Inorg. Chem. **2008**, *47*, 10046−10052

Inorganic Chemistry
Article

Fluorinated β-Diketonates of the First Row Divalent Transition Metals: New Approach to the Synthesis of Unsolvated Species

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Received July 15, 2008

An original low-temperature solid-state route for the preparation of metal β-diketonates in their unsolvated forms has been suggested. Four new first row divalent transition metal β-diketonates, $M(hfac)_2$ (M = Mn (**1**), Fe (**2**), Co (**3**), and Ni (**4**); hfac = hexaluoroacetylacetonate), have been isolated in quantitative yield. Compounds **1**−**3** have been obtained by comproportionation reaction between the corresponding $M(hfac)_3$ and metal powder. $Ni(hfac)_2$ (**4**) has been synthesized by oxidation of metallic nickel with $Cu(hfac)_2$. All products have been characterized spectroscopically and by X-ray powder and single crystal diffraction techniques. The solid state structures of **1**−**4** feature polynuclear molecules, in which the coordinatively unsaturated metal centers fulfill an octahedral environment by Lewis acid−base interactions with the oxygen atoms of diketonate ligands acting in chelating-bridging fashion. Title transition metal diketonates have been shown to retain their polynuclear structures upon sublimation-deposition procedure as well as in solutions of non-coordinating solvents. In coordinating solvents the molecules of **1**−**4** quickly form the mononuclear $M(hfac)_2L_2$ (L = donor solvent) complexes.

Introduction

Transition metal β-diketonates have attracted considerable attention as metal organic chemical vapor deposition (MOCVD) precursors because of their volatility and low-temperature clean decomposition patterns.[1] A number of first row divalent transition metal diketonates have been reported as starting materials in the synthesis of supramolecular aggregates,[2] cubane-type metallic clusters,[3] and heterometallic complexes.[4] In addition, it has also been shown that these compounds may play an important role in catalysis.[5]

Our renewed interest in the title compounds comes from the recent foray into the preparation of heterometallic β-diketonates[6] and their potential application as single-source precursors for the synthesis of mixed-metal oxide materials. We have suggested several low-temperature solid-state synthetic methods for the preparation of heterometallic diketonates that can incorporate a wide variety of s, p, d, and f-metals. The most common and convenient approach was described as the reaction between two unsolvated β-diketonates with at least one of those being coordinatively unsaturated:

$$M(\beta\text{-dik})_x + M'(\beta\text{-dik})_y \rightarrow MM'(\beta\text{-dik})_{x+y} \qquad (1)$$

Importantly, we have found that in several cases the above reaction could result in a different M/M′ ratio than other synthetic tactics. To this end, we were especially interested in using divalent transition metal unsolvated diketonates that are capable of providing coordinatively unsaturated fragments $M(\beta\text{-dik})_2$ in the vapor phase.

Since the pioneering work on nickel(II) acetylacetonate,[7] many unsolvated $M(\beta\text{-dik})_2$ (M = Cr−Zn) compounds with sterically uncongested ligands have been synthesized.[8] However, those are mostly limited to acetylacetonate (acac) and dibenzoylmethanate (DBM) species. These compounds

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10.1021/ic801320p CCC: $40.75

can be obtained in a dehydrated form by recrystallization from non-coordinating solvents as well as by thermal treatment or sublimation in vacuum in the presence of water-absorbing agents. The resulting M(β-dik)$_2$ products (except for Cr and Cu) exhibit a great variety of polynuclear structures in the solid state, built on M···O intermolecular contacts.[8b,f,g,9] At the same time, unsolvated divalent transition metal β-diketonates with electron-withdrawing ligands such as hexafluoroacetylacetonate (hfac) are considerably more difficult to isolate. Only diketonates of those metals that do not strongly require an octahedral environment can be obtained relatively easily. The first of those, Cu(hfac)$_2$, has been reported a while ago by Maverick[2a] to exhibit a square-planar mononuclear structure with long Cu···F intermolecular contacts. Another member of that family, Zn(hfac)$_2$, has been described by us[6a] to have a monomeric structure with tetrahedrally coordinated zinc atoms. No β-diketonates of Mn, Fe, Co, and Ni with hexafluoroacetylacetonate ligands have been characterized despite some reports[4c,8c,10] mentioning their isolation.

Herein, we suggest a new synthetic method for the preparation of unsolvated divalent transition metal diketonates by reduction of the M(β-dik)$_3$ compounds with the corresponding metal and describe their structures and properties.

