Inorg. Chem. **2006**, *45*, 3074–3085

Inorganic Chemistry
Article

The Imidazole Role in Strontium β-Diketonate Complexes Formation

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Received November 15, 2005

A selection of new strontium β-diketonate derivatives $(imH_2)_2[Sr_2(\beta\text{-dike})_6]$ [where imH = imidazole and β-dike = tfac (tfacH = 1,1,1-trifluoro-2,4-pentanedione), tfbz (tfbzH = 1,1,1-trifluoro-4-phenyl-2,4-butanedione), or hfac (hfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione)], $[Sr_2(tfac)_4(Meim)_2(H_2O)_2]$, $(MeimH)_2[Sr(\beta\text{-dike})_4]$ (where Meim = 1-methylimidazole and β-dike = tfbz or hfac), $[Sr_2(thd)_4(imH)_2(EtOH)]$, and $[Sr_2(thd)_4(Meim)_2(EtOH)]$ (where thdH = 2,2,6,6-tetramethyl-3,5-heptanedione) have been synthesized and fully characterized. $(imH_2)_2[Sr_2(\beta\text{-dike})_6]$ and $(MeimH)_2[Sr(\beta\text{-dike})_4]$ are di- and mononuclear Sr anionic complexes, respectively, while $[Sr_2(tfac)_4(Meim)_2(H_2O)_2]$, $[Sr_2(thd)_4(imH)_2(EtOH)]$, and $[Sr_2(thd)_4(Meim)_2(EtOH)]$ are neutral dinuclear molecular derivatives. The derivative $(imH_2)_2[Sr_2(hfac)_6]$ slowly decomposes in solution under aerobic conditions, giving $(imH_2)_2[Sr(H_2O)_2(tfa)_3](tfa)$ (tfaH = trifluoroacetic acid), which is an ionic compound containing polynuclear anionic chains composed of $Sr(H_2O)_2(tfa)_3$ units. When a deficiency of imH is employed, the thdH proligand forms not only the dinuclear derivative $[Sr_2(thd)_4(imH)_2(EtOH)]$ but also an additional product with the formula $[Sr(thd)_2(H_2O)_2(EtOH)]$, in which the Sr atom is seven-coordinated. A complete solid-state characterization has been accomplished by comparing X-ray and solid-state ^{13}C NMR data. Elucidation of the H-bond interaction between the heterocyclic rings and metal complexes by cross-polarization magic-angle-spinning ^{15}N NMR is also reported.

Introduction

There is a growing interest in the chemistry of the alkaline-earth metal ions, particularly in the research area of strontium-based materials in the form of thin films. This is due to several possible applications in luminescent and electronic devices.[1,2] For example, Ln-doped strontium sulfide and Sr-containing fluoride glasses, such as $SrAlF_5$, show interesting electroluminescent and optical features,[3−5] whereas $SrTiO_3$ and Bi−Sr−Ca−Cu or Sr−Bi−Ta mixed oxides are of interest for their applications respectively as high-K materials in DRAMs,[6−8] as HTSC materials,[9,10] and as ferroelectric nonvolatile random access memories FeRAM.[11,12] Among several techniques used to synthesize them, probably the most viable route for industry seems to be metal−organic chemical vapor deposition (MOCVD) because of the superior step coverage compared to other deposition techniques.[13] Several strontium diketonates have been proposed as molecular precursors for MOCVD. Most of them are derivatives of 2,2,6,6-tetramethyl-3,5-heptane-

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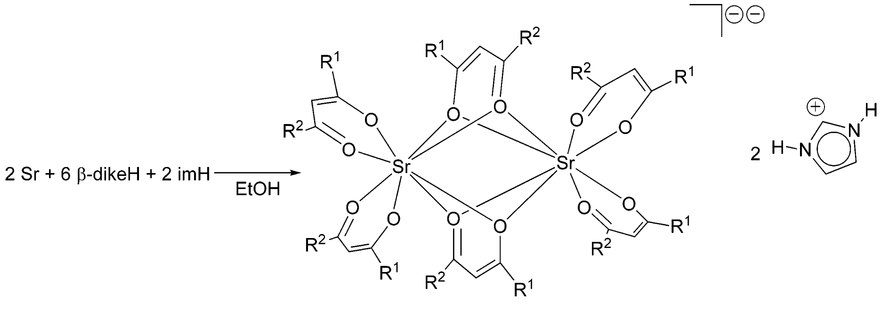
10.1021/ic051972g CCC: $33.50

Scheme 1



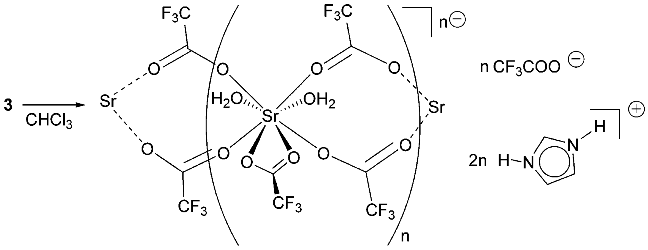
1, β-dikeH = tfacH, $R^1 = CH_3$, $R^2 = CF_3$
2, β-dikeH = tfbzH, $R^1 = C_6H_5$, $R^2 = CF_3$
3, β-dikeH = hfacH, $R^1 = R^2 = CF_3$

dione (thdH) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH).[14,15] The Sr complexes show oligomeric or polymeric structures and are sensitive to moisture because of the low coordination numbers (CNs) of the central atoms.[14,15] To prevent oligomerization, which generally decreases the volatility of complexes, several ancillary donors, such as polyethers, *β*-amino alcohols, and phenanthroline, have been used, with the aim of saturating the Sr coordination sphere and increasing stability.[14,15] We have recently reported a new type of alkaline-earth metal compounds containing a new class of *β*-diketones, namely, 4-acyl-5-pyrazolones, and their adducts with several ancillary donors, such as phenanthroline,[16] polyethers,[16,17] and imidazoles.[18] The presence of imidazoles in the reaction mixture causes the unexpected formation of ionic dinuclear strontium diketonate complexes, which are either soluble or very soluble in nonpolar solvents.[18] Similar Ba- and Sr(thd) derivatives stabilized by pyrazoles show good volatility in a vacuum and were suggested as CVD precursors.[19] Here we extend our studies to the interaction of Sr with *β*-diketonates (tfac, tfbz, hfac, and thd) and nitrogen monodentate donors, such as imidazole or 1-methylimidazole, to compare the structural and physicochemical features of the new derivatives with those of the previous ones[18,19] and to find new molecular precursors suitable for CVD. Several structural typologies of the derivatives will be reported and the importance of tuning reaction conditions, electronic properties, and steric crowding of the ancillary ligands discussed.

Results and Discussion

Synthesis of the Complexes. Via the interaction of Sr with the simple imidazole and fluorinated ligands (tfacH, tfbzH, and hfacH) in a 1:1:3 metal/imidazole/*β*-diketone ratio in absolute ethanol, the complexes **1**−**3** of the formula $(imH_2)_2[Sr(\beta\text{-dike})_4]$ (*β*-dike = tfac, tfbz, or hfac) have been obtained (Scheme 1). They are very soluble in most common organic solvents such as alcohols, chlorinated solvents, acetonitrile, acetone, and dimethyl sulfoxide (DMSO).

Scheme 2



4

Attempts to recrystallize compound **3** gave good-quality crystals, which were identified as $(imH)_2[Sr(H_2O)_2(tfa)_3](tfa)$ (**4**; tfa = CF_3COO). Derivative **4** is a decomposition product of **3**, arising from the cleavage of hfac ligands and the subsequent formation of tfa anions. Examples of the cleavage of fluorinated *β*-diketonates to form the trifluoroacetate anion, by the action of water molecules during or after the complex formation, are well-known.[20−23] Derivative **4** is an ionic compound in the solid state containing anionic polynuclear chains where Sr atoms are interconnected through bridging tfa groups (see the Crystallographic X-ray Studies section; Scheme 2).

By the interaction of Sr with 1-methylimidazole and *β*-diketonate in absolute ethanol, novel complexes of the formulas $[Sr_2(tfac)_4(Meim)_2(H_2O)_2]$ (**5**) and $(MeimH)_2[Sr(\beta\text{-dike})_4]$ (**6** and **7**; *β*-dike = tfbz or hfac) were formed (Scheme 3). These are very soluble in many organic solvents.

The different structure of **5** with respect to **6** and **7** has been mainly suggested by solid-state ^{13}C and ^{15}N NMR (see below).

Conductivity data of **1**−**3**, **6**, and **7** in acetone indicate the occurrence of equilibrium processes such as those in eqs

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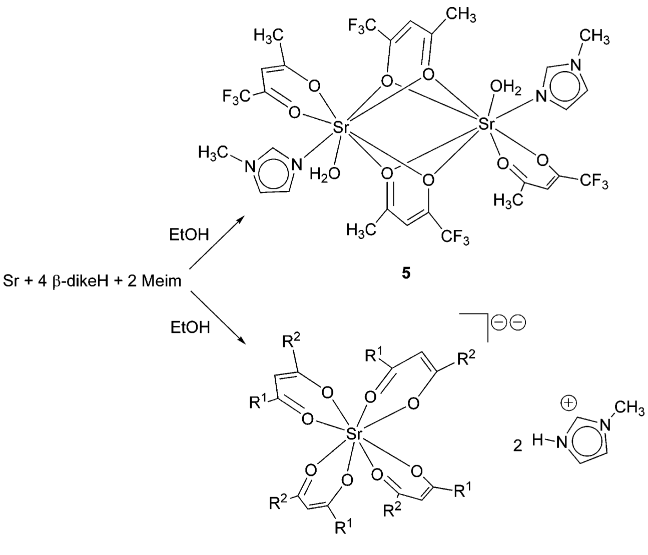
Scheme 3



6, β-dikeH = tfbzH, $R^1 = C_6H_5$, $R^2 = CF_3$
7, β-dikeH = hfacH, $R^1 = R^2 = CF_3$

