Synthesis and characterization of volatile, thermally stable bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)barium-, -strontium- and -calcium·polyether complexes, suitable as precursors in chemical vapour deposition

Klaas Timmer, Karel I. M. A. Spee, Adri Mackor, Harry A. Meinema*
TNO-Industrial Research, Department of Industrial Chemistry, P.O. Box 108, 3700 AC Zeist (Netherlands)

Anthony L. Spek and Paul van der Sluis
Laboratory of Crystallography, University of Utrecht, Padualaan 8, 3584 CH Utrecht (Netherlands)

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Abstract

Complexes of the type M(hfac)$_2$·polyether, bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)M·polyether (M = Ba, Sr, polyether = tetraglyme; M = Ba, polyether = hexaglyme; M = Ca, polyether = triglyme), are obtained in high yield upon reaction of M(hfac)$_2$ with one equivalent of polyether. The complexes thus obtained appear to be sublimable, non-hygroscopic, thermally stable solids. They have been characterized by elemental analysis, molecular weight determinations, NMR spectroscopy, mass spectrometry, IR and TG-DTA analysis. The complex Ba(hfac)$_2$·tetraglyme has been characterized by an X-ray structure determination. The barium atom is found to be coordinated by all nine oxygen atoms, with the polyether ligand wrapped around barium in a plane, with one hfac ligand on top of this plane and another below. The absence of short intermolecular interactions explains why the compound sublimes easily without decomposition.

Introduction

There is a considerable interest in the development of chemical vapour deposition processes for the deposition of thin films of high-Tc superconducting oxides, such as Y–Ba–Cu, Bi–Sr–Ca–Cu and Tl–Ba–Ca–Cu oxides. This requires the availability of suitable precursors with sufficient volatility and thermal stability for gas-phase transport to the deposition site and a proper decomposition behaviour to give the desired material. At present, various types of metal β-diketonates are generally applied [1–9]. However, the low volatility and thermal instability of the alkaline-earth metal β-diketonates at temperatures > 200 °C, required to achieve a sufficient mass transport, forms a bottleneck in the development of a practical MO-CVD process.

Investigations into the development of volatile alkaline-earth metal compounds have now resulted in the synthesis and characterization of a series of complexes of Ca-, Sr- and Ba-bis(hexafluoroacetylacetonates), bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)calcium, -strontium and -barium, M(hfac)$_2$, with polyethers. These complexes appear to possess a much higher volatility than the polyether-free, non-coordinated alkaline-earth metal β-diketonates. They meet the requirements for MO-CVD precursors for HTcS at evaporation temperatures $T \leqslant 150$ °C. They actually are the most volatile Ca, Sr and Ba compounds presently available [10–12].

In this paper the synthesis and characterization of these complexes are described. A communication on the X-ray crystal structure determination of Ba(hfac)$_2$·tetraglyme has been published elsewhere [13]. The synthesis and characterization of the corresponding crown ether complex, Ba(hfac)$_2$·18-crown-6, has also been reported [12, 14].

Experimental

Synthetic procedures were performed in dry, freshly distilled analytical-grade solvents.

Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-barium, -strontium or -calcium, M(hfac)$_2$ (M = Ba, Sr or Ca), obtained from Strem Chemicals, were

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*Author to whom correspondence should be addressed.

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stored under dry nitrogen. Elemental analyses of Ba(hfac)$_2$ point to the additional presence of 1 mol of H_2O. *Anal.*Calc. for $C_{10}H_2O_4F_{12}Ba \cdot H_2O$: C, 21.08; H, 0.70; F, 40.05. Found: C, 21.09; H, 0.82: F, 40.15%. Tetraglyme (2,5,8,11,14-pentaoxapentadecane) $CH_3O(CH_2CH_2O)_4CH_3$ and triglyme (2,5,8,11-tetraoxadodecane) $CH_3O(CH_2CH_2O)_3CH_3$ were purchased from Aldrich, hexaglyme (2,5,8,11,14,17,20-heptaoxaheneicosane) $CH_3O(CH_2CH_2O)_6CH_3$ from Riedel-de Häen. All compounds were used as received.

Elemental analyses and molecular weight determinations (osmometry in benzene) were carried out at the element-analytical department of the Institute of Applied Chemistry TNO, Zeist. NMR spectra were recorded on a Varian VXR-400. ^{1}H NMR chemical shifts are given in units of δ, relative to TMS. Couplings are given in Hz. Mass spectra were recorded with a Finnigan 4500 quadrupole mass spectrometer, using the direct insertion probe. For electron impact studies, the electron energy was 70 eV and the source temperature was 130 °C. For positive and negative chemical ionization, methane was used as reagent gas and the source temperature was kept at 100 °C. For all experiments, the direct insertion probe was heated from 40 to 250 °C at a rate of 30 °C/min. IR spectra were measured as KBr pellets on a Perkin-Elmer 1750 Fourier-Transform infrared spectrophotometer (4000–400 cm^{-1}).

TG-DTA analyses were carried out on a SETARAM TG-DTA92 instrument, which simultaneously performs thermogravimetry (TG) and differential thermal analysis (DTA); $\Delta T/\Delta t = 5$ °C/min from ambient temperature up to 500 °C. Experiments were performed in ambient air, both at atmospheric and at reduced pressure.