Experimental Section

General Procedures. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk line and glovebox techniques. Mn(hfac)$_3$,[6b] Fe(hfac)$_3$,[11] and Cu(hfac)$_2$[2a] were synthesized as reported. Manganese, iron, cobalt, and nickel metals, CoF$_3$, hexafluoroacetylacetone (Hhfac), and all anhydrous solvents were purchased from Aldrich and used as received. UV−vis spectra were acquired using a Hewlett-Packard 8452A diode array spectrophotometer. The attenuated total reflection (ATR) and solution IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained using a Bruker Avance 400 spectrometer at 400 MHz for ^{1}H and at 376.47 MHz for ^{19}F. Chemical shifts (δ) are given in ppm relative to residual solvent peak for ^{1}H and to CFCl$_3$ for ^{19}F. Thermogravimetric measurements were carried out under nitrogen at a heating rate of 5 °C/min using a TGA 2050 thermogravimetric analyzer, TA Instruments, Inc. Elemental analysis was performed by Maxima Laboratories Inc., Ontario, Canada.

Synthesis. Mn(hfac)$_2$ (1). A mixture of Mn(hfac)$_3$ (0.20 g, 0.30 mmol) and manganese powder (0.02 g, 0.36 mmol) 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 80 °C for 3 days to allow yellow crystals to be deposited in the cold section of the container where the temperature was set approximately 5 °C lower. Yield is about 90% (crystals collected). The purity of the bulk product has been confirmed by comparison of the powder diffraction pattern with the theoretical one calculated on the basis of single crystal data analysis. Elemental analysis (%) calcd for C$_{10}$H$_2$O$_4$F$_{12}$Mn: C 25.59, H 0.43, O 13.65, F 48.61; found: C 25.65, H 0.46, O 13.21, F 48.78; ATR-IR (cm^{-1}): 3147w, 1643s, 1613m, 1565m, 1538s, 1460s, 1347w, 1256s, 1219s, 1203s, 1137s, 1103s, 1090s, 950w; UV/vis (CH$_2$Cl$_2$, 22 °C): $\lambda_{\max}$ (ε, M$^{-1}\cdot$cm^{-1}) = 232(521), 310(3146) nm.

When acetone solution of **1** was layered with hexanes in an NMR tube and placed in a freezer at −10 °C, yellow crystals of Mn(hfac)$_2$(OCMe$_2$)$_2$ (**5**) were obtained in a few days.

Fe(hfac)$_2$ (2). A mixture of Fe(hfac)$_3$ (0.20 g, 0.30 mmol) and iron powder (0.02 g, 0.36 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace. The ampule was kept at 110 °C for 3 days to allow orange crystals to be deposited in the cold section of the container where the temperature was set approximately 5 °C lower. Yield is about 90% (crystals collected). ^{1}H NMR (d_6-acetone, 22 °*C*): δ = 7.48(s); ^{19}F NMR (d_6-acetone, 22 °C): δ = −79.21(s). ATR-IR (cm^{-1}): 3149w, 1629m, 1603s, 1564m, 1539m, 1470m, 1433m, 1414m, 1349w, 1254s, 1199s, 1136s, 1100s, 951w; UV/vis (CH$_2$Cl$_2$, 22 °C): $\lambda_{\max}$ (ε, M$^{-1}\cdot$cm^{-1}) = 302(3086) nm.

Co(hfac)$_3$. A slurry of CoF$_3$ (0.10 g, 0.86 mmol) was stirred for 3 days at room temperature in 10 mL of CHCl$_3$ that contains 0.5 mL (3.6 mmol) of Hhfac. The reaction mixture was filtered, and the filtrate was dried under vacuum. The solid was dissolved in 15 mL of hexanes and filtered to remove any insoluble impurities. The solution was then evaporated, and the resulting solid was resublimed

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Table 1. Crystallographic Data and Structure Refinement Parameters for **1**−**4a**