1−4 or ionic couple formation, which is likely via H-bond interactions involving imidazolates,[24] whereas in a strong polarizing solvent such as DMSO, Λ_m values fall into the range reported for 1:1 species.[24] These values seem to indicate further fragmentation of the dianionic dinuclear species into monoanionic mononuclear ones. Acetone and DMSO solutions of derivative **4** show higher Λ_m values with respect to **1**−**3**, **6**, and **7**. A disruption of the polynuclear solid structure of **4** seems likely in these solvents.

$$(\mathrm{imH_2}^+)_2[\mathrm{Sr_2}(\beta\text{-dike})_6]^{2-} \rightleftharpoons \mathrm{Sr_2}(\beta\text{-dike})_4 + 2(\beta\text{-dikeH}) + 2\mathrm{imH} \tag{1}$$

$$(\mathrm{imH_2}^+)_2[\mathrm{Sr_2}(\beta\text{-dike})_6]^{2-} \rightleftharpoons 2[\mathrm{Sr}(\beta\text{-dike})_4\beta\text{-dikeH}] + 2\mathrm{imH} \tag{2}$$

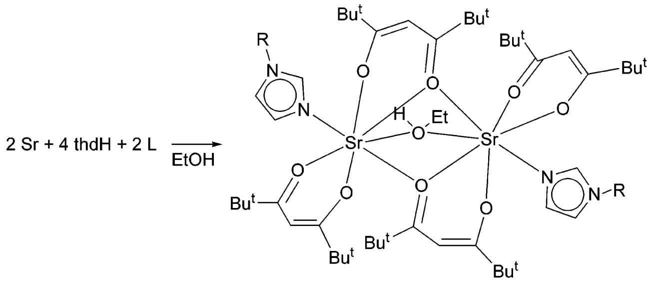
$$(\mathrm{imH_2}^+)_2[\mathrm{Sr_2}(\beta\text{-dike})_6]^{2-} \rightleftharpoons 2[\mathrm{Sr}(\beta\text{-dike})_2(\mathrm{imH})] + 2(\beta\text{-dikeH}) \tag{3}$$

$$(\mathrm{MeimH}^+)_2[\mathrm{Sr}(\beta\text{-dike})_4]^{2-} \rightleftharpoons \mathrm{Sr}(\beta\text{-dike})_2(\mathrm{Meim})_2 + 2(\beta\text{-dikeH}) \tag{4}$$

In contrast with fluorinated diketones, the sterically hindered thd ligand gave rise to the neutral dinuclear complexes **8** and **9**, containing two bridging κ^1,κ^2-O_2-thd, two terminal thd, two monodentate neutral imidazole or methylimidazole groups, and a bridging ethanol molecule (Scheme 4).

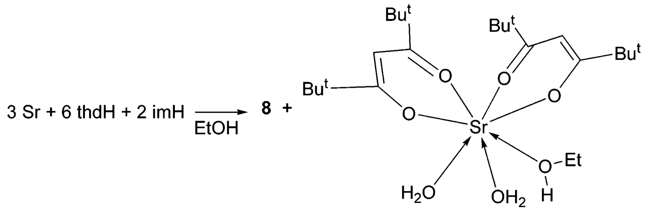
The attempted reaction between Sr, imH, and thdH in ethanol in a 3:2:6 ratio gave a mixture containing derivative **8** and a new compound with the formula $[Sr(thd)_2(H_2O)_2(EtOH)]$ (**10**), which was isolated from recrystallization in chloroform (Scheme 5). **10** contains two bidentate terminal thd, two water molecules, and an ethanol molecule coordinated to the Sr atom.

Scheme 4



8, L = imH, R = H
9, L = Meim, R = Me

Scheme 5



10

All derivatives are quite stable in the solid state; however, prolonged contact with air and moisture leads to slow decomposition and the formation of strontium carbonate. In solution, they slowly undergo hydration, with the subsequent formation of ionic polynuclear species containing carboxylate anions coming from β-diketonate ligand cleavage.

In the IR spectra of **1**−**3** and **5**−**10**, the ν(C═O) + ν(C═C) combination bands of β-diketonates shift to lower frequencies upon complex formation,[25−28] and the broad absorption between 2300 and 3000 cm^{-1}, due to OH···O of the keto−enol form in the IR spectra of free neutral diketones, disappears. This indicates the coordination of the ligands in the anionic bidentate form.[19] The IR spectrum of **4** shows a very large and broad absorption between 2300 and 3600 cm^{-1}, due to water molecules and imidazolium cations involved in H-bond interactions. The presence of several broad ν(COO) bands in the range 1500−1860 cm^{-1} is in accordance with several types of CF_3COO groups differently coordinated to Sr, either as terminal O_2-bidentate, bridging O_2-bidentate, or anionic noncoordinated ligands.[29] In the range of 300−500 cm^{-1}, several medium-to-strong absorptions have been detected and assigned to ν(Sr−O).

The IR spectrum of **5** shows a very large and broad band due to $\nu(H_2O)$ centered at 3458 cm^{-1}. The broad bands observed over 3000 cm^{-1}, in **1**−**3** and **6**−**8**, are due to the N−H bonds of imidazoles or imidazolates likely to be involved in some kind of H bonding (see the the Crystallographic X-ray Studies section). In the far-IR region (300−500 cm^{-1}), new strong absorption bands have always been

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Table 1. Crystallographic Data and Some Details of Data Collection and Refinement for the Sr Complexes

	2	**4**	**6**	**8**	**10**
molecular formula	$C_{60}H_{50}F_{18}N_4O_{14}Sr_2$	$C_{14}H_{14}F_{12}N_4O_{10}Sr$	$C_{48}H_{38}F_{12}N_4O_{14}Sr_2$	$C_{52}H_{90}N_4O_9Sr_2$	$C_{24}H_{48}O_7Sr$
fw	1640.34	713.91	1114.44	1090.52	536.24
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/n$
a/Å	11.760(3)	17.378(4)	17.102(3)	15.808(3)	25.845(5)
b/Å	12.497(3)	15.522(3)	13.460(3)	15.396(3)	9.474(1)
c/Å	13.415(4)	9.966(3)	21.828(4)	25.457(5)	27.667(6)
α/deg	99.87(3)	90	90	90	90
β/deg	93.80(3)	92.57(3)	93.19(3)	100.18(3)	117.08(3)
γ/deg	115.85(2)	90	90	90	90
V/Å^3	1725.7(8)	2686(1)	5017(29	6098(2)	6032(2)
Z	1	4	4	4	8
abs coeff/mm^{-1}	1.660	2.144	1.175	1.188	1.821
cryst size/mm	0.5 × 0.3 × 0.3	0.5 × 0.3 × 0.3	0−40 × 0.25 × 0.25	0.7 × 0.4 × 0.4	0.50 × 0.34 × 0.13
T/K	298	170	170	160	180
θ(max)/deg	28.2	28.1	28.0	28.1	29.2
reflns collected/independent	12572/7644	19384/5962	18756/6007	19720/7286	44563/15501
data/param in refinement	6799/532	5305/499	5064/331	4598/308	10684/644
wR2 (on F^2)	0.0918	0−0861	0.2993	0.2053	0.1342
R1 [$I \geq 2\sigma(I)$]	0.0413	0.0357	0.0839	0.0648	0.0548
largest diff peak and hole/e Å^{-3}	0.506/−0.646	0.403/−0.602	0.748/−0.806	0.517/−0.904	0.803/−0.633

Table 2. Coordination of the Sr atom (Distances in Å) in the Crystal Structures

distance	**2**	distance	**4**	distance	**6**	distance	**8**	distance	**10**, Sr1	**10**, Sr2
Sr−O1	2.707(3)	Sr−O1	2.633(2)	Sr−O1	2.567(4) × 2	Sr−O1	2.466(4)	Sr−O1	2.470(3)	2.526(3)
Sr−O1′	2.835(3)	Sr−O2	2.925(3)	Sr−O2	2.569(4) × 2	Sr−O2	2.541(4)	Sr−O2	2.558(4)	2.464(4)
Sr−O2	2.642(2)	Sr−O3	2.618(2)	Sr−O3	2.684(5) × 2	Sr−O3	2.514(4)	Sr−O3	2.542(4)	2.572(4)
Sr−O2′	2.644(3)	Sr−O4	2.557(2)	Sr−O4	2.529(5) × 2	Sr−O3′	2.596(4)	Sr−O4	2.565(3)	2.559(3)
Sr−O3	2.523(2)	Sr−O5	2.593(2)			Sr−O4	2.470(4)	Sr−O9	2.539(4)	2.574(5)
Sr−O4	2.509(2)	Sr−O6	2.486(3)			Sr−O5	2.667(5)	Sr−O10	2.611(4)	2.615(4)
Sr−O5	2.557(3)	Sr−O9	2.595(2)			Sr−N1	2.674(5)	Sr−O11	2.595(4)	2.583(5)
Sr−O6	2.556(3)	Sr−O10	2.614(2)							

detected upon coordination, likely as a result of ν(Sr−O) stretching modes.[25−28]

Crystallographic X-ray Studies. To investigate the structural typologies of our compounds in the solid state, X-ray single-crystal structural studies were undertaken for derivatives **2**, **4**, **6**, **8**, and **10**. Crystal data and relevant distance lengths are reported in Tables 1 and 2, respectively.

The crystal structure of **2**, $(imH_2)_2[Sr_2(tfbz)_6]\cdot 2H_2O$, contains an anionic dinuclear Sr unit (Figure 1), an imidazolium cation, and a water molecule.

The anion $[Sr_2(tfbz)_6]^{2-}$ is centrosymmetric with a Sr···Sr distance of 3.734 Å. The square-antiprismatic environment of Sr (CN = 8) is composed of four tfbz ligands acting as terminal donors and the remaining two as bridging O_2-μ^4-diketonates.