Preparation of Ba(hfac)$_2$·tetraglyme (1)

In a dry atmosphere, 8.42 g (37.93 mmol) of tetraglyme was added dropwise in 15 min to a stirred suspension of 20.91 g (37.93 mmol) of Ba(hfac)$_2$ in 250 ml of toluene. Stirring was continued for 2 h. The resulting, slightly turbid, solution was filtered and evaporated to dryness. The remaining off-white solid was stirred with 250 ml of pentane for 1 h. After setting for 1 h, the pentane was decanted and the colourless, crystalline product thus obtained was dried *in vacuo* at 50 °C for 4 h. Yield 25.80 g (88%) of **1**. Melting point: 147–150 °C. *MW* Calc.: 774. Found: 766. *Anal.* Calc. for $C_{20}H_{24}O_9F_{12}Ba$: C, 31.03; H, 3.10. Found: C, 31.12; H, 3.06%. After exposure to ambient air for two months: Found: C, 30.96; H, 3.14%. IR data: 2938(m), 2900(w), 1670(s), 1530(s), 1478(m), 1460(w), 1258(s), 1205(s), 1148(vs), 1093(s), 1032(w), 959(m), 861(w), 840(w), 800(m), 760(w), 665(m), 583(m), 530(w) cm^{-1}. The complex rapidly and almost quantitatively sublimes at 150 °C/0.03 mm Hg. ^{1}H NMR of the sublimate showed that the composition of the complex had not changed.

Single crystals of Ba(hfac)$_2$·tetraglyme were obtained from pentane by slow evaporation of a saturated solution. Experimental details on the X-ray crystal structure determination are presented in ref. 13.

Preparation of Ba(hfac)$_2$·hexaglyme (2)

Prepared as described for **1** from 2.70 g (8.72 mmol) of hexaglyme and 4.81 g (8.72 mmol) of Ba(hfac)$_2$. The compound was recrystallized from pentane. Yield 5.64 g (75.1%) of **2** as a colourless solid. Melting point: 59–62 °C. *MW* Calc.: 862. Found: 845. *Anal.* Calc. for $C_{24}H_{32}O_{11}F_{12}Ba$: C, 33.44; H, 3.72; F, 26.47. Found: C, 33.35; H, 3.80; F, 26.25%. After exposure to ambient air for two weeks: Found: C, 33.53; H, 3.79%. IR data: 2940(m), 2900(w), 1675(s), 1538(s), 1475(m), 1460(sh), 1260(s), 1198(s), 1151(vs), 1100(s), 1031(w), 961(m), 950(w), 863(w), 840(w), 797(m), 760(w), 662(m), 581(m), 530(w) cm^{-1}. The complex rapidly and almost quantitatively sublimes at 145 °C/0.02 mm Hg. ^{1}H NMR of the sublimate showed that the composition of the complex had not changed.

Preparation of Sr(hfac)$_2$·tetraglyme (3)

Prepared as described for **1** from 4.53 g (20.39 mmol) of tetraglyme and 10.23 g (20.39 mmol) of Sr(hfac)$_2$. Yield 12.91 g (87.5%) of **3** as a colourless solid. Melting point: 137–139 °C. *MW* Calc.: 724. Found: 719. *Anal.* Calc. for $C_{20}H_{24}O_9F_{12}Sr$: C, 33.17; H, 3.32; F, 31.51. Found: C, 33.28; H, 3.34; F, 31.30%. After exposure to ambient air for one month: Found: C, 33.11; H, 3.35%. IR data: 2950(m), 2900(w), 1678(s), 1538(s), 1478(m), 1460(m), 1261(s), 1200(s), 1150(vs), 1090(s), 1038(m), 958(m), 862(m), 846(w), 799(m), 760(w), 665(m), 584(m), 532(w) cm^{-1}. The complex rapidly and almost quantitatively sublimes at 115 °C/0.01 mm Hg. ^{1}H NMR of the sublimate showed that the composition of the complex had not changed.

Preparation of Ca(hfac)$_2$·triglyme (4)

Prepared as described for **1** from 4.12 g (23.12 mmol) of triglyme and 10.50 g (23.12 mmol) of Ca(hfac)$_2$. Yield 10.90 g (74.6%) of **4** as a colourless solid. Melting point: 120–122 °C. *MW* Calc.: 632. Found: 628. *Anal.* Calc. for $C_{18}H_{20}O_8F_{12}Ca$: C, 34.17; H, 3.16; F, 36.07. Found: C, 34.22; H, 3.22; F, 35.61%. After exposure to ambient air for one month: Found: C, 34.08; H, 3.20%. IR data: 2962(m), 2910(w), 1662(s), 1538(s), 1480(m), 1460(m), 1258(s), 1202(s), 1145(vs), 1090(s), 1071(m), 1021(w), 957(m), 880(w), 858(w), 800(m), 761(w), 665(m), 583(m), 530(w) cm^{-1}. The complex rapidly and almost quantitatively sublimes at 100 °C/0.02 mm Hg. