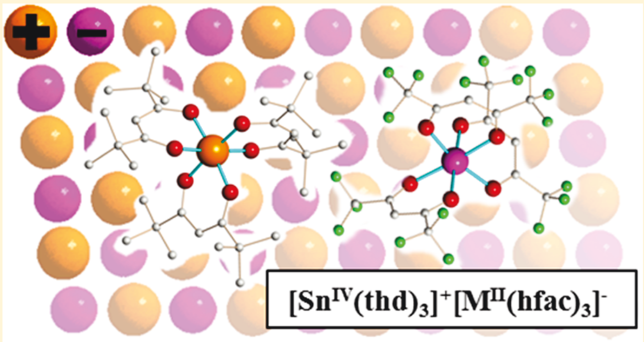
Inorganic Chemistry
Article
Cite This: *Inorg. Chem.* 2018, 57, 2308−2313
pubs.acs.org/IC

Expanding the Structural Motif Landscape of Heterometallic β-Diketonates: Congruently Melting Ionic Solids

Matthew C. Barry,[†] Craig M. Lieberman,[†] Zheng Wei,[†] Rodolphe Clérac,[‡,§] Alexander S. Filatov,[∥] and Evgeny V. Dikarev*,[†]

[†]Department of Chemistry, University at Albany, Albany, New York 12222, United States
[‡]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[§]Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France
[∥]Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, United States

Supporting Information



ABSTRACT: The first example of ionic β-diketonates in which both the cation and anion are octahedral coordinatively saturated metal diketonate moieties are reported. Heterometallic tin−transition-metal heteroleptic diketonates were obtained through solid-state redox reactions and are formulated as $\{[Sn^{IV}(thd)_3]^+[M^{II}(hfac)_3]^-\}$ (M^{II} = Mn (**1**), Fe (**2**), Co (**3**); thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, hfac = hexafluoroacetylacetonate). X-ray single-crystal structural investigations along with DART mass spectrometry, multinuclear NMR, and magnetic susceptibility measurements have been used to confirm an assignment of metal oxidation states in compounds **1**−**3**. Ionic compounds were found to melt congruently at temperatures below the decomposition point. As such, they represent prospective materials that can be utilized as ionic liquids as well as reagents for the soft transfer of diketonate ligands. An unexpected volatility of ionic compounds **1**−**3** was proposed to occur through a transport reaction, in which the transport agent is one of the products of their partial decomposition in the gas or condensed phase.

INTRODUCTION

β-Diketonates demonstrate an unparalleled ability to form coordination compounds with the majority of the elements in the Periodic Table.[1,2] For decades, chemists have continued to explore the unique properties of β-diketonate complexes and have unambiguously established the relationship between their volatility and structure/composition.[3] The latter has led to widespread applications of metal β-diketonates[4] as molecular precursors in various CVD and MOCVD processes.[5,6] At the same time, the research into tunable/controllable properties has also made metal β-diketonates useful in both laser[1] and fuel[7] technologies, as well as NMR shift reagents,[8,9] catalysts,[10,11] and gas sensors.[12] Even more, diketonate compounds have been explored for their ability to move alkali-metal ions across biological membranes,[13] antibacterial activity,[14] and environmental protection through metal chelation in sewage.[15]

The simplest form of *homoleptic* β-diketonate complexes is a mononuclear structure in which all ligands are chelating a coordinatively saturated metal center. This structure type is known for a number of di-,[16] tri-,[17] and tetravalent[18] complexes $M(\beta\text{-dik})_x$ (x = 2−4). However, if the number (and size) of chelating ligands does not satisfy the coordination requirements for the metal ion, β-diketonate oxygens appear to act in a chelating-bridging fashion. In the absence of donor solvent molecules, the latter leads to the formation of *polynuclear* species featuring a variety of dimeric,[9,19] trimeric,[20] tetrameric,[21] hexameric,[22] and, ultimately, polymeric structures.[23] An application of two or more different metals results in an even greater diversity of structure types for *heterometallic* β-diketonates.[8,24]

Chisholm eventually suggested an additional way for metals in *unsolvated* diketonates to achieve coordinational saturation: the formation of metal−metal bonds. His quadruply bonded dimolybdenum(II,II) diketonate structure[16] still stands as the only example of such a compound, even though heterometallic diketonates with a single metal−metal bond[25] have later been discovered.

A relatively common type of diketonate structure, in which metal centers are forming *ionic* fragments, can be separated into two distinct groups. The first of these includes heterometallic compounds, in which formally cationic and anionic fragments constitute parts of the molecular/polymeric structure and are bridged by diketonate ligands. The anionic fragments are often represented by $[M(\beta\text{-dik})_3]^-$ (M = divalent 3d transition metal)[26] and $[M(\beta\text{-dik})_4]^-$ (M = trivalent lanthanide or