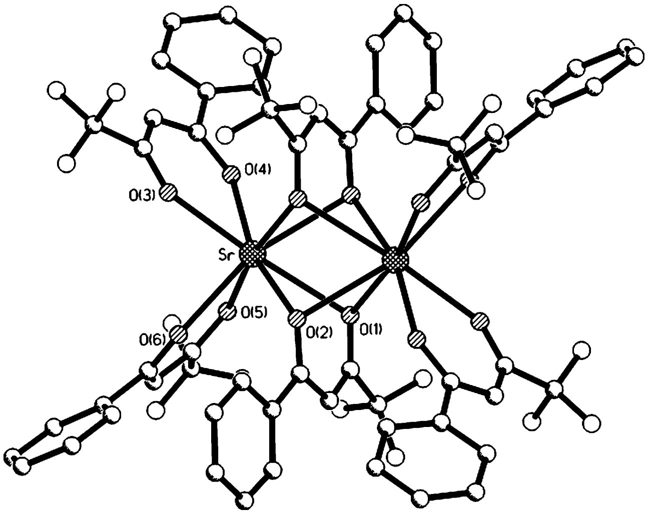

Figure 1. Structure of the anion of derivative **2**.

The average terminal Sr−O$_{tfbz}$ distances, 2.536 Å, are shorter than the bridging Sr−O$_{tfbz}$ ones, 2.707 Å, thus resembling an analogous structure of $(imH_2)_2[Sr_2$(acylpyrazolonate)$_6]$.[18] The imidazolium cations are involved in weak H bonding with an O atom in the dimeric anion [N2−H2···O5, 2.750(8) Å] and with the O atom of water [N1−H1···O7, 2.728(8) Å]. The water molecule is involved in H bonding also with the O atoms of a terminal tfbz, with distances of 2.767 Å (O7−H71···O3) and 2.912 Å (O7−H72···O6).

The compound **4** represents a mixed anionic imidazolium salt containing polynuclear $[Sr(tfa)_3(H_2O)_2]_\infty$ anionic chains with bridging and terminal O_2-bidentate trifluoroacetate groups (Figure 2). The Sr atom is eight-coordinated with two additional terminal water molecules and an average Sr−O distance of 2.628 Å. Imidazolium cations are connected to the anionic chain and the trifluoroacetate anion with N−H···O hydrogen bonds at distances of 2.70−2.91 Å [N1···O8, 2.697(5) Å; N2···O3, 2.853(5) Å; N3···O7, 2.747(5) Å; N4···O10, 2.908(5) Å].

Derivative **6** is also an ionic compound; however, a subtle change in such systems, such as the employment of 1-methyl-substituted imidazole, surprisingly affords a mononuclear $[Sr(tfbz)_4]^{2-}$ anionic complex, consisting of a Sr center surrounded by four terminal bidentate tfbz donors (Figure 3).

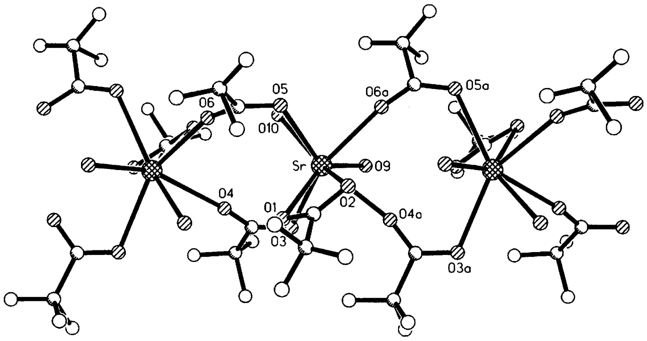

Figure 2. Structure of the polymeric anionic part of derivative **4**.

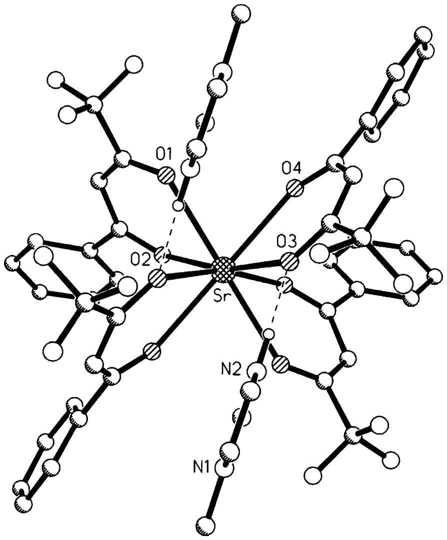

Figure 3. Structure of the anion of derivative **6**.

Two 1-methylimidazolium cations are involved in H-bonding interactions with the O atoms of tfbz in the anionic unit, with the distance N2···O3 being 2.803(10) Å. This causes the elongation of the Sr−O3 distance (2.684 Å) with respect to the other Sr−O_{tfbz} ones (av 2.555 Å), which are very similar to those in the analogous ionic (tmedaH)-$[Sr(tfac)_4]_2$ compound.[15] In both structures **2** and **6**, the metal possesses a CN = 8 in a square-prismatic arrangement independent from the complex nuclearity.

In contrast with **2** and **6**, derivative **8** is composed of discrete dinuclear $[Sr_2(thd)_4(imH)_2(EtOH)]$ molecules. Each Sr atom is surrounded by two O atoms from a terminal thd, two O atoms from a bridging η^1,η^2-O_2-thd, an O atom by a second bridging η^1,η^2-O_2-thd, an O atom of a bridging EtOH molecule, and a N atom from a terminal imidazole (Figure 4).

Also, this structure is centrosymmetric like that of **2**, with the Sr···Sr distance being 3.747 Å. Such structural behavior is well-known in alkaline-earth β-diketonate chemistry such as, for example, in the structure of $[Sr(thd)_2(diethylenetriamine)]_2$.[30] However, in compound **8**, the Sr atom is only seven-coordinated, thus demonstrating that a CN lower than 8 can occur in the structures of Sr complexes.[15] As in the structure of **6**, the average distances of the terminal Sr−O_{thd} groups are shorter than those in the bridging ones, as expected, and the bridging Sr−O_{EtOH} distance is the longest. The Sr−N distance (2.674 Å) is shorter than those found in previous Sr(thd) derivatives containing poly(ethyleneamines) as ancillary donors.[27]

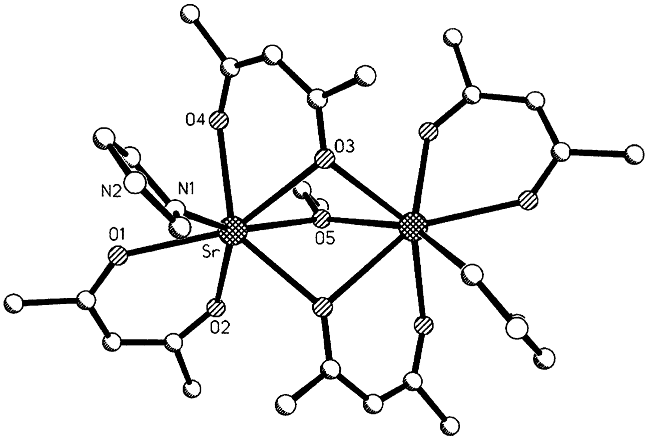

Figure 4. Molecular structure of derivative **8**.

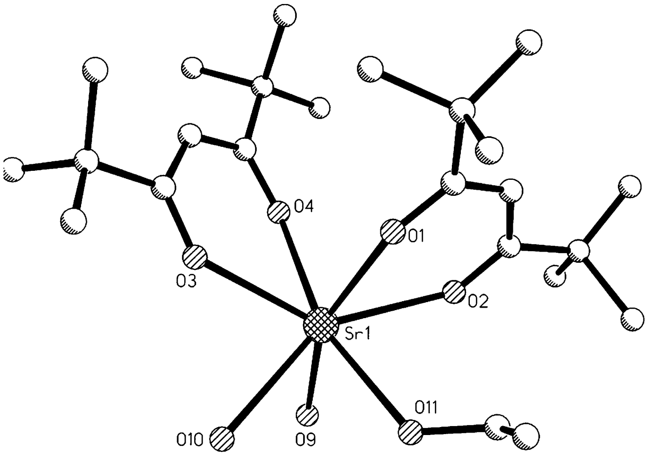

Figure 5. Molecular structure of derivative **10**.

Crystals of compound **10** contain discrete mononuclear $[Sr(thd)_2(H_2O)_2(EtOH)]$ units (Figure 5) similar to those found in $[Ba(thd)_2(H_2O)_2(MeOH)_2]$.[14] This result seems to indicate the weakness of the Sr ← N bonding and is in full accordance with Pearson's theory of soft and hard acids and bases.

Both the Sr1 and Sr2 atoms in the two crystallographically independent molecules are surrounded by seven O atoms each from two thd ligands, two water molecules, and an ethanol molecule. The average Sr−O distance, 2.555 Å, is shorter than that of the mononuclear complex **5** (2.587 Å). The very irregular arrangement of O donor atoms around the Sr atoms can be explained by the existence of the very weak additional bonding of O9 to the Sr atom of the neighboring molecule at the distance of 3.17 Å. In this way, weakly bonded infinite chains of molecules are formed.

Solid-State NMR Studies. The solid-state ^{13}C and ^{15}N NMR data of the Sr derivatives, except for **7**, which is in a liquid form, and **10**, which does not contain N-donor ligands and which was obtained in poor yield, are listed in Table 3. The ^{13}C NMR spectra (see Figures 6, 8, and 10) are

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(30) Park, J. W.; Kim, J. T.; Koo, S. M.; Kim, C. G.; Kim, Y. S. *Polyhedron* **2000**, *19*, 2547−2555.