	1	**2**	**3**	**4a**
formula	$Mn_3O_{12}C_{30}H_6F_{36}$	$Fe_2O_8C_{20}H_4F_{24}$	$Co_3O_{12}C_{30}H_6F_{36}$	$Ni_3O_{12}C_{30}H_6F_{36}$
fw	1407.17	939.93	1419.14	1418.48
crystal system	trigonal	monoclinic	monoclinic	monoclinic
space group	$R\bar{3}c$	$C2/c$	$P2_1/c$	$P2_1/n$
a (Å)	11.1975(13)	20.479(3)	17.6557(15)	13.515(3)
b (Å)	11.1975(13)	7.6582(10)	16.2242(14)	16.995(3)
c (Å)	11.1975(13)	20.547(3)	16.9102(15)	20.016(4)
α (deg)	109.942(17)	90.00	90.00	90.00
β (deg)	109.942(17)	108.853(1)	115.201(1)	96.33(3)
γ (deg)	109.942(17)	90.00	90.00	90.00
V (Å^3)	1061.5(2)	3049.5(7)	4382.9(7)	4569.4(16)
Z	1	4	4	4
ρ_{calcd} (g·cm^3)	2.201	2.047	2.151	2.062
μ (mm^{-1})	1.098	1.142	1.335	1.427
transm factors	0.8795− 0.9271	0.7329−0.8751	0.7904−0.9007	0.6350−0.7634
temp (K)	173(2)	173(2)	90(2)	120(2)
data/restr/params	866/1/69	2982/72/289	10200/18/763	8997/126/817
$R1$,[a] $wR2$[b]				
$I > 2\sigma(I)$	0.0608, 0.1252	0.0766, 0.2063	0.0425, 0.0896	0.0529, 0.1345
all data	0.0726, 0.1296	0.0836, 0.2137	0.0707, 0.1021	0.0605, 0.1414
quality-of-fit[c]	1.200	1.123	1.005	1.058

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**4**[a]

	M−O$_c$	M−O$_{c\text{-}b}$	M···O$_b$	M···M	O···M···O
Mn(hfac)$_2$ (**1**)	2.11	2.22	2.20	3.11	76.4, 103.6, 180
Fe(hfac)$_2$ (**2**)	1.97, 1.98	1.97	2.87, 3.02	3.28	72.9, 72.2
Co(hfac)$_2$ (**3**)	1.95−2.07	2.04−2.08	2.09−2.42	2.97, 2.98	72.7, 107.8, 72.3
Ni(hfac)$_2$ (**4a**)	1.94−1.99	1.99−2.02	2.06−2.43	2.87, 2.89	72.9, 103.8, 71.5

[a] c - chelating; c-b - chelating-bridging; b - bridging.

twice under vacuum at 50−60 °C to obtain dark-green crystals of Co(hfac)$_3$. Yield is about 50%. ^{1}H NMR (CDCl$_3$, 22 °C): $\delta = 6.58$(s); ^{19}F NMR (CDCl$_3$, 22 °C): $\delta = -74.43$(s). ATR-IR (cm^{-1}): 3153w, 1625s, 1605s, 1557m, 1530m, 1448m, 1422s, 1352m, 1250s, 1228s, 1199s, 1160s, 1143s, 1108s, 961w; UV/vis (CH$_2$Cl$_2$, 22 °C): λ_{max} (ε, M^{-1}·cm^{-1}) = 272(1921), 298(2005) nm.

Co(hfac)$_2$ (3). A mixture of Co(hfac)$_3$ (0.10 g, 0.15 mmol) and cobalt powder (0.01 g, 0.17 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace. The ampule was kept at 80 °C for 2 days to allow reddish-brown crystals to be deposited in the cold section of the container where the temperature was set approximately 5 °C lower. Yield is about 90% (crystals collected). The purity of the bulk product has been confirmed by X-ray powder diffraction. ATR-IR (cm^{-1}): 3149w, 1641s, 1613m, 1564m, 1538m, 1465s, 1349w, 1256s, 1218s, 1203s, 1140s, 1104s, 1091s, 946w; UV/vis (CH$_2$Cl$_2$, 22 °C): λ_{max} (ε, M^{-1}·cm^{-1}) = 302(5318) nm.

Ni(hfac)$_2$ (4). A mixture of Cu(hfac)$_2$ (0.10 g, 0.21 mmol) and nickel powder (0.03 g, 0.51 mmol) was sealed in an evacuated glass ampule and placed in an electric furnace. The ampule was kept at 120 °C for 7 days to allow green crystals of Ni(hfac)$_2$ to be deposited in the cold section of the container where the temperature was set approximately 5 °C lower. Yield is about 70% (crystals collected). X-ray diffraction pattern revealed the presence of two compounds in the bulk crystalline sample. Those were later identified as two polymorph modifications of Ni(hfac)$_2$ by collecting single crystal data for both major (**4a**) and minor (**4b**) components. ATR-IR (cm^{-1}): 3150w, 1643s, 1613m, 1564m, 1537m, 1463s, 1349w, 1256s, 1218s, 1203s, 1142s, 1092s, 952w; UV/vis (CH$_2$Cl$_2$, 22 °C): λ_{max} (ε, M^{-1}·cm^{-1}) = 302(4036) nm.