Received: December 19, 2017
Published: February 7, 2018

DOI: 10.1021/acs.inorgchem.7b03166
Inorg. Chem. 2018, 57, 2308−2313

actinide)[27] and offer their diketonate oxygens for coordination of "naked" metal ions. The cationic counterparts are typically main-group-metal fragments such as [Pb(β-dik)]$^+$ [28] and [Bi(β-dik)$_2$]$^+$ [29] that are coordinatively unsaturated and require additional bridging interactions by oxygens from anionic units. The second group comprises compounds with coordinatively saturated isolated ions that cocrystallize with common organic/inorganic counterions. The cationic diketonates are represented by tetra- and pentavalent ions such as [M^{IV}(β-dik)$_3$]$^+$ (M^{IV} = Ti, V, Ge)[30−32] and [Ta^V(β-dik)$_4$]$^+$,[33] while isolated metal diketonate anions are usually stabilized by various noncoordinating cations and include transition-metal and lanthanide fragments similar to those in the first group.[34,35]

In this work, we report a new class of β-diketonates, ionic compounds, in which both the cation and anion are coordinatively saturated metal β-diketonate fragments, free of exogenous ligands or solvent molecules. The tin−transition-metal complexes formulated as {[Sn^{IV}(thd)$_3$]$^+$[M^{II}(hfac)$_3$]$^-$} (M = Mn, Fe, Co) consist of counterions that exist as isolated moieties and cocrystallize without any bridging interactions.

RESULTS AND DISCUSSION

Heterometallic β-diketonates [SnM(thd)$_3$(hfac)$_3$] (M = Mn (**1**), Fe (**2**), Co (**3**)) were obtained in evacuated glass ampules at 85−95 °C by the solid-state redox reaction between divalent tin and trivalent transition-metal homometallic diketonate reagents (see Table S1 in the Supporting Information):

$$\begin{aligned} &2\mathrm{Sn(hfac)_2} + 2\mathrm{M(thd)_3} \\ &\quad \rightarrow \mathrm{SnM(thd)_3(hfac)_3} + \text{“}\mathrm{SnM(thd)_3(hfac)}\text{”} \end{aligned} \qquad (1)$$

The title products can be purified by multiple washings of the reaction mixture with dry, deoxygenated hexanes and appear as yellow (**1**), purple-red (**2**), or orange (**3**) solids. The purity of collected products was confirmed (Figure 1a) by the Le Bail fit of X-ray powder diffraction patterns using single-crystal data (Figures S1−S3 and Table S2 in the Supporting Information).

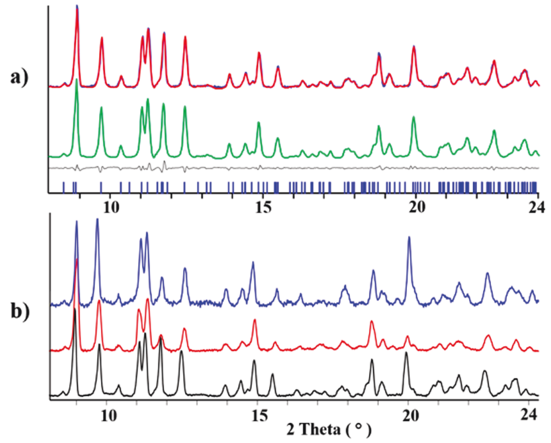


Figure 1. (a) X-ray powder diffraction pattern of {SnMn(thd)$_3$(hfac)$_3$} (**1**) and the Le Bail fit for triclinic unit cell (space group $P\bar{1}$). Blue and red curves are experimental and calculated patterns overlaid, respectively. The green curve is a calculated pattern, the gray line is the difference curve, and theoretical peak positions are shown at the bottom as blue lines. (b) Comparison of X-ray powder diffraction patterns of heterometallic diketonates **1** (black), **2** (red), and **3** (blue).

Comparison of the powder diffraction spectra also indicates (Figure 1b) that compounds **1**−**3** are isomorphous.

The second reaction product, "[SnM(thd)$_3$(hfac)]", has not been isolated; however, a number of similar tin(II)−transition-metal(II) heterometallic diketonates have been obtained[36] by direct reactions between divalent Sn(β-dik)$_2$ and M(β-dik)$_2$ reagents. At the same time, if the appearance of reaction products is taken into account, the presence of decomposition residues (vide infra) cannot be excluded. Partial decomposition of heterometallic diketonates could also explain the low yields, especially for the products **2** and **3**.

Heterometallic products **1**−**3** are not air- and moisture-sensitive at ambient temperatures and can be handled without the use of a glovebox in the course of characterization studies. Compounds were found to be soluble only in polar solvents such as dichloromethane, chloroform, acetone, and THF. In addition, the products were shown to display similar melting points of 179 ± 3 (**1**), 178 ± 2 (**2**), and 180 ± 3 °C (**3**).

Block-shaped crystals of **1**−**3** suitable for X-ray structural investigation were selected directly from the initial reaction mixtures. Diffraction studies confirmed that heterometallic diketonates **1**−**3** are isomorphous and exhibit similar parameters of the centrosymmetric triclinic unit cells (Table S3 in the Supporting Information). Their structures consist of two *homoleptic* tris-chelated mononuclear moieties [Sn(thd)$_3$] and [M(hfac)$_3$] (Figure 2) with no significant contacts between them.