Table 3. ^{13}C and ^{15}N NMR Chemical Shift Data for Compounds **1**−**9**

compound	δ ^{13}C (ppm)	δ ^{15}N (ppm)
$(imH_2)_2[Sr_2(tfac)_6]$ (**1**)	198.0 CH_3-C_q-O 169.4 CF_3-C_q-O 166.8 CF_3-C_q-O 133.0 N−CH−N imH_2 119.8 CF_3 and imH_2 94.2 CH 28.0 CH_3	151.2 N−H (imH_2)
$(imH_2)_2[Sr_2(tfbz)_6]$ (**2**)	190.7 Ph−C_q−O 187.5 Ph−C_q−O 169.7 CF_3-C_q-O 140.5 C_q (C_6H_5) 137.5 N−CH−N imH_2 129.2 C_6H_5 and imH_2 119.7 CF_3 imH_2 92.7 CH 90.6 CF_3	148.7 N−H (imH_2)
$(imH_2)_2[Sr_2(hfac)_6]$ (**3**)	177.7 CF_3-C_q-O 130.7 N−CH−N imH_2 118.2 CF_3 and imH_2 88.2 CH	146.2 N−H (imH_2)
$[Sr_2(tfac)_4(Meim)_2(H_2O)_2]$ (**5**)	199.3 CH_3-C_q-O 170.4 CF_3-C_q-O 138.1 N−CH−N ($imHCH_3$) 126.7 imH_2 122.7 CF_3 and imH_2 95.8 CH 34.4 sh CH_3 ($imHCH_3$) 32.1 sh CH_3 ($imHCH_3$) 28.8 CH_3	219.6 N-Sr 135.8 N−CH_3 123.2 N−CH_3
$(MeimH)_2[Sr(tfbz)_4]$ (**6**)	191.7 Ph−C_q−O 189.1 Ph−C_q−O 169.3 CF_3-C_q-O 140.7 C_q (C_6H_5) 129.3 C_6H_5 and $imHCH_3$ 127.3 C_6H_5 and $imHCH_3$ 122.8 sh (119.7 NQS) CF_3 90.9 CH 34.4 CH_3 ($imHCH_3$)	142.6 N−CH_3
$[Sr_2(thd)_4(imH)_2(EtOH)]$ (**11**)[a]	203.0 202.0 199.6 136.9 N−CH−N imH 134.9 N−CH−N imH 127.4 imH 119.2 imH 117.4 imH 91.1 CH 41.9 C_q Bu^t 29.8 Me Bu^t	221.4 N−Sr 218.6 N−Sr 140.1 N−H 138.0 sh N−H

[a] See text.

characterized by peaks at about 28 and 35 ppm, which are associated with the methyl and methylimidazole moieties, respectively. The CF_3 groups give rise to a broader peak centered in the range 118−122 ppm, due to indirect coupling with fluorine atoms, while the imidazole carbons fall in the region between 115 and 144 ppm (the latter assigned to the N−*C*H−N carbon). The high-frequency region is dominated by ligand resonances: at about 169, 189, and 198 ppm fall CF_3-C_q-O, Ph−C_q−O, and CH_3-C_q-O, respectively, while the CH carbon can be found at 90 ppm. In the ^{15}N NMR spectra (see Figures 7, 9, and 11), the peaks at about 137.8 and 226.1 ppm are assigned to the N−H and −N═ atoms, respectively. This is straightforward on the basis of the previously reported data.[31]

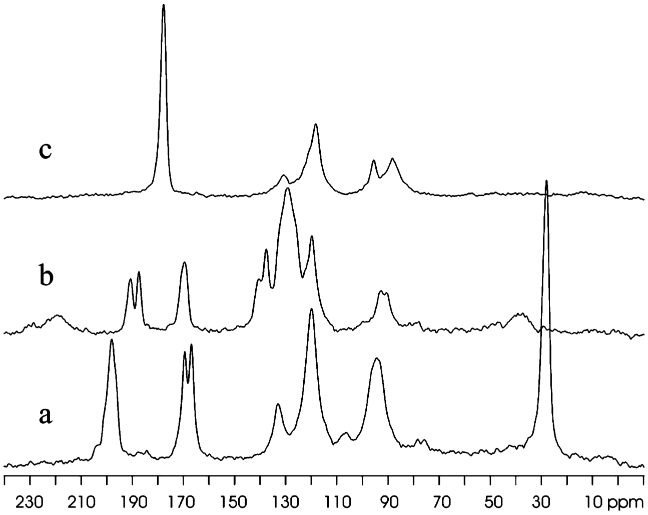

Figure 6. CPMAS ^{13}C NMR spectra of derivatives **1** (a), **2** (b), and **3** (c) recorded at 67.9 MHz, at a spinning speed of about 6.0 kHz.

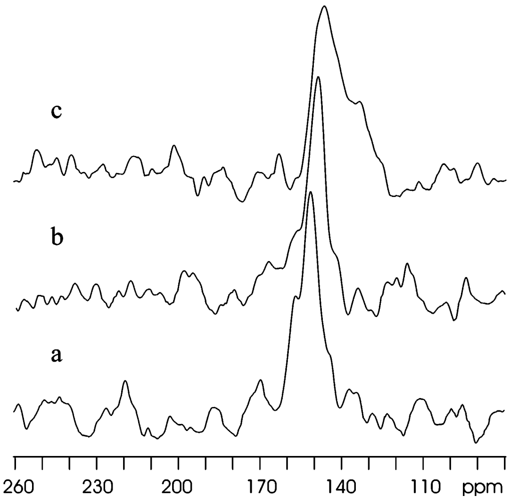

Figure 7. CPMAS ^{15}N NMR spectra of derivatives **1** (a), **2** (b), and **3** (c) recorded at 27.25 MHz, at a spinning speed of 5.0 kHz.

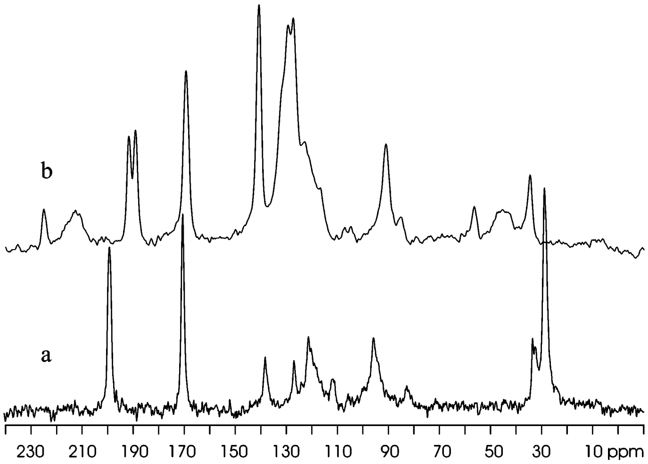

Figure 8. CPMAS ^{13}C NMR spectra of derivatives **5** (a) and **6** (b) recorded at 67.9 MHz, at a spinning speed of about 6.0 kHz.

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(31) Ueda, T.; Masui, H.; Nakamura, N. *Solid State NMR* **2001**, *20*, 145−155.

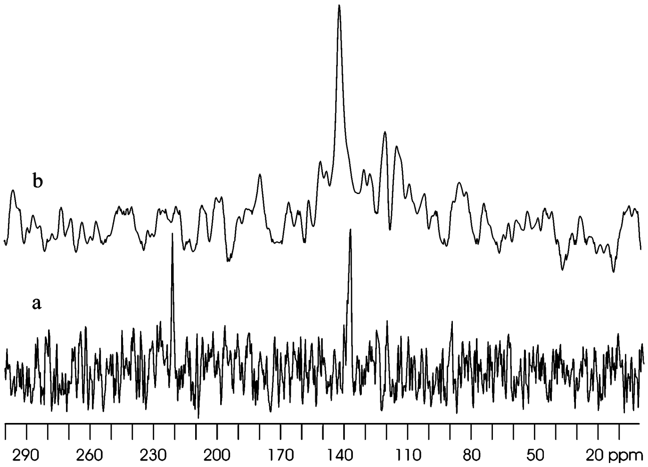

Figure 9. CPMAS ^{15}N NMR spectra of derivatives **5** (a) and **6** (b) recorded at 27.25 MHz, at a spinning speed of 5.0 kHz.

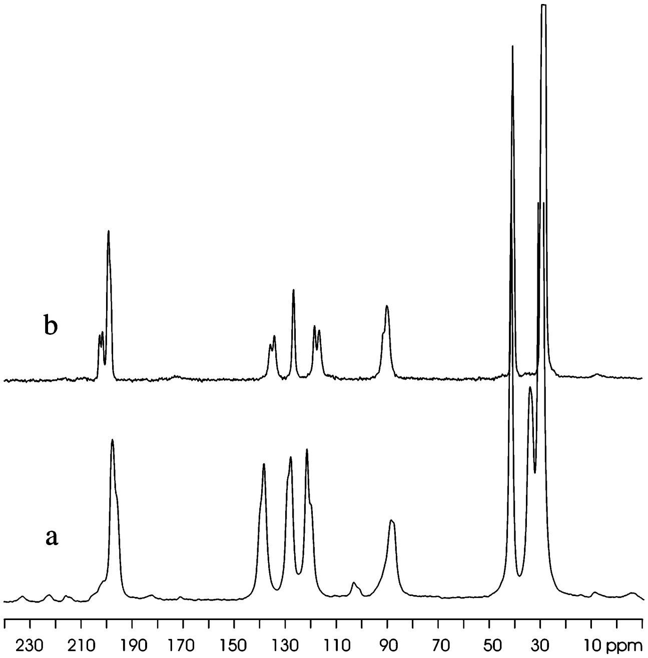

Figure 10. CPMAS ^{13}C NMR spectra of derivatives **9** (a) and **11** (b) recorded at 67.9 MHz, at a spinning speed of about 6.0 kHz.

An interesting characteristic of the ^{13}C NMR spectrum of **1** (Figure 6a) is the presence of two signals in the relative ratio 1:1 for the CF_3-C_q-O groups at 169.4 and 166.8 ppm, whereas only a single peak can be detected at 198.0 ppm for the CH_3-C_q-O carbons, probably as a result of casual overlapping. Then different CF_3-C_q-O groups in the unit cell can be postulated on the basis of the ^{13}C NMR data. A resonance at 151.2 ppm is detected in the ^{15}N NMR spectrum (Figure 7a) for the two equivalent N−H units of the imidazole ring.

^{13}C NMR data similar to those of derivative **1** are observed for compound **2** (Figures 6b and 7b), but now two signals are present for the $Ph-C_q-O$ moieties at 190.7 and 187.5 ppm, whereas there is only one resonance at 169.7 ppm for the CF_3-C_q-O groups. This is in agreement with the presence of a single signal for the six CF_3-C_q-O groups and by the occurrence of two different $Ph-C_q-O$ carbon atoms whose difference depends on the relative position of the phenyl moiety in space, as observed in the single-crystal X-ray structure (Figure 1). The former $Ph-C_q-O$ peak is due to the two tfbz ligands bridging the metal atoms, while the latter is attributed to the four terminal tfbz symmetric ligands. The ^{15}N NMR spectrum of product **2** (Figure 7b) shows a single resonance at 148.7 ppm in agreement with the presence of two crystallographically identical imidazole molecules observed in the X-ray structure. It is worth noting that both N atoms are involved in intermolecular N−H···O H-bond interaction. Although the N atoms are bonded to different moieties, to an O atom of a CF_3-C_q-O moiety and to a water molecule O, respectively, the two interactions appear to be really quite similar both for the N···O atom distance (2.749 and 2.730 Å) and for the chemical shift.

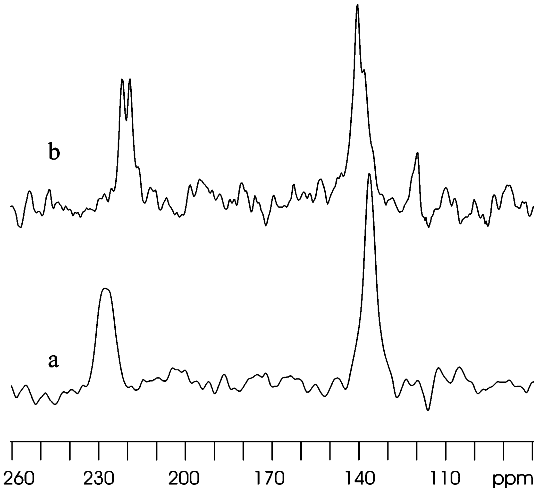

Figure 11. CPMAS ^{15}N NMR spectra of derivatives **9** (a) and **11** (b) recorded at 27.25 MHz, at a spinning speed of about 5.0 kHz.

The presence of only four signals, observed in the ^{13}C NMR spectrum of compound **3** (Figure 6c), at 177.7, 130.7, 118.2, and 88.2 ppm, suggests a high symmetry for the complex. Indeed, because the R1 and R2 substituents are identical, a D_{2h} symmetry is present in the molecule. The resonances are attributed to the hfacH C_q, to the N−CH−N (imH_2), to the CF_3, and to the CH carbons, respectively.

The ^{15}N NMR spectrum (Figure 7c), as for compounds **1** and **2**, is characterized by a single resonance at 146.2 ppm for the four N atoms. Nevertheless, in this case the signal is broader and even more shifted to lower frequency (toward the free imidazole N−H signal) than the other derivatives. It is interesting to analyze these shifts in terms of the H-bond interaction: indeed, it is known that, in the case of aromatic molecules, the N resonance is expected in the low-frequency region when the lone pair is involved in bonding by protonation.[32] In this case, the observed high-frequency shift of 4.5 ppm on passing from **3** to **1** indicates a progressive deprotonation of the N imidazole: in other words, the substituent electronic effects and the crystal packing in **1**

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(32) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience: New York, 1979.

elongate the N−H distance with respect to **3**, where the situation is similar to that observed for free imidazole.

The ^{13}C NMR spectrum of **5** (Figure 8a) is characterized by a peak at 199.3 ppm for the CH_3-C_q-O groups and by a signal at 170.4 ppm for the CF_3-C_q-O moieties. This is evidence of the high symmetry of the ligands around the metal atom. The particular features of compound **5**'s ^{15}N NMR spectrum (Figure 9a) are the occurrence of a peak at 219.6 ppm. We reasonably attribute this resonance to a Sr−N nitrogen atom because it is well-known that the coordination of a N atom to a metal leads to very wide shift.[32,33] Furthermore, we observe a similar peak for compound **8** confirmed by the X-ray structure (see below). This is clear evidence of the coordination of both imidazole molecules to the metal center. Thus, the structure of compound **5** hypothesized from solid-state NMR data is quite different from the those of the homologues **6** and **7**. Another signal is present at 135.8 ppm, attributed to the $N-CH_3$ nitrogen atoms.

As reported above, the special feature of compound **6** is the presence of two imidazole molecules H-bonded through N−H···O2 and N−H···O3 interactions (see Figure 3). It is worth noting that the $Ph-C_q-O$ carbon atom is more influenced by the H-bond interaction than the CF_3-C_q-O carbon atom. This is confirmed by the larger difference in the C_q-Ph distances (1.480 Å for the H-bonded ligand and 1.503 Å for the normal ligand) with respect to the C_q-CF_3 distances (1.538 Å for the H-bonded ligand and 1.528 Å for the normal ligand). This difference is also stressed by the high symmetry of the CF_3 group with respect to rotation about the C_q-CF_3 bond, compared with the phenyl asymmetry. Such observations indicate the presence of two different $Ph-C_q-O$ groups and four equivalent CF_3-C_q-O groups per molecule, which cause two signals at 191.7 and 189.1 ppm for the former and only one at 169.3 ppm for the latter in the cross-polarization magic-angle-spinning (CP-MAS) ^{13}C NMR spectrum (Figure 8b). Although several attempts have been performed with different experimental conditions (variation in the temperature, contact time, pulse delay, etc.), the ^{15}N NMR spectrum (Figure 9b) shows only one resonance at 142.6 ppm. We assigned the peak to the N−H nitrogen atoms that are involved in a N−H···O hydrogen bond. Comparing this chemical shift value with those of derivatives **1**−**3**, we conclude that, for sample **6**, the proton is closer to the N atom, leading to a weaker and longer H bond (N···O, 2.803 Å). The lack of other resonances in the ^{15}N NMR spectrum is probably due to the unfavorable nuclear Overhauser effect because the negative γ value of ^{15}N can annihilate the signal.[32]

Attempts to perform the ^{13}C NMR spectrum of compound **8** result in a structural change in the sample. The spectrum suggests a different structure with respect to that observed from the X-ray studies. There is no evidence of the ethanol ligand probably because, being lightly bonded, it evaporates during the rotor spinning. Hereafter, we refer to this new derivative as **11**. In the carbonyl region (Figure 10b), **11** exhibits two small and one more intense resonance at 203.0, 202.0, and 199.6 ppm respectively in the relative intensity 1:1:6. The imidazole region shows five resonances (one of which has double intensity) for the C atoms in the ^{13}C NMR spectrum, suggesting the presence of two independent imidazole molecules in the asymmetric unit cell. This is confirmed by the ^{15}N NMR spectrum (Figure 11b), which is characterized by two close resonances at 221.4 and 218.6 ppm for the N−Sr atoms and by a peak at 140.1 ppm (with a shoulder at 138 ppm) for the N−H nitrogen atoms. Although it is not possible to propose a structure based only on the solid-state NMR data, we conclude that derivative **11** is a Sr_2 complex with four dike and two imidazole ligands and has a lower symmetry with respect to compound **8**.

Derivative **9** presents some differences in the ^{13}C NMR spectrum (Figure 10a) with respect to sample **11**; indeed, it seems to have a higher symmetry. This is confirmed by the presence of one signal at 197.7 ppm for all thd C_q carbon atoms, one signal (without a shoulder) at 88.5 ppm for the thd CH carbon atoms, and three peaks at 138.4 (N−CH−N), 127.9, and 121.5 ppm for the two equal imidazole molecules. Unfortunately, there is no clear evidence of the ethanol ligand whose signals would fall at 41.3 ppm (CH_2) and at 29.7 ppm (CH_3) under the *tert*-butyl peaks. The ^{15}N NMR spectrum (Figure 11a) presents two resonances at 228.1 and 136.4 ppm attributed to the N−Sr and $N-CH_3$ atoms, respectively.

Solution NMR and Electrospray Ionization Mass Spectrometry (ESIMS) Studies. The ^{1}H, $^{19}F\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra, recorded in acetone-d_6, show all of the expected resonances in accordance with the formulation proposed on the basis of previous analytical and spectroscopic data. However, in the NMR spectra of compounds **1**−**3**, **5**, **8**, and **9**, only one set of signals has been detected at room temperature, thus indicating exchange processes between terminal and bridging β-diketonate ligands around the metal centers in solution. Another possibility is that the dinuclear units break, giving rise to mononuclear fragments with equivalent β-diketonate ligands. The unique doublet for H_4 and H_5 of the imidazoles and the integration of the broad signal for N−H indicate the presence of imidazolium units in **1**−**3**.[18] The same pattern has also been observed in the ^{1}H NMR spectra of **1** and **2** recorded in DMSO-d_6. This is in accordance with conductivity data, typical of 1:1 electrolytes.[24] In the low-temperature ^{1}H NMR spectra (193 K) of **1** and **3** recorded in acetone-d_6, one set of broad resonances arising from β-diketonate moieties was detected. The broadening could be due to an unresolved splitting of signals for the terminal and bridging β-diketonate ligands or to the presence of different neutral species such as those hypothesized in eqs 1−3 by conductivity measurements. Instead, the azole protons give rise to two resonances, one for H_4 and H_5 and the other for H_2, in accordance with the presence of the imidazolium cation.

In the ^{1}H NMR spectra of compounds **6** and **7**, two resonances due to H_4 and H_5 and a broad one due to N−H give evidence for the formation of the 1-methylimidazolium

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(33) Strohmeier, M.; Orendt, A. M.; Facelli, J. C.; Solum, M. S.; Pugmire, R. J.; Parry, R. W.; Grant, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 7114−7120.

cation. Instead, the two doublets for H_4 and H_5 of the imidazole in the ^{1}H NMR spectra of compounds **8** and **9** indicate the presence of neutral azoles in these compounds. In all cases, H resonances fall at lower fields with respect to starting neutral O_2- and N-donor ligands, indicating the existence of the complexes in an acetone solution.

The ^{19}F NMR spectra of compounds **1**−**3** and **5**−**7** show a unique resonance at ca. −76 ppm, further confirming the fluxionality of the complexes at room temperature previously hypothesized on the basis of the ^{1}H NMR spectra. The ^{19}F NMR spectra of derivative **4**, carried out in acetone-d_6 and DMSO-d_6, show two different resonances between −69 and −78 ppm, due to Sr-bonded and anionic uncoordinated tfa ligands, respectively.