Magnetic Measurements. The magnetic susceptibility measurements for **1** were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for direct current (dc) applied fields ranging from −7 to 7 T. Measurements were performed on finely ground crystalline sample (23.60 mg) prepared in a glovebox under argon and sealed in a plastic bag to avoid any contact with air or water. The presence of ferromagnetic impurities has been checked by measuring the magnetization as a function of the field at 100 K. A perfect linear field dependence of the magnetization was found indicating the absence of any ferromagnetic impurities. The alternating current (ac) susceptibility has been measured with an oscillating ac field of 3 Oe, and the ac frequencies ranging from 1 to 1500 Hz, with no out-of-phase ac signal been detected above 1.8 K. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

X-ray Diffraction Procedures. X-ray powder diffraction data were collected using an automated Bruker D8 Advance diffractometer (Cu K$_\alpha$ radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step 0.01° 2θ, 20 °C). The crystalline samples under investigation were grounded and placed in the dome-like airtight zero-background holders inside glovebox.

Selected single crystals suitable for X-ray crystallographic analysis were used for structure determination. The X-ray intensity data were measured at 173(2) K (**1**, **2**, and **5**), 120(2) K (**4a**), and at 90(2) K (**3**, **4b**) (Bruker KRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. The data collection and refinement procedures have been described elsewhere.[6b] In the process of structure solution, it was found that the fluorine atoms of some CF$_3$ groups appeared to be disordered over three rotational orientations. This disorder was modeled in each individual case. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorines. The hydrogen atoms were located and refined independently. Relevant crystallographic data are summarized in Table 1. Selected bond lengths and angles for compounds **1**−**4** are given in Table 2.

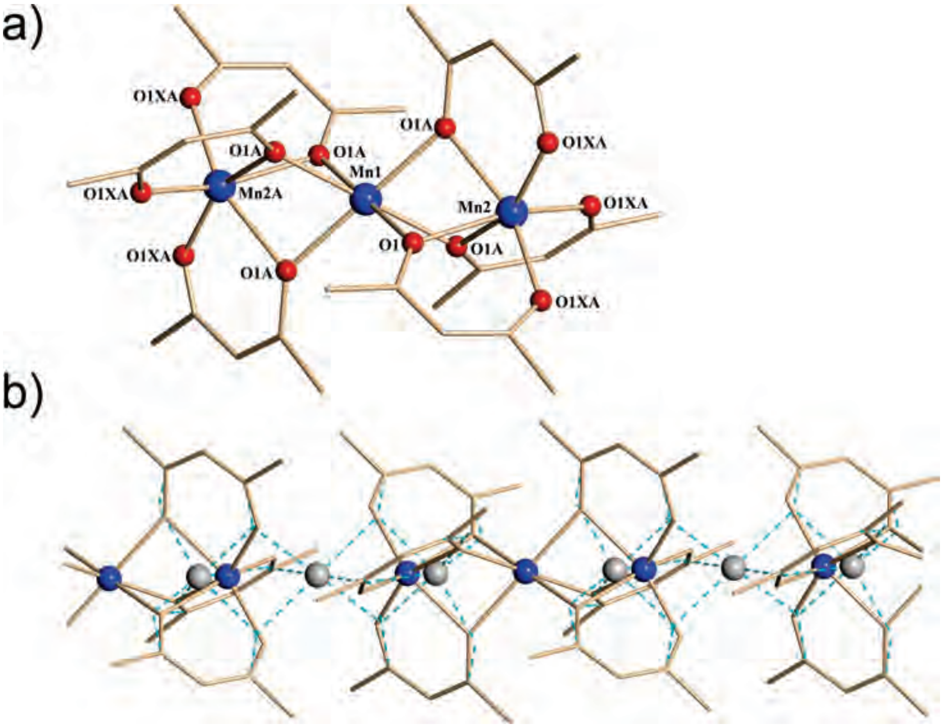

Figure 1. (a) Molecular structure of $Mn(hfac)_2$ (**1**). Fluorine and hydrogen atoms are omitted for clarity. (b) Disorder in the crystal structure of **1**. Blue balls and solid lines correspond to one orientation of a trinuclear unit, gray balls and dashed lines represent the other.

Results and Discussion

The first-row transition metal unsolvated hexafluoroacetylacetonates $M(hfac)_2$ (M = Mn (**1**), Fe (**2**), and Co (**3**)) were synthesized by comproportionation reactions between $M(hfac)_3$ and the corresponding metal powder:

$$2M(hfac)_3 + M \rightarrow 3M(hfac)_2 \qquad (2)$$

All trivalent diketonates show good oxidation activity toward metals, and compounds **1**−**3** can be isolated with quantitative yields under relatively mild conditions in a course of few days. Because of the unavailability of nickel(III) diketonate, unsolvated $Ni(hfac)_2$ (**4**) was isolated by the solid-state redox reaction of nickel powder with copper(II) hexafluoroacetylacetonate:

$$Cu(hfac)_2 + Ni \rightarrow Ni(hfac)_2 + Cu \qquad (3)$$

All transition metal(II) hexafluoroacetylacetonates are highly volatile and can be further purified by resublimation at 70−80 °C in a sealed ampule, if needed. Compounds are readily soluble in coordinating solvents, such as acetone and THF, and partially soluble in non-coordinating solvents, such as dichloromethane and chloroform. Products **1**−**4** are air- and moisture-sensitive, especially $Fe(hfac)_2$ (**2**), which loses its crystallinity in a few hours even when kept in a glovebox and should be used immediately after preparation. In open atmosphere, **2** is oxidized to Fe^{III} species within seconds, while other compounds quickly turn into the corresponding dihydrate complexes. According to thermogravimetric analysis (TGA) data, the thermal decomposition of $M(hfac)_2$ upon heating in nitrogen starts above 100 °C and is accompanied by an apparent loss of β-diketonates to sublimation.

The solid state structure of $Mn(hfac)_2$ (**1**) contains trinuclear molecules, in which one manganese center is sandwiched between two $[Mn(hfac)_3]$ fragments (Figure 1a). The structure has been solved and refined in the trigonal space group $R\bar{3}c$ with one trinuclear molecule per unit cell. The whole molecule of manganese(II) β-diketonate is disordered over two translational orientations in the crystal structure (Figure 1b). The disordered structure appeared to contain $[Mn_2(hfac)_3]_\infty$ infinite chains, but refinement of the structure and the coordination environment around Mn atoms both suggest the formula of $Mn_3(hfac)_6$, which is further confirmed by the results of elemental analysis. The coordination of metal atom in the $[Mn(hfac)_3]$ units is distorted octahedral with three of the Mn−O bond distances (2.22 Å) being essentially longer than the others (2.11 Å, Table 2) because of the bridging coordination of oxygen atoms to the central Mn in the former. The Mn−O bond distances in **1** are close to those reported for the $[Mn^{II}(hfac)_3]^-$ anion[6b,10,12] and the $Mn^{II}(hfac)_2L_2$ adducts[6b,12a] (2.13−2.18 Å) but are significantly longer than the corresponding distances in $Mn^{III}(hfac)_3$[12b] (2.00 Å), which indicates that the oxidation state of manganese is +2 in complex **1** giving its formula as $\{Mn^{2+}[Mn(hfac)_3]_2^-\}$. This formulation has also been confirmed by magnetic measurements for **1** (vide infra). The trinuclear molecule is held together by six bridging Mn···O contacts between the central Mn and diketonate oxygens at 2.20 Å. It is worth mentioning that these bridging contacts are even shorter than some of the chelating Mn−O bonds (2.22 Å, Table 2).

Another previously reported homometallic Mn^{II} diketonate, $Mn(acac)_2$,[8b] exhibits a trinuclear structure similar to **1** with

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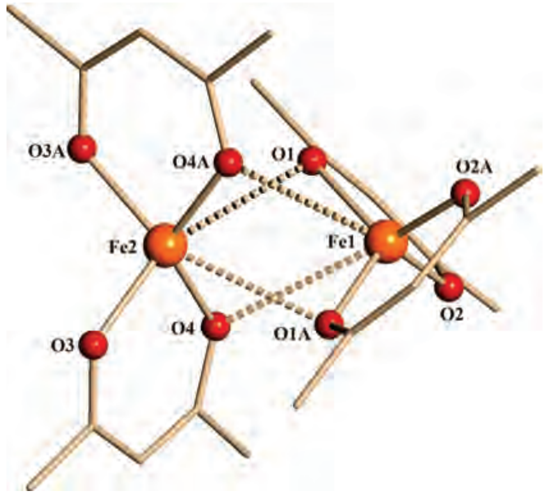

Figure 2. Molecular structure of Fe(hfac)$_2$ (**2**). Fluorine and hydrogen atoms are omitted for clarity.

the Mn−O bond distances of 2.10−2.25 Å and the Mn···O bridging contacts of 2.17 Å. The other structural analogues of **1** include homometallic Mg(acac)$_2$,[13a] a Ni(*tert*-butyl acetoacetato)$_2$,[8g] as well as heterometallic CdMn$_2$(hfac)$_6$[6b] and PbMn$_2$(hfac)$_6$[13b] complexes.

Compound Fe(hfac)$_2$ (**2**) crystallizes in the monoclinic space group *C*2/*c* with two crystallographically independent iron atoms both occupying special positions. Each iron atom is chelated by two symmetry related *β*-diketonate ligands, and the oxidation state of iron is +2. However, the Fe−O bond distances in **2**, averaged to 1.97 Å, are significantly shorter than those reported for the $[\text{Fe}^{\text{II}}(\text{hfac})_3]^-$ anion[10] and the Fe$^{\text{II}}$(hfac)$_2$L$_2$ adducts,[14] while very close to the corresponding distances in Fe$^{\text{III}}$(hfac)$_3$.[11] The latter observation can be explained by the fact that each iron atom in **2** is four-coordinate with two additional interactions being quite long. The dinuclear structure is held together by four Fe···O bridging contacts between two Fe(hfac)$_2$ units at 2.87 and 3.02 Å (Table 2), and with inclusion of these interactions the coordination environment of iron can be considered as a very distorted octahedral (Figure 2). To understand the degree of distortion, one should imagine two octahedra around neighboring iron atoms that share four vertices. No strong interactions are observed between the dinuclear complexes, with the shortest Fe···O intermolecular contact measured at 3.59 Å, which is already longer than the sum of the corresponding van der Waals radii (3.52 Å).

The structure of **2** is similar to that of another reported dinuclear Fe$^{\text{II}}$ diketonate, Fe(acac)$_2$.[9a,e] However, the latter exhibits significantly shorter Fe···O bridging contacts (2.18−2.32 Å) and Fe···Fe distance (3.02 Å) compared to **2** (2.87−3.02 and 3.28 Å, respectively), which is likely due to the self-repulsion effect of the CF$_3$ groups,[15] restricting the two Fe(hfac)$_2$ units to come closer to each other.

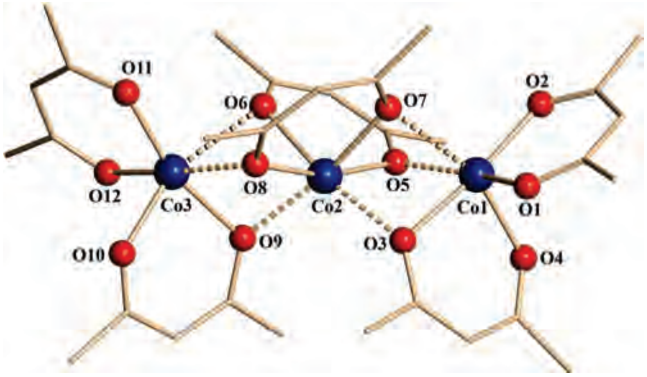

Figure 3. Molecular structure of Co(hfac)$_2$ (**3**). Fluorine and hydrogen atoms are omitted for clarity.

The solid state structure of Co(hfac)$_2$ (**3**) consists of trinuclear molecules, in which three Co(hfac)$_2$ units are held together by six Co···O interactions (Figure 3). Unlike another trinuclear molecule **1**, each cobalt atom in **3** has two chelating *β*-diketonate ligands and fulfills its distorted octahedral coordination environment with two Lewis acid−base contacts (2.09−2.42 Å) to the oxygens from the neighboring Co(hfac)$_2$ unit/units. The chelating Co−O distances (Table 2) range from 1.95 to 2.08 Å and are typical for the Co$^{\text{II}}$ compounds with diketonate ligands.[12b,14a,16] In the polyhedral representation, the structure of **3** can be viewed similar to compound **1** as a chain of three octahedra, in which the central one is sharing opposite faces with two others. The cobalt atoms are nearly aligned, with the Co···Co separations being about 2.98 Å.