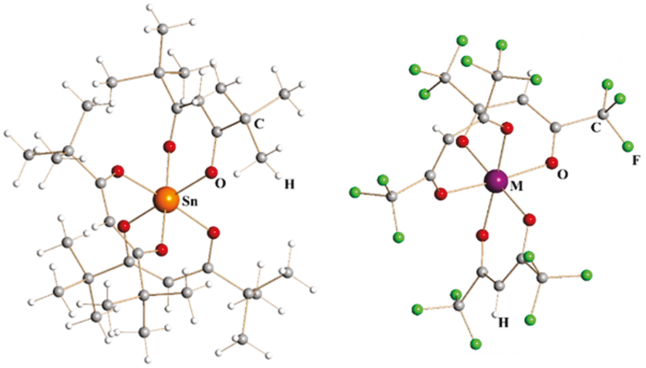


Figure 2. Ball and stick model representations of [Sn(thd)$_3$]$^+$ and [M(hfac)$_3$]$^-$ moieties in structures **1**−**3** drawn side-by-side for clarity. The views of structures **1**−**3** featuring thermal ellipsoids can be found in Figures S4−S6 in the Supporting Information.

Both metal centers exhibit an almost perfect octahedral geometry with all diketonate ligands acting in a purely chelating mode. The analysis of M−O bonds in compounds **1**−**3** (Table 1) reveals that transition-metal fragments perfectly correspond to known [M^{II}(hfac)$_3$]$^-$ anions, while having distances significantly longer than those in neutral [M^{III}(hfac)$_3$] molecules. Specifically notable is the lack of Jahn−Teller distortion in the [Mn(hfac)$_3$] portion of **1**. This makes the other counterpart the cationic fragment [Sn^{IV}(thd)$_3$]$^+$ featuring tetravalent tin. Indeed, there is no manifestation of a lone electron pair that is characteristic of all known Sn^{II} diketonates. Moreover, the Sn−O distances in **1**−**3** are about 0.16 Å shorter than those in Sn^{II}(thd)$_2$ (**4**, CN = 4; Figure S7 and Table S7 in the Supporting Information) and even shorter than corresponding bonds in the only known tetravalent tin oxo diketonate, [Sn$_3$(acac)$_6$O$_3$].[41]

Table 1. Comparison of the Average Sn−O and M−O Bond Lengths (Å) in the Structures of 1−3 with Those in Related Compounds[a]

	ref	Sn^{IV}−O	Sn^{II}−O	M^{III}−O	M^{II}−O
$[Sn^{IV}(thd)_3]^+[Mn^{II}(hfac)_3]^-$ (**1**)	*b*	2.031(2)			2.157(2)
$[Fe(C_5H_5)_2]^+[Mn^{II}(hfac)_3]^-$	37				2.158(4)
$Mn^{III}(hfac)_3$	38			2.144(3) (2×), 1.922(3) (4×)	
$[Sn^{IV}(thd)_3]^+[Fe^{II}(hfac)_3]^-$ (**2**)	*b*	2.032(2)			2.087(2)
$[Fe(2PyBN)_2(hfac)]^+[Fe^{II}(hfac)_3]^-$ [c]	39				2.085(4)
$Fe^{III}(hfac)_3$	40			1.999[d]	
$[Sn^{IV}(thd)_3]^+[Co^{II}(hfac)_3]^-$ (**3**)	*b*	2.030(3)			2.064(3)
$[C_{14}Py]^+[Co^{II}(hfac)_3]^-$ [e]	35				2.061(2)
$Co^{III}(hfac)_3$	36			1.872(2)	
$Sn^{II}(thd)_2$ (**4**)	*b*		2.195(1)		
$Sn^{IV}_3(acac)_6O_3$	41	2.099(2)			

[a] The full list of metal−oxygen distances can be found in Tables S4−S6 in the Supporting Information. [b] This work. [c] 2PyBN = *N*-*tert*-butyl-*α*-(2-pyridyl)nitrone. [d] Standard deviations are not reported. [e] $C_{14}Py$ = *n*-tetradecylpyridinium.

On the basis of the above considerations, compounds **1**−**3** were formulated as $\{[Sn^{IV}(thd)_3]^+[M^{II}(hfac)_3]^-\}$ (M = Mn (**1**), Fe (**2**), Co (**3**)). To the best of our knowledge, the title heterometallic compounds constitute the first examples of entirely ionic diketonates, in which both the cation and anion are represented by metal *β*-diketonate moieties that are not engaged in any extended structure by bridging interactions. They also feature the first Sn^{IV} diketonate fragment without any exogenous ligands. The distribution of diketonate ligands in compounds **1**−**3** is notable and confirms the known pattern[28,29] of the ligand with electron-donating groups (thd) to be located on the high-valent main-group metal, while the back-donating transition metal(II) ion is chelated by diketonates with electron-withdrawing substituents (hfac).

Analysis of the crystal packing of complex symmetric ions in the structures of **1**−**3** suggests the triclinically distorted NaCl type (Figure S8 in the Supporting Information). Inspection of interionic interactions revealed the shortest contacts were C−F···H−C between the trifluoromethyl groups of the anions and *tert*-butyl hydrogens of the cations. The corresponding distances of 2.6−2.9 Å and the lack of C−F bond lengthening indicate moderate, mostly electrostatic[42] hydrogen-bonding interactions.

Compounds **1**−**3** were found to melt at 178−180 °C, shortly before decomposition that occurs above 200 °C. The melting process has been studied in an anaerobic environment in order to prevent the oxidation of heterometallic diketonates, as well as under nongradient conditions, to ensure that the title compounds do not partially decompose (vide infra). By using X-ray powder diffraction analysis, it was found that under the above conditions the compounds **1**−**3** are melting congruently, as the phase composition does not change upon melting/crystallization process (Figure 3 and Figures S9−S11 and Table S8 in the Supporting Information).