The ^{13}C NMR spectra show a unique set of β-diketonate resonances that fall at lower fields with respect to the neutral free ligands. The C_4 and C_5 of the azoles resonate at the same frequency for compounds **1**−**3**, whereas two signals have been detected for 1-methylimidazolium in compounds **6** and **7** and for the neutral imidazole in compounds **8** and **9**, as expected. The $^1J_{C-F}$ values are in the range 280−290 Hz in **1**−**3** and **5**−**7**. These coupling constants are similar to those found in other alkaline-earth compounds containing the same donors.[14,15]

Negative ESIMS spectra of compounds **1**−**3** (the most relevant data are reported in the Experimental Section) indicate that, in solution, the dinuclear $[Sr_2(\beta\text{-dike})_6]^{2-}$ anion of these derivatives undergoes fragmentation into two $\{Sr(\beta\text{-dike})_3\}^-$ units and loses a β-diketonate with the formation of the $\{Sr_2(\beta\text{-dike})_5\}^-$ species. This is in accordance with Λ_m values in DMSO. Moreover, peaks of lower intensity have been found because of the association of Sr fragments with the formation of $\{Sr_3(\beta\text{-dike})_7\}^-$.

In the negative ESIMS spectrum of compounds **5**−**7**, several species have been identified, such as the species $\{Sr(\beta\text{-dike})_3\}^-$ arising from the loss of one β-diketonate donor from the parent $[Sr(\beta\text{-dike})_4]^{2-}$. Also, aggregates such as $\{Sr_2(\beta\text{-dike})_5\}^-$, $\{Sr_3(\beta\text{-dike})_7\}^-$, $\{Sr(\beta\text{-dike})_2(tfa)^-$, $\{Sr_2(\beta\text{-dike})_4(tfa)\}^-$, and $\{Sr_2(\beta\text{-dike})_3(tfa)_2\}^-$ have been found; the tfa arises from the cleavage of a fluorinated β-diketonate ligand in an acetonitrile solution.

It was not possible to perform the ESIMS spectrum of compounds **4** and **8**−**10** because of their limited solubility in acetonitrile. However, when an acetonitrile sample of **3** is left in contact with air for 1 week and then its negative spectrum is recorded, some new peaks emerged, clearly as a result of the cleavage of (hfac)$^-$ ligands and the formation of (tfa)$^-$ compounds. Species such as $\{Sr(hfac)_2(tfa)\}^-$, $\{Sr_2(hfac)_2(tfa)\}^-$, $\{Sr_3(hfac)_6(tfa)\}^-$, and $\{Sr_3(hfac)_5(tfa)_2\}^-$ were identified as successive products of the decomposition pattern of **3** with the formation of derivative **4**.

Conclusion

The interaction of the Sr metal with β-diketones and imidazoles results in the formation of four different typologies of compounds, depending on the nature of the β-diketone and imidazole employed: ionic species $(MeimH)_2[Sr(\beta\text{-dike})_4]$ containing an anionic mononuclear $Sr(\beta\text{-dike})_4$ fragment, ionic species $(imH_2)_2[Sr_2(\beta\text{-dike})_6]$ with anionic dinuclear $(\beta\text{-dike})_2Sr(\mu^2\text{-}\beta\text{-dike})Sr(\beta\text{-dike})_2$ units, neutral dinuclear derivatives with coordinated azoles of the type $Sr_2(\beta\text{-dike})_4(Meim)_2(H_2O)_2$ with two bridging μ^2-β-dike ligands, and $Sr_2(\beta\text{-dike})_2(\mu^1\text{-}\beta\text{-dike})_2(imH)_2(\mu^2\text{-EtOH})$ with two bridging μ^1-β-dike ligands. While the ionic species **1**−**3**, **6**, and **7** were obtained only with fluorinated β-diketonate ligands, neutral derivatives **5**, **8**, and **9** were formed when the tfac or thd donors were employed. The thd ligand is sterically very hindered and is likely to be responsible for the prevention of steric crowding on the Sr atom, giving derivatives **8** and **9** with lower metal CN (7 instead of 8). The lack of the imH ligand with respect to the amount of Sr again gives derivative **8**, together with a minor product (derivative **10**) containing only thd, H_2O, and EtOH ligands coordinated to Sr. Derivative **5** is a neutral dinuclear species, whose solid-state structure has been deduced by solid-state ^{13}C and ^{15}N NMR, further confirming the potentials of this spectroscopic method when X-ray structural data are not available. Also, compound **4**, which is the decomposition product of derivative **3**, has been isolated and fully characterized, consisting of polynuclear $[Sr(tfa)_3(H_2O)_2]_\infty$ anionic chains and of imidazolium cations connected to the anionic chain and trifluoroacetate anions through N−H···O hydrogen bonds.

Some preliminary results[34] indicate that derivatives **8** and **9** possess interesting physicochemical features, such as good volatility and correct thermal stability in the gas phase, making them suitable as molecular precursors in CVD experiments. They are currently under investigation in order to optimize experimental conditions for the deposition of Sr- and Ti-containing mixed oxides.

Experimental Section

Materials and Methods. All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. Solvent evaporations were always carried out under vacuum using a rotary evaporator. The samples for microanalysis were dried in vacuo to a constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. All solvents were degassed with dry nitrogen prior to use. Elemental analyses (C, H, and N) were performed in-house with a Fison Instrument 1108 CHNS−O elemental analyzer. IR spectra were recorded from 4000 to 200 cm^{-1} with a Perkin-Elmer system 2000 Fourier transform IR instrument. ^{1}H, ^{19}F, and ^{13}C{^{1}H} NMR spectra were recorded on a VXR-300 Varian instrument operating at room temperature (300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 282.2 MHz for ^{19}F). H and C chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$, whereas F chemical shifts are reported in ppm from $CFCl_3$ (^{1}H, ^{19}F, and ^{13}C NMR calibration by an internal deuterium solvent lock). Peak multiplicities are abbreviated as follows: singlet, s; doublet, d; triplet, t; multiplet, m. Melting points are uncorrected and were taken on an Stuart SMP3 scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_m, reported as Ω^{-1} cm^2 mol^{-1}) of acetone or DMSO solutions of complexes were taken with a Crison CDTM 522 conductimeter at

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(34) Battiston, G. A.; Gerbasi, R.; Carta, G.; Marchetti, F.; Pettinari, C.; Barreca, D.; Maragno, C.; Tondello, E. *Proceedings of the SAMIC 2005*, Brixen, Italy, Dec 4−7, 2005; University of Padua: Padua, 2005; p P11.

room temperature. The negative ESIMS spectra were obtained with a Hewlett Packard series 1100 MSI detector spectrometer using an acetonitrile mobile phase. Solutions (3 mg mL^{-1}) for ESIMS were prepared using reagent-grade acetonitrile. For the ESIMS data, masses and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.[35] Peaks containing Sr(II) ions are identified as the center of an isotopic cluster. Solid-state ^{13}C and ^{15}N NMR studies were performed on a JEOL 270GSX equipped with a Doty CPMAS probe. The ^{13}C and ^{15}N NMR resonances at the magnetic field of 6.34 T are 67.8 and 27.25 MHz, respectively. The samples were spun in a 5-mm zirconia rotor at about 5000−6000 Hz. For both ^{13}C and ^{15}N NMR spectra, a standard cross-polarization experiment with a 90° pulse to flip the magnetization back was used with a recycle delay of about 10 s and a contact time of about 3500−4000 μs. For the ^{13}C NMR characterization, nonquaternary-suppression (NQS) experiments have been performed. For the ^{13}C NMR spectra, a 90° pulse of 3.5 μs with a spectral width of 40 kHz for about 1000−1500 transients was used. A 90° pulse of 4.7 μs was used for the ^{15}N NMR experiments with a 32-kHz spectral width during 3000−4000 scans. ^{15}N NMR chemical shifts were referenced via the resonance of solid $(NH_4)_2SO_4$ (−355.8 ppm with respect to CH_3NO_2), while the ^{13}C NMR chemical shift was referenced via the methyl hexamethylbenzene peak set at 17.4 ppm with respect to the tetramethylsilane resonance.

Syntheses of Complexes. Preparation of $(imH_2)_2[Sr_2(tfac)_6]$ (1). Imidazole (imH; 136 mg, 2 mmol) and 1,1,1-trifluoromethyl-2,4-pentanedione (tfacH; 925 mg, 6 mmol) were dissolved in 20 mL of absolute ethanol. Then Sr (powder, 175 mg, 2 mmol) was added. Upon stirring and gentle heating (ca. 50 °C), the Sr dissolved and a colorless precipitate slowly formed. After 1 h, the mixture was filtered off and the precipitate was washed with diethyl ether (10 mL) and dried under reduced pressure to constant weight and is shown to be compound **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Yield: 77%. Mp: 195−197 °C. Elem anal. Calcd for $C_{36}H_{34}F_{18}N_4O_{12}Sr_2$: C, 35.10; H, 2.78; N, 4.55. Found: C, 34.78; H, 2.74; N, 4.13. Λ_m (acetone, 298 K): 9.9 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 66.8 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3320m, 3156m, 3098w ν(N−H), 1644vs, 1624s, 1600m, 1522vs ν(C=O) + ν(C=C), 395vs ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.97s (18H, CH_{3tfac}), 5.57s (6H, CH_{tfac}), 7.35d (4H, H_4 and H_5 of imH_2), 8.34s (2H, H_2 of imH_2), 8.90br (4H, N*H* of imH_2). ^{1}H NMR (acetone-d_6, 193 K): δ 1.90br (18H, half-height = 30 Hz, CH_{3tfac}), 4.20br (4H, N*H* of imH_2), 5.41br (6H, CH_{tfac}), 7.73br, 7.90br (4H, H_4 and H_5 of imH_2), 9.05br, 9.10br (2H, H_2 of imH_2). ^{1}H NMR (DMSO-d_6, 298 K): δ 2.00s (18H, CH_{3tfac}), 5.24s (6H, CH_{tfac}), 7.41d (4H, H_4 and H_5 of imH_2), 8.00br (4H, N*H* of imH_2), 8.49s (2H, H_2 of imH_2). ^{19}F NMR (acetone-d_6, 298 K): δ −76.8s (CF_{3tfac}). ^{19}F NMR (acetone-d_6, 193 K): δ −74.8br (CF_{3tfac}). ^{13}C NMR (acetone-d_6, 298 K): δ 29.5 (s, CH_{3tfac}), 94.3 (s, CH_{tfac}), 120.3 (q, $^1J_{C-F}$ = 286.4 Hz, CF_{3tfac}), 121.2 (s, C_4 and C_5 of imH_2), 136.3 (s, C_2 of imH_2), 169.8 (q, $^2J_{C-F}$ = 30.0 Hz, *C*O−CF_{3tfac}), 196.3 (s, *C*OCH_{3tfac}). ESIMS (MeCN): *m/z* (%) 547 (100) $\{Sr(tfac)_3\}^-$, 941 (75) $\{Sr_2(tfac)_5\}^-$, 1335 (18) $\{Sr_3(tfac)_7\}^-$.