It is interesting, that among compounds **1**−**4**, Co(hfac)$_2$ (**3**) is the only one that has a structure different from its acetylacetonate analogue. The Co(acac)$_2$ is known[9b] to contain tetranuclear molecules in the solid-state structure of its unsolvated form. Instead, the Co(hfac)$_2$ is very similar to Ni(hfac)$_2$ (**4**, Figure 4), though in the latter molecule all corresponding distances are a bit shorter than in **3** (Table 2) in accord with well-established ionic radius trends. Two polymorph modifications of Ni(hfac)$_2$ (**4a** and **4b**) are different in the way in which trinuclear molecules are being packed in the crystal structure. The minor polymorph **4b** is isomorphous to Co(hfac)$_2$ (**3**).

A number of Ni(II) diketonates have been reported[8g,17] with four of them exhibiting trinuclear structures. Ni(acac)$_2$,[7,8e,9c] Ni(DBM)$_2$,[8f] and Ni(3-phenylpentane-2,4-dionato)$_2$[8g] have a structure similar to that of **4**, while Ni(*tert*-butyl acetoacetato)$_2$[8g] bears the structural analogy with Mn(hfac)$_2$ (**1**).

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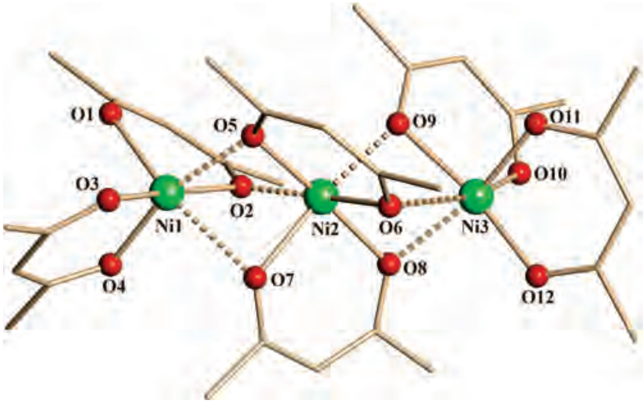

Figure 4. Molecular structure of Ni(hfac)$_2$ (**4a**). Fluorine and hydrogen atoms are omitted for clarity.

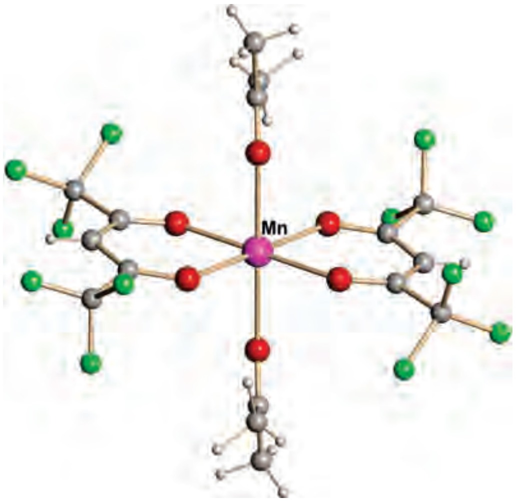

Figure 5. Molecular structure of *trans*-Mn(hfac)$_2$(Me$_2$CO)$_2$ (**5**).

Table 3. Infrared C−H Stretching Frequencies (cm^{-1}) for Compounds **1**−**4**

compound	solid state	CHCl$_3$ solution	acetone solution
Mn(hfac)$_2$ (**1**)	3147	3147	3136
Fe(hfac)$_2$ (**2**)	3149	3148	3138
Co(hfac)$_2$ (**3**)	3149	3149	3138
Ni(hfac)$_2$ (**4**)	3150	3149	3140

In the presence of coordinating donor molecules, the M(hfac)$_2$ compounds instantly loose their polynuclear structures and convert to octahedrally coordinated mononuclear species M(hfac)$_2$L$_2$. One of such species, Mn(hfac)$_2$(OCMe$_2$)$_2$ (**5**), was isolated from the acetone solution of **1** to confirm the collapse of a trinuclear structure in coordinating solvents. The crystal structure of **5** contains Mn^{II} atoms in an octahedral environment of two chelating β-diketonates located in a plane and two acetone groups occupying the trans-positions (Figure 5).