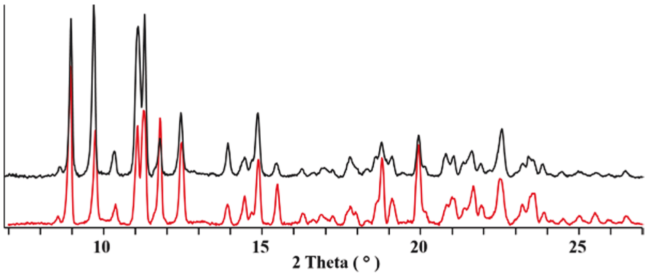


Figure 3. Comparison of X-ray powder diffraction patterns of $\{[Sn(thd)_3]^+[Mn(hfac)_3]^-\}$ (**1**) before (black) and after (red) recrystallization from the melt.

To our great surprise, we have discovered that, despite their ionic character, single crystals of heterometallic diketonates **1**−**3** can be obtained by sublimation of bulk materials in sealed evacuated ampules placed in a gradient furnace at ca. 150 °C (days) or 170 °C (hours). With the recent findings that some ionic liquids exhibit limited volatility at elevated temperatures under reduced pressure,[43] a series of experiments were run to understand the volatility of **1**−**3**. It was found that the sublimation of heterometallic compounds over a small temperature gradient (ca. 5 °C) yields a large amount of colored melt along with crystalline products **1**−**3**, whose identity can be confirmed by both X-ray powder and single-crystal diffraction methods. Upon extraction of crystalline materials from the mixture, the sublimation can be repeated a number of times, resulting in a similar loss of the product until, eventually, only melt is observed in the cold zone of the reaction vessel. We proposed that the volatility of heterometallic ionic compounds **1**−**3** can possibly be explained by a transport reaction, in which the transport agent is one of the thermal decomposition products. Apparently, the partial decomposition of title compounds under temperature gradient conditions is also a contributing factor to the low reaction yields observed upon initial preparation of heterometallic diketonates **1**−**3**.

Although the volatility among ionic liquids is known, the gas-phase behavior of these compounds remains a mystery.[44] To gain a better understanding of the processes that occur in the gas phase, a DART (direct analysis in real time) mass spectrometry investigation was undertaken on solid samples of **1**−**3**. DART mass spectrometry has recently begun to show great promise in the assignments of metal oxidation states in heterometallic diketonate complexes.[45] Furthermore, a careful analysis of all peaks in the spectrum may give a hint of how the species are breaking apart in the gas phase. In the positive mode spectra of solid $\{[Sn(thd)_3]^+[Mn(hfac)_3]^-\}$ (**1**), the most prevalent peak corresponds to the homometallic $[Sn^{IV}(thd)_3]^+$ (measd/calcd *m*/*z* 669.3177/669.3170) ion with a characteristic isotope distribution pattern (Figure 4a). Likewise, in the negative mode, the most abundant peak is associated with $[Mn^{II}(hfac)_3]^-$ (measd/calcd *m*/*z* 675.8650/675.9028) ion (Figure 4b). Similar pictures are observed for both positive and negative mode spectra of **2** and **3** (Figures S12−S17 in the

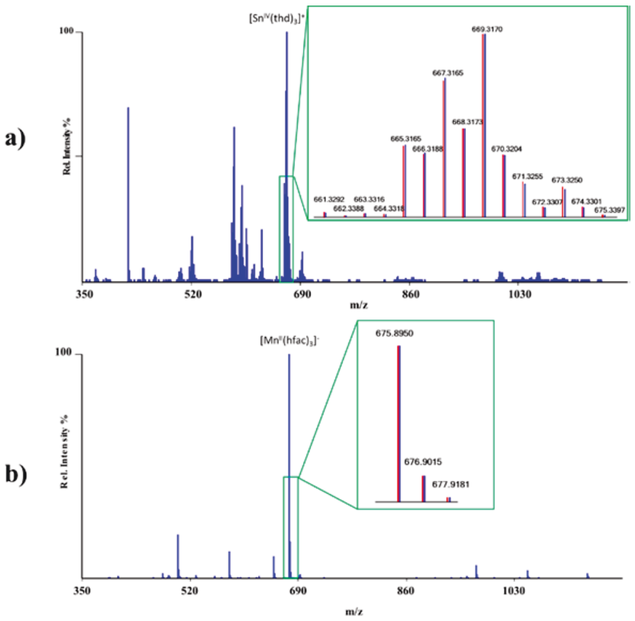


Figure 4. Positive (a) and negative ion (b) DART mass spectra of $\{[\mathrm{Sn(thd)_3}]^+[\mathrm{Mn(hfac)_3}]^-\}$ (**1**). The isotope distribution patterns for $[\mathrm{Sn^{IV}(thd)_3}]^+$ and $[\mathrm{Mn^{II}(hfac)_3}]^-$ peaks are shown in the insets.