Preparation of $(imH_2)_2[Sr_2(tfbz)_6]$ (2). Compound **2** was synthesized similarly to **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Slow evaporation of the chloroform solution of **2** gave colorless crystals suitable for X-ray diffraction studies. Yield: 85%. Mp: 175−178 °C. Elem anal. Calcd for $C_{66}H_{46}F_{18}N_4O_{12}Sr_2$: C, 49.41; H, 2.89; N, 3.49. Found: C, 49.18; H, 2.80; N, 3.31. Λ_m (acetone, 298 K): 17.2 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 39.0 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3365m, 3153m ν(N−H), 1635vs, 1612s, 1572s, 1528vs ν(C=O) + ν(C=C), 424m, 356s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 6.44s (6H, CH_{tfbz}), 7.27d (4H, H_4 and H_5 of imH_2), 7.40−7.55m, 7.99d (30H, C_6H_{5tfbz}), 8.18s (2H, H_2 of imH_2), 9.15br (4H, N*H* of imH_2). ^{1}H NMR (DMSO-d_6, 298 K): δ 6.13s (6H, CH_{tfbz}), 7.45m, 7.86d (30H, C_6H_{5tfbz}), 7.53d (4H, H_4 and H_5 of imH_2), 8.76s (2H, H_2 of imH_2), 9.80br (4H, N*H* of imH_2). ^{19}F NMR (acetone-d_6, 298 K): δ −76.8s (CF_{3tfbz}). ^{13}C NMR (acetone-d_6, 298 K): δ 90.9 (s, CH_{tfbz}), 120.3 (s, C_4 and C_5 of imH_2), 119.6 (q, $^1J_{C-F}$ = 285.9 Hz, CF_{3tfbz}), 127.5, 128.4, 131.4, 139.9 (s, C_6H_{5tfbz}), 135.9 (s, C_2 of imH_2), 171.2 (q, $^2J_{C-F}$ = 31.2 Hz, *C*O−CF_{3tfbz}), 187.6 (s, *C*OC_6H_{5tfbz}). ESIMS (MeCN): *m/z* (%) 733 (100) $\{Sr(tfbz)_3\}^-$, 1251 (42) $\{Sr_2(tfbz)_5\}^-$, 1769 (12) $\{Sr_3(tfac)_7\}^-$.

Preparation of $(imH_2)_2[Sr_2(hfac)_6]$ (3). Compound **3** was synthesized similarly to **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Yield: 83%. Mp: 230−234 °C dec. Elem anal. Calcd for $C_{36}H_{16}F_{36}N_4O_{12}Sr_2$: C, 27.79; H, 1.04; N, 3.60. Found: C, 28.15; H, 1.02; N, 3.96. Λ_m (acetone, 298 K): 22.1 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 42.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3158m ν(N−H), 1660vs, 1642s, 1598s, 1531vs ν(C=O) + ν(C=C), 449m, 364s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 5.81s (6H, CH_{hfac}), 7.84d (4H, H_4 and H_5 of imH_2), 9.15s (2H, H_2 of imH_2), 10.50br (4H, N*H* of imH_2). ^{1}H NMR (acetone-d_6, 193 K): δ 5.68br (6H, CH_{hfac}), 7.91d (4H, H_4 and H_5 of imH_2), 9.23s (2H, H_2 of imH_2), 14.30br (4H, N*H* of imH_2). ^{19}F NMR (acetone-d_6, 298 K): δ −76.6s (CF_{3hfac}). ^{19}F NMR (acetone-d_6, 193 K): δ −76.0br (CF_{3hfac}). ^{13}C NMR (acetone-d_6, 298 K): δ 86.7 (s, CH_{hfac}), 119.3 (q, $^1J_{C-F}$ = 287.4 Hz, CF_{3hfac}), 120.6 (s, C_4 and C_5 of imH_2), 135.8 (s, C_2 of imH_2), 175.3 (q, $^2J_{C-F}$ = 31.4 Hz, *C*O−CF_{3hfac}). ESIMS (MeCN): *m/z* (%) 709 (100) $\{Sr(hfac)_3\}^-$, 1212 (22) $\{Sr_2(hfac)_5\}^-$, 1713 (8) $\{Sr_3(hfac)_7\}^-$. ESIMS (MeCN) performed after a week: *m/z* (%) 615 (12) $\{Sr(hfac)_2(tfa)\}^-$, 709 (100) $\{Sr(hfac)_3\}^-$, 1116 (5) $\{Sr_2(hfac)_4(tfa)\}^-$, 1212 (22) $\{Sr_2(hfac)_5\}^-$, 1525 (4) $\{Sr_3(hfac)_5(tfa)_2\}^-$, 1619 (8) $\{Sr_3(hfac)_6(tfa)\}^-$, 1713 (6) $\{Sr_3(hfac)_7\}^-$.

Preparation of $(imH_2)_2[Sr(H_2O)_2(tfa)_3](tfa)$ (4). From the recrystallization of **3** in a chloroform solution under aerobic conditions, a second type of crystal was received, which was analyzed with analytical and spectroscopic methods and diffraction techniques and shown to be derivative **4**. Elem anal. Calcd for $C_{14}H_{14}F_{12}N_4O_{10}Sr$: C, 23.53; H, 1.98; N, 7.85. Found: C, 23.40; H, 2.05; N, 7.60. Λ_m (acetone, 298 K): 69.5 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 124.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3560−2300 vbr ν(N−H) + ν(H_2O), 1856wbr, 1795mbr, 1670vsbr, 1605m, 1534s ν(COO), 446m, 439m, 417w, 363s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 2.90br (4H, H_2O), 6.90br (4H, N*H* of imH_2), 7.62d (4H, H_4 and H_5 of imH_2), 8.82s (2H, H_2 of imH_2). ^{1}H NMR (DMSO-d_6, 298 K): δ 3.00br (4H, H_2O), 7.49d (4H, H_4 and H_5 of imH_2), 8.45br (4H, N*H* of imH_2), 8.69s (2H, H_2 of imH_2). ^{19}F NMR (acetone-d_6, 298 K): δ −76.3s, −77.8 (CF_{3tfa}). ^{19}F NMR (acetone-d_6, 193 K): δ −75.8s, −77.3 (CF_{3tfa}). ^{19}F NMR (DMSO-d_6, 298 K): δ −69.3s, −71.2s (CF_{3tfa}).

Preparation of $[Sr_2(tfac)_4(Meim)_2(H_2O)_2]$ (5). Compound **5** was synthesized similarly to **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Yield: 81%. Mp: 81−83 °C. Elem anal. Calcd for $C_{28}H_{32}F_{12}N_4O_{10}Sr_2$: C, 34.05; H, 3.27; N, 5.67. Found: C, 33.52; H, 3.08; N, 5.92. Λ_m (acetone, 298 K): 12.1 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 3.8 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3458br ν(H_2O), 3112m, 3078m ν(C−H), 1645vs, 1624s, 1599s, 1564vs, 1525s ν(C=O) + ν(C=C), 454m, 396s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.95s (12H,

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C$H_{3\text{tfac}}$), 3.85s (6H, N−CH_3 of Meim), 5.50 (4H, CH_{tfac}), 5.75br (4H, H_2O), 7.16br, 7.23br (4H, H_4 and H_5 of Meim), 7.97s (2H, H_2 of Meim). ^{1}H NMR (chloroform-d_6, 298 K): δ 2.13s (12H, C$H_{3\text{tfac}}$), 3.71s (6H, N−CH_3 of Meim), 5.43br (4H, CH_{tfac}), 5.76br (4H, H_2O), 6.89br, 7.07br (4H, H_4 and H_5 of Meim), 7.56s (2H, H_2 of Meim). ^{19}F NMR (acetone-d_6, 298 K): δ −75.2s (C$F_{3\text{tfac}}$). ^{13}C NMR (acetone-d_6, 298 K): δ 31.7 (s, CH$_{3\text{tfac}}$), 34.4 (s, N-CH$_3$ of Meim), 93.9 (s, CH$_{\text{tfac}}$), 120.5 (q, $^1J_{\text{C-F}} = 286.8$ Hz, CF$_{3\text{tfac}}$), 122.1, 126.4 (s, C_4 and C_5 of Meim), 138.5 (s, C_2 of Meim), 169.5 (q, $^2J_{\text{C-F}} = 29.2$ Hz, CO−CF$_{3\text{tfbz}}$), 196.3 (s, COC$_6$H$_{5\text{tfac}}$). ESIMS (MeCN): m/z (%) 507 (61) {Sr(tfac)$_2$(tfa)}$^-$, 547 (100) {Sr(tfac)$_3$}$^-$, 860 (12) {Sr$_2$(tfac)$_3$(tfa)$_2$}$^-$, 941 (9) {Sr$_2$(tfac)$_5$}$^-$.