All compounds **1**−**4** show similar IR spectra with the same C−H stretching positions in the solid state and chloroform solution, while in acetone solution, the C−H peaks down shift about 10 cm^{-1} (Table 3). This difference is related to the change in coordination mode of diketonate ligands from chelating-bridging to pure chelating.[6b] These observations support the assumption that compounds **1**−**4** retain their polynuclear structures in non-coordinating solvents while they dissociate into mononuclear species in coordinating solvents.

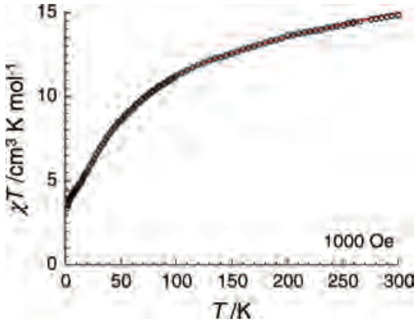

Figure 6. χT vs T plot for **1** at 1000 Oe (χ being the magnetic susceptibility equal to M/H normalized by trinuclear complex). The solid red line is the best fit of the experimental data with the model described in the text.

Magnetic Susceptibility Studies for Mn(hfac)$_2$ (1). At room temperature, the χT product of **1** (15 cm^3 K/mol) is in good agreement with the presence of three $S = 5/2$ Mn^{II} metal ions (for each $S = 5/2$ Mn^{II} metal ion: $C = 4.375$ cm^3 K/mol expected for $g = 2$) and with a theoretical value of 13.125 cm^3 K/mol. It is worth mentioning that this result confirms the assignment of the Mn oxidation states based on the structural data (vide supra). Upon decreasing the temperature, the χT product at 1000 Oe decreases and reaches 3.4 cm^3 K/mol at 1.8 K (Figure 6). This thermal behavior indicates the presence of dominating antiferromagnetic interactions between Mn^{II} metal ions in the trinuclear complex. Below 5 K, the decrease of χT seems to be more important, likely indicating weak antiferromagnetic interactions between the [Mn$_3$] units.

On the basis of the molecular structure of **1**, the magnetic properties were modeled using a Heisenberg trimer model of $S = 5/2$ Mn^{II}. The χT product was simulated by taking into account only isotropic intra-complex magnetic interactions between the manganese sites. Application of the van Vleck equation[18] to Kambe's vector coupling scheme[19] allows one to determine an analytical expression of the magnetic susceptibility[20] from the following Hamiltonian: $\mathbf{H} = -2J\{\mathbf{S}_{\mathrm{Mn(2)}}\cdot\mathbf{S}_{\mathrm{Mn(1)}}+\mathbf{S}_{\mathrm{Mn(1)}}\cdot\mathbf{S}_{\mathrm{Mn(2A)}}\}$, where J is the exchange interaction between Mn^{II} ions in the trimer and S_i is the spin operator for each metal ion ($S = 5/2$ for Mn(1), Mn(2) and Mn(2A)). Fitting the experimental data above 15 K to avoid the effects of inter-complex magnetic interactions, the best set of parameters was found as $J/k_B = -3.1(1)$ K and $g = 2.00(5)$ (solid line in Figure 6). On the basis of these considerations, the magnetic interactions between Mn^{II} metal ions through the (μ-O)$_3$ bridges are antiferromagnetic which lead to the $S_T = 5/2$ spin ground-state for this complex.

In summary, four first row divalent transition metal (M^{II} = Mn (**1**), Fe (**2**), Co (**3**), and Ni (**4**)) β-diketonates have been isolated in their unsolvated form with high yields using low-temperature solid-state oxidation of the corresponding metals. In general, this technique provides access to an

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important class of starting materials for the reactions, in which the presence of solvent molecules can interfere with the formation of specific reaction products. In our particular case, these unsolvated *β*-diketonates are employed in the synthesis of new heterometallic species, which structures are built on the Lewis acid−base interactions that cannot withstand the presence of donor solvent molecules. In addition to that, the synthetic approach described in this work can be applied to the preparation of a wide variety of homo- and heterometallic *β*-diketonates. We have already reported[6b] on the use of this method for the synthesis of Mn/M (M = Cd, Hg, and In) compounds, and other examples will be following soon after.

Acknowledgment. Financial support from the National Science Foundation (CHE-0718900 and CHE-0619422, X-ray diffractometer) as well as from the Donors of the American Chemical Society Petroleum Research Fund (44770-AC3) is gratefully acknowledged. R.C. thanks the University of Bordeaux, the CNRS, and the Région Aquitaine for financial support.

Supporting Information Available: X-ray crystallographic files for **1**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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