Supporting Information). Careful analysis of peaks throughout the spectra did not yield any indication of the presence of $\mathrm{Sn^{II}}$- and $\mathrm{M^{III}}$-based ions (Tables S9−S14 in the Supporting Information), regardless of ionization strength or temperature applied. Importantly, upon further investigation of the high-mass region, we were able to identify *heterometallic* ions that contain acetate ligands, such as $[\mathrm{SnMn(thd)(hfac)_3(CH_3COO)}]^+$ (measd/calcd m/z 1037.9196/1037.9563) and $[\mathrm{SnMn(hfac)_4(CH_3COO)}]^+$ (measd/calcd m/z 1061.7996/1061.8058). Obviously, the acetates that probably appear from decomposition of thd groups can act as bridging ligands in the identified heterometallic fragments. These observations support the idea of partial decomposition in the gas or condensed phase followed by a transport reaction that promotes the sublimation of ionic heterometallic diketonates **1**−**3**.

NMR investigation of heterometallic ionic diketonates in a solution of polar solvent ($\mathrm{CDCl_3}$) predictably revealed peaks corresponding to only the $[\mathrm{Sn^{IV}(thd)_3}]^+$ cation. The ^{1}H NMR spectrum (Figure 5, left) features aromatic and methyl proton signals (ca. 1:18 ratio) that are significantly broadened due to the presence of high-spin transition-metal anions. The ^{119}Sn NMR spectrum (Figure 5, right) contains a singlet peak at −723 ppm. The latter corresponds well to analogous octahedrally (6O) coordinated tetravalent tin compounds $\mathrm{Sn(acac)_2(OR)_2}$ (acac = acetylacetonate; OR = OMe, O^{i}Pr, OBu).[46] The resonance signal is sharp, which indicates no ligand exchange on the NMR time scale, and this is also supported by the lack of any signals in the ^{19}F NMR spectrum. The absence of tin−tin (117/119) coupling points to the monomeric nature of tin species in solution.

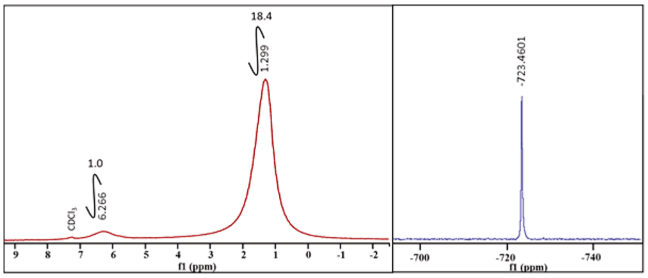


Figure 5. ^{1}H (left) and ^{119}Sn (right) NMR spectra of $\{[\mathrm{Sn(thd)_3}]^+[\mathrm{Mn(hfac)_3}]^-\}$ (**1**) in $\mathrm{CDCl_3}$ recorded at room temperature.

The results of magnetic susceptibility measurements for the heterometallic diketonate $\{[\mathrm{Sn(thd)_3}][\mathrm{Mn(hfac)_3}]\}$ (**1**) fully support the assignment of manganese oxidation/spin state drawn from the structural data. At room temperature, the χT product is estimated at 4.62(5) cm^3 K/mol, which corresponds exactly to one $S = 5/2$ $\mathrm{Mn^{II}}$ magnetic center as expected. The temperature dependence of the magnetic susceptibility follows almost a perfect Curie law (at 1.8 K, $\chi T = 4.54(5)$ cm^3 K/mol; Figure 6), indicating the excellent magnetic separation of the $S = 5/2$ $[\mathrm{Mn(hfac)_3}]^-$ moieties as envisaged from the ionic crystal structure and the long separations between magnetic centers. The field dependence of the magnetization also confirms the presence of isolated $\mathrm{Mn^{II}}$ centers, as the M vs H/T data can be all scaled on a single master curve and fit to an $S = 5/2$ Brillouin function with $g = 2.15(5)$ (Figure S22 in the Supporting Information).

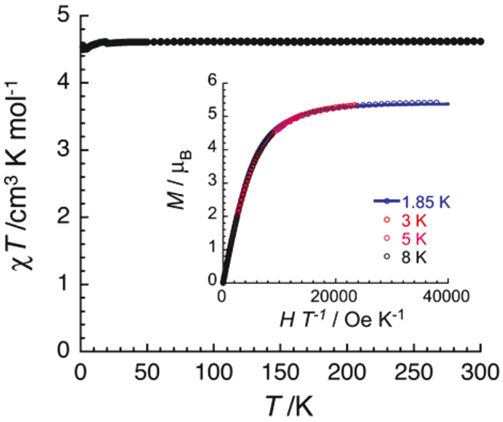


Figure 6. Temperature dependence of the χT product at 0.1 T for $\{[\mathrm{Sn^{IV}(thd)_3}]^+[\mathrm{Mn^{II}(hfac)_3}]^-\}$ (**1**). χ is defined as the magnetic susceptibility, equal to M/H per mole of **1**. The inset shows the field dependence of the magnetization below 8 K for **1** shown as an M vs H/T plot. The blue solid line is the best fit of the experimental data to the $S = 5/2$ Brillouin function described in the text.

■ CONCLUSIONS

The new class of heterometallic β-diketonates $\{[\mathrm{Sn^{IV}(thd)_3}]^+[\mathrm{M^{II}(hfac)_3}]^-\}$ (M = Mn (**1**), Fe (**2**), Co(**3**)), in which both the cation and anion are coordinatively saturated metal diketonate fragments, is reported. The title compounds were found to melt congruently at relatively low temperatures. Importantly, ligand substitution at either the cation or anion in the structures of **1**−**3** may offer endless opportunities for tuning the melting temperatures of ionic diketonates. Such a control over the physical properties would make these compounds promising candidates to be explored as *ionic liquids*. Furthermore, compounds of this type could potentially serve for a soft ligation of metals/metalloids either through the redox reaction $[\mathrm{Sn^{IV}}(\beta\text{-dik})_3]^+ + \mathrm{M'} \rightarrow [\mathrm{Sn^{II}}(\beta\text{-dik})_2] + [\mathrm{M'}(\beta\text{-dik})_x]^+$ or through sharing the ligands to yield new heterometallic diketonates $[M^{II}(\beta\text{-dik})_3]^- + M'^+ \rightarrow [MM'(\beta\text{-dik})_3]$.

EXPERIMENTAL SECTION

General Procedures. All of the manipulations were carried out under a dry, oxygen-free argon atmosphere by employing standard Schlenk and glovebox techniques. The attenuated total reflection (ATR) spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained on a Bruker Avance 400 spectrometer at 400 MHz for ^1H and at 376.47 MHz for ^{19}F. ^{119}Sn NMR spectra were acquired on a Bruker 500 MHz AVIIIHD system equipped with a cryogenically cooled multinuclear NMR probe with coils and preamplifiers operating at liquid nitrogen temperature. Mass spectra were acquired using a DART-SVP ion source (IonSense) coupled to a JEOL AccuTOF time-of-flight mass spectrometer (JEOL USA) in positive and negative ion modes. X-ray powder diffraction data were collected on a Bruker D8 Advance diffractometer (Cu Kα radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step of 0.02° 2θ, 20 °C). Le Bail fits for powder diffraction patterns were performed using the TOPAS version 4 software package (Bruker AXS, 2006). Magnetic measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer at temperatures between 1.8 and 300 K and dc magnetic fields ranging from −7 to + 7 T. The single-crystal diffraction data for **1**, **3**, and **4** were measured at 100 K on a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). The single crystal diffraction data for **2** were measured at 100 K on a Bruker D8 fixed-chi with Pilatus1 M CdTe pixel array detector using ϕ scans (synchrotron radiation at λ = 0.41328 Å) located at the Advanced Photon Source, Argonne National Laboratory (ChemMatCARS, Sector 15). More details on characterization techniques can be found in the Supporting Information.

Synthesis. Heterometallic diketonates **1**−**3** have been obtained via a one-step solid-state reaction. Typically, a mixture of two powdered reagents, $Sn(hfac)_2$ and $M(thd)_3$, was sealed in an evacuated glass ampule and placed in an electric furnace having a temperature gradient along the length of the tube. The ampule was kept at constant temperature for 1 day (**1**) or 3 days (**2**, **3**), allowing products to be deposited in the cold section of the container, where the temperature was set approximately 5 °C lower. Ampules were cooled to room temperature, and the reaction products were washed with several portions of hexanes to yield insoluble yellow (**1**), purple-red (**2**), and orange-brown (**3**) crystalline powders. The yield was calculated in each case on the basis of the amount of product isolated after washings. The experimental conditions for the synthesis of **1**−**3** are summarized in Table S1 in the Supporting Information.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b03166.

> Full synthetic and characterization details, MS, NMR, and IR spectra, X-ray powder diffraction patterns, full details on interatomic distances and angles in the structures of **1**−**4**, crystal packing in ionic solids, magnetic susceptibility measurement plots (PDF)

Accession Codes

CCDC 1811491−1811494 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for E.V.D.: edikarev@albany.edu.

ORCID

Rodolphe Clérac: 0000-0001-5429-7418
Evgeny V. Dikarev: 0000-0001-8979-7914

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation (CHE-1152441), CNRS, the University of Bordeaux, the Région Nouvelle Aquitaine, the GdR MCM-2, and the MOLSPIN COST action CA15128 is gratefully acknowledged. ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1346572. Use of the PILATUS3 X CdTe 1M detector is supported by the National Science Foundation under the grant number NSF/DMR-1531283. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

DEDICATION

Dedicated to the memory of Malcolm H. Chisholm, educator, mentor, and friend.

REFERENCES

(1) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic: New York, 1978.

(2) Garnovskii, A. D.; Kharisov, B. I.; Blanco, L. M.; Garnovskii, D. A.; Burlov, A. S.; Vasilchenko, I. S.; Bondarenko, G. I. Some aspects of competitive coordination of β-diketones and nitrogen-containing ligands. *J. Coord. Chem.* **1999**, *46*, 365−395.

(3) Bazuev, G. V.; Kurbatova, L. D. Chemistry of volatile β-diketonates and their application in synthesis of high-temperature superconducting thin films. *Russ. Chem. Rev.* **1993**, *62*, 981.

(4) Fahlman, B. D.; Barron, A. R. Substituent effects on the volatility of metal β-diketonates. *Adv. Mater. Opt. Electron.* **2000**, *10*, 223−232.

(5) Tiitta, M.; Niinisto, L. Volatile metal β-diketonates. ALE and CVD precursors for electroluminescent device thin films. *Chem. Vap. Deposition* **1997**, *3*, 167−182.

(6) Ozawa, T. Volatility of metal β-diketonates for chemical vapor deposition of oxide superconductors. *Thermochim. Acta* **1991**, *174*, 185−99.

(7) Poonia, N. S.; Bajaj, A. V. Coordination chemistry of alkali and alkaline earth cations. *Chem. Rev.* **1979**, *79*, 389−445.

(8) Lindoy, L. F.; Lip, H. C.; Louie, H. W.; Drew, M. G. B.; Hudson, M. J. Interaction of lanthanide shift reagents with coordination complexes; direct observation of nuclear magnetic resonance signals for free and complexed tris(pentane-2,4-dionato)cobalt(III) at ambient temperature, and x-ray crystal and molecular structure of the 1:1 adduct formed. *J. Chem. Soc., Chem. Commun.* **1977**, 778−870.

(9) Holm, R. H.; Cotton, F. A. Spectral investigations of metal complexes of β-diketones. I. Nuclear magnetic resonance and ultraviolet spectra of acetylacetonates. *J. Am. Chem. Soc.* **1958**, *80*, 5658−5663.

(10) Akturk, E. S.; Scappaticci, S. J.; Seals, R. N.; Marshak, M. P. Bulky β-Diketones Enabling New Lewis Acidic Ligand Platforms. *Inorg. Chem.* **2017**, *56*, 11466−11469.

(11) Ligtenbarg, A. G. J.; Hage, R.; Feringa, B. L. Catalytic oxidations by vanadium complexes. *Coord. Chem. Rev.* **2003**, *237*, 89−101.

(12) Harvey, S. D. Method and apparatus for selective capture of gas phase analytes using metal beta-diketonate polymers. US20100203652A1, 2010.

(13) Vigato, P. A.; Peruzzo, V.; Tamburini, S. The evolution of β-diketone or β-diketophenol ligands and related complexes. *Coord. Chem. Rev.* **2009**, *253*, 1099−1201.

(14) Verma, P. N.; Juneja, H. D. Antibacterial screening of some novel metal β-diketonates. *J. Pharm. Res. Clin. Pract.* **2012**, *2*, 6−12.

(15) Urbaniak, W.; Jurek, K.; Witt, K.; Goraczko, A.; Staniszewski, B. Properties and application of diketones and their derivatives. *Chemik* **2011**, *65*, 273−282.

(16) Onuma, S.; Shibata, S. Structure of bis(acetylacetonato)-beryllium(II), Be(C5H7O2)2, at 119 K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 1181−1183.

(17) Morosin, B.; Brathovde, J. R. The crystal structure and molecular configuration of trisacetylacetonatomanganese(III). *Acta Crystallogr.* **1964**, *17*, 705−711.

(18) Titze, H. Crystal structure of α-tetrakis(acetylacefonato)cerium-(IV). *Acta Chem. Scand.* **1974**, *28a*, 1079−1088.

(19) Wei, X.-H.; Coles, M. P.; Hitchcock, P. B.; Lappert, M. F. Synthesis and Structures of Five Crystalline Organometallic (Li/Y, Mg/Mg) or Coordination (Mg, CrII, Y/Y) Complexes. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1807−1813.

(20) Zhang, H.; Li, B.; Sun, J.; Clerac, R.; Dikarev, E. V. Fluorinated β-Diketonates of the First Row Divalent Transition Metals: New Approach to the Synthesis of Unsolvated Species. *Inorg. Chem.* **2008**, *47*, 10046−10052.

(21) Drozdov, A. A.; Troyanov, S. I. New oligomeric structures of barium dipivaloylmethanate, $Ba_4(thd)_8$, and its pivalate derivative $Ba_5(thd)_9(piv)$. *Polyhedron* **1992**, *11*, 2877−2882.

(22) Waldmueller, D.; Mayer, B.; Braun, M.; Hanuschik, A.; Krueger, C.; Guenot, P. Crystal structure and gas-phase investigations of lithiated tert-butyl acetoacetate. *Chem. Ber.* **1992**, *125*, 2779−2782.

(23) Filatov, E. S.; Baidina, I. A.; Igumenov, I. K. Crystal structure of lithium(I) 1,1,1,-trifluoro-5,5-dimethyl-2,4-hexanedionate. *J. Struct. Chem.* **2006**, *47*, 484−488.

(24) Bennett, M. J.; Cotton, F. A.; Legzdins, P.; Lippard, S. J. Crystal structure of cesium tetrakis(hexafluoroacetylacetonato)yttrate(III). Novel stereoisomer having dodecahedral eight-coordination. *Inorg. Chem.* **1968**, *7*, 1770−1776.

(25) Zhang, H.; Li, B.; Dikarev, E. V. Mn(III) Hexafluoroacetylacetonate as an Oxidative Agent in the Synthesis of Heterobimetallic β-Diketonates. *J. Cluster Sci.* **2008**, *19*, 311−321.

(26) Wei, Z.; Filatov, A. S.; Dikarev, E. V. Volatile Hetero-metallic Precursors for the Low-Temperature Synthesis of Prospective Sodium Ion Battery Cathode Materials. *J. Am. Chem. Soc.* **2013**, *135*, 12216−12219.

(27) Barry, M. C.; Wei, Z.; He, T.; Filatov, A. S.; Dikarev, E. V. Volatile Single-Source Precursors for the Low-Temperature Preparation of Sodium-Rare Earth Metal Fluorides. *J. Am. Chem. Soc.* **2016**, *138*, 8883−8887.