Preparation of (MeimH)$_2$[Sr(tfbz)$_4$] (6). Compound **6** was synthesized similarly to **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Slow evaporation of a chloroform solution of **6** gave colorless crystals suitable for X-ray diffraction studies. Yield: 88%. Mp: 143−146 °C. Elem anal. Calcd for $C_{48}H_{38}F_{12}N_4O_8Sr$: C, 51.73; H, 3.44; N, 5.03. Found: C, 51.45; H, 3.28; N, 4.86. Λ_m (acetone, 298 K): 19.7 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 37.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3130m, 3071m ν(N−H), 1632vs, 1616s, 1597s, 1576vs, 1531s ν(C=O) + ν(C=C), 421m, 360s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 3.94s (6H, N−CH_3 of MeimH), 6.57s (4H, CH_{tfbz}), 7.26d, 7.33d (4H, H_4 and H_5 of MeimH), 7.50−7.70m, 8.14d (20H, C$_6H_{5\text{tfbz}}$), 8.14s (2H, H_2 of MeimH), 9.20br (2H, NH of MeimH). ^{19}F NMR (acetone-d_6, 298 K): δ −75.7s (C$F_{3\text{tfbz}}$). ^{13}C NMR (acetone-d_6, 298 K): δ 34.7 (s, N−CH$_3$ of MeimH), 90.8 (s, CH$_{\text{tfbz}}$), 119.1 (q, $^1J_{\text{C-F}} = 282.7$ Hz, CF$_{3\text{tfbz}}$), 122.3, 125.3 (s, C_4 and C_5 of MeimH), 128.2, 129.2, 132.4, 138.1 (s, C_6H$_{5\text{tfbz}}$), 140.0 (s, C_2 of MeimH), 173.0 (q, $^2J_{\text{C-F}} = 28.3$ Hz, CO−CF$_{3\text{tfbz}}$), 188.0 (s, COC$_6$H$_{5\text{tfbz}}$). ESIMS (MeCN): m/z (%) 631 (67) {Sr(tfbz)$_2$(tfa)}$^-$, 733 (100) {Sr(tfbz)$_3$}$^-$, 1047 (8) {Sr$_2$(tfbz)$_3$(tfa)$_2$}$^-$, 1149 (8) {Sr$_2$(tfbz)$_4$(tfa)}$^-$, 1251 (10) {Sr$_2$(tfbz)$_5$}$^-$.

Preparation of (MeimH)$_2$[Sr(hfac)$_4$] (7). Compound **7** was synthesized similarly to **1**. It is soluble in alcohols, chloroform, dichloromethane, acetone, acetonitrile, and DMSO. Yield: 75%. It is a dense oil. Elem anal. Calcd for $C_{28}H_{18}F_{24}N_4O_8Sr$: C, 31.08; H, 1.68; N, 5.18. Found: C, 31.34; H, 1.76; N, 5.36. Λ_m (acetone, 298 K): 25.2 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 41.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3131s ν(N−H), 1682vs, 1611s, 1598s, 1565vs ν(C=O) + ν(C=C), 445m, 374s, 355s ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 3.36br (2H, NH of MeimH), 3.98sbr (6H, N−CH_3 of MeimH), 5.84s (4H, CH_{hfac}), 6.80br, 6.92br (4H, H_4 and H_5 of MeimH), 7.46s (2H, H_2 of MeimH). ^{19}F NMR (acetone-d_6, 298 K): δ −77.1s (C$F_{3\text{hfac}}$). ^{13}C NMR (acetone-d_6, 298 K): δ 33.6 (s, N−CH$_3$ of MeimH), 88.7 (s, CH$_{\text{hfac}}$), 118.2 (q, $^1J_{\text{C-F}} = 286.4$ Hz, CF$_{3\text{hfac}}$), 120.4, 127.9 (s, C_4 and C_5 of MeimH), 138.5 (s, C_2 of MeimH), 176.4 (q, $^2J_{\text{C-F}} = 31.8$ Hz, CO−CF$_{3\text{hfac}}$). ESIMS (MeCN): m/z (%) 615 (54) {Sr(hfac)$_2$(tfa)}$^-$, 709 (100) {Sr(hfac)$_3$}$^-$, 1022 (5) {Sr$_2$(hfac)$_3$(tfa)$_2$}$^-$, 1116 (9) {Sr$_2$(hfac)$_4$(tfa)}$^-$, 1210 (12) {Sr$_2$(hfac)$_5$}$^-$.

Preparation of [Sr$_2$(thd)$_4$(imH)$_2$(EtOH)] (8). Compound **8** was synthesized similarly to **1**, by using Sr, imH, and thdH in a 1:1:2 ratio, respectively. Slow evaporation of the chloroform solution of **8** gave colorless crystals suitable for X-ray diffraction studies. It is soluble in alcohols, acetone, chloroform, dichloromethane, and DMSO and also slightly soluble in acetonitrile and n-hexane. Yield: 74%. Mp: 132−136 °C. Elem anal. Calcd for $C_{52}H_{90}N_4O_9Sr_2$: C, 57.27; H, 8.32; N, 5.14. Found: C, 56.98; H, 8.24; N, 4.96. Λ_m (acetone, 298 K): 3.5 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 1.3 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3180m ν(N−H), 1591vs, 1576vs, 1534s, 1502vs ν(C=O) + ν(C=C), 473m, 394m, 351w ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.17s (72H, C(CH_3)$_{3\text{thd}}$), 1.26t (3H, CH_3CH$_2$OH), 2.99s (1H, CH$_3$CH$_2$OH), 3.68qbr (2H, CH$_3$CH_2OH), 5.58s (4H, CH_{thd}), 7.11d, 7.23d (4H, H_4 and H_5 of imH), 7.78s (2H, H_2 of imH), 11.2br (2H, NH of imH). ^{13}C NMR (acetone-d_6, 298 K): δ 26.1 (s, CH$_3$CH$_2$OH), 27.7 (s, C(CH$_3$)$_{3\text{thd}}$), 40.2 (CH$_3$$CH_2$OH), 46.6 (s, C(CH$_3$)$_{3\text{thd}}$), 91.5 (s, CH$_{\text{thd}}$), 128.1, 128.9 (s, C_4 and C_5 of imH$_2$), 136.1 (s, C_2 of imH$_2$), 199.9 (s, CO$_{\text{thd}}$).

Preparation of [Sr$_2$(thd)$_4$(Meim)$_2$(EtOH)] (9). Compound **9** was synthesized similarly to **1**, by using Sr, imH, and thdH in a 1:1:2 ratio, respectively. It is soluble in alcohols, acetone, chloroform, dichloromethane, and DMSO and also slightly soluble in acetonitrile and n-hexane. Yield: 84%. Mp: 53−54 °C. Elem anal. Calcd for $C_{54}H_{94}N_4O_9Sr_2$: C, 57.98; H, 8.47; N, 5.01. Found: C, 58.12; H, 8.58; N, 5.25. Λ_m (acetone, 298 K): 4.0 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 1.8 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3183m, 3117m ν(N−H), 1593vs, 1575vs, 1530s ν(C=O) + ν(C=C), 471vs, 395s, 383s, 352m ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.13t (3H, CH_3CH$_2$OH), 1.17s (72H, C(CH_3)$_{3\text{thd}}$), 2.80br (1H, CH$_3$CH$_2$OH), 3.58q (2H, CH$_3$CH_2OH), 3.73s (6H, N−CH_3 of Meim), 5.56s (4H, CH_{thd}), 6.95br, 7.03br (4H, H_4 and H_5 of Meim), 7.55s (2H, H_2 of Meim). ^{13}C NMR (acetone-d_6, 298 K): δ 25.8 (s, CH$_3$CH$_2$OH), 26.1 (s, C(CH$_3$)$_{3\text{thd}}$), 33.5 (CH$_3$$CH_2$OH), 41.1 (s, C(CH$_3$)$_{3\text{thd}}$), 90.6 (s, CH$_{\text{thd}}$), 120.1, 129.9 (s, C_4 and C_5 of imH$_2$), 138.5 (s, C_2 of imH$_2$), 200.5 (s, CO$_{\text{thd}}$).

Preparation of [Sr(thd)$_2$(H$_2$O)$_2$(EtOH)] (10). Compound **10** was synthesized similarly to **1**, by using Sr, imH, and thdH in a 3:2:6 ratio, respectively. The colorless precipitate formed was shown from ^{1}H NMR to be a mixture of previous derivative **8** and of a new compound. The mixture powder was recrystallized from cold chloroform, and pale-yellow crystals slowly formed. These were filtered off, dried under reduced pressure to constant weight, and shown to be compound **10** (from the filtrate, colorless crystals of **8** slowly afforded after a longer time). Compound **10** is slightly soluble in alcohols and acetone and soluble in acetonitrile, chloroform, dichloromethane, and DMSO. Yield: 27%. Mp: 130 °C dec. Elem anal. Calcd for $C_{52}H_{90}N_4O_9Sr_2$: C, 53.75; H, 9.02. Found: C, 53.38; H, 9.23. Λ_m (acetone, 298 K): 2.6 Ω^{-1} cm^2 mol^{-1}. Λ_m (DMSO, 298 K): 1.8 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 3350sbr ν(O−H), 1586vs, 1572vs, 1536s, 1507vs ν(C=O) + ν(C=C), 451m, 414m, 363sbr ν(Sr−O). ^{1}H NMR (acetone-d_6, 298 K): δ 1.12s (36H, C(CH_3)$_{3\text{thd}}$), 1.22t (3H, CH_3CH$_2$OH), 3.65qbr (2H, CH$_3$CH_2OH), 5.57s (2H, CH_{thd}), 2.93s (5H, H_2O and CH$_3$CH$_2$OH). ^{13}C NMR (acetone-d_6, 298 K): δ 26.0 (s, CH$_3$CH$_2$OH), 27.5 (s, C(CH$_3$)$_{3\text{thd}}$), 40.1 (CH$_3$$CH_2$OH), 46.8 (s, C(CH$_3$)$_{3\text{thd}}$), 91.3 (s, CH$_{\text{thd}}$), 201.2 (s, CO$_{\text{thd}}$).

X-ray Diffraction Studies. The experimental data for compounds **2**·2H$_2$O, **4**, **6**, **8**, and **10** were collected on an image plate diffractometer (Stoe) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Numerical absorption correction was applied to the crystals of all compounds. The structures were solved by direct methods (*SHELXS-97*[36]) and refined anisotropically for all non-H atoms using full-matrix least-squares procedures (*SHELXL-97*[37]). In structures **4** and **6**, some CF$_3$ groups were found to be disordered between two positions. H atoms were included in the calculated positions and refined in a riding mode. Crystallographic data and some details of data collection and structure refinement are listed in Table 1. The interatomic distances for the Sr environment are listed in Table 2.

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Acknowledgment. We thank the University of Camerino, “Carima Foundation”, and INTAS (Research Grant 00-469) for financial support. Financial support from A. Rodriguez of the Canary Islands Government, Spain (B.O.C. 11-25-2003), is gratefully acknowledged.

Supporting Information Available: Full crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051972G