(28) Lieberman, C. M.; Navulla, A.; Zhang, H.; Filatov, A. S.; Dikarev, E. V. Mixed-Ligand Approach to Design of Heterometallic Single-Source Precursors with Discrete Molecular Structure. *Inorg. Chem.* **2014**, *53*, 4733−4738.

(29) Lieberman, C. M.; Wei, Z.; Filatov, A. S.; Dikarev, E. V. Mixed-Ligand Approach to Changing the Metal Ratio in Bismuth-Transition Metal Heterometallic Precursors. *Inorg. Chem.* **2016**, *55*, 3946−3951.

(30) Ito, T.; Toriumi, K.; Ueno, F. B.; Saito, K. The absolute configuration of the (-)589-tris(acetylacetonato)germanium(IV) ion. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 2998−3001.

(31) Thewalt, U.; Adam, T. Preparation and structure of tris(acetylacetonato)titanium(IV) perchlorate. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 142−145.

(32) Hambley, T. W.; Hawkins, C. J.; Kabanos, T. A. Synthetic, structural, and physical studies of tris(2,4-pentanedionato)vanadium-(IV) hexachloroantimonate(V) and tris(1-phenyl-1,3-butanedionato)-vanadium(IV) hexachloroantimonate(V). *Inorg. Chem.* **1987**, *26*, 3740−3745.

(33) Davies, H. O.; Jones, A. C.; Motevalli, M. A.; McKinnell, E. A.; O'Brien, P. Synthesis and structure of a tantalum(V) tetrakis-O, O chelate: $[Ta(tmhd)_4][TaCl_6]$. *Inorg. Chem. Commun.* **2005**, *8*, 585−587.

(34) Clark, K. D.; Purslow, J. A.; Pierson, S. A.; Nacham, O.; Anderson, J. L. Rapid preconcentration of viable bacteria using magnetic ionic liquids for PCR amplification and culture-based diagnostics. *Anal. Bioanal. Chem.* **2017**, *409*, 4983−4991.

(35) Zhang, P.; Gong, Y.; Lv, Y.; Guo, Y.; Wang, Y.; Wang, C.; Li, H. Ionic liquids with metal chelate anions. *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 2334−2336.

(36) Dikarev, E. V. Crystal Structures of tin(II)-transition metal(II) heterometallic diketonates; personal communication.

(37) Bryant, J. R.; Taves, J. E.; Mayer, J. M. Oxidations of Hydrocarbons by Manganese(III) Tris(hexafluoroacetylacetonate). *Inorg. Chem.* **2002**, *41*, 2769−2776.

(38) Bouwman, E.; Caulton, K. G.; Christou, G.; Folting, K.; Gasser, C.; Hendrickson, D. N.; Huffman, J. C.; Lobkovsky, E. B.; Martin, J. D.; Michel, P.; Tsai, H.-L.; Xue, Z. Doubly-hydrated hexafluoroacetylacetone as a tetradentate ligand: synthesis, magnetochemistry, and thermal transformations of a dimanganese(III) complex. *Inorg. Chem.* **1993**, *32*, 3463−3470.

(39) Villamena, F. A.; Crist, D. R. Metal-nitrone complexes: spin trapping and solution characterization. *J. Chem. Soc., Dalton Trans.* **1998**, 4055−4062.

(40) Pfluger, C. E.; Haradem, P. S. Coordination sphere geometry of tris(acetylacetonato)metal(III) complexes: the crystal and molecular structure of tris(1,1,1,5,5,5-hexafluoroacetylacetonato)iron(III). *Inorg. Chim. Acta* **1983**, *69*, 141−146.

(41) Verdenelli, M.; Parola, S.; Lecocq, S.; Hubert-Pfalzgraf, L. G. Crystal structure of tris[oxobis(2,4-pentanedionato)tin(IV)], $[SnO(acac)_2]_3$. *Z. Kristallogr. - New Cryst. Struct.* **2001**, *216*, 295−296.

(42) *An Introduction to Hydrogen Bonding*; Jeffrey, G. A., Ed.; Oxford University Press: Oxford, U.K., 1997.

(43) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831−834.

(44) Leal, J. P.; Esperanca, J. M. S. S.; Da Piedade, M. E. M.; Lopes, J. N. C.; Rebelo, L. P. N.; Seddon, K. R. The Nature of Ionic Liquids in the Gas Phase. *J. Phys. Chem. A* **2007**, *111*, 6176−6182.

(45) Lieberman, C. M.; Barry, M. C.; Wei, Z.; Rogachev, A. Y.; Wang, X.; Liu, J.-L.; Clerac, R.; Chen, Y.-S.; Filatov, A. S.; Dikarev, E. V. Position Assignment and Oxidation State Recognition of Fe and Co Centers in Heterometallic Mixed-Valent Molecular Precursors for the Low-Temperature Preparation of Target Spinel Oxide Materials. *Inorg. Chem.* **2017**, *56*, 9574−9584.

(46) Chandler, C. D.; Fallon, G. D.; Koplick, A. J.; West, B. O. The structure of mono and bis β-diketonate tin(IV) alkoxide complexes. *Aust. J. Chem.* **1987**, *40*, 1427−1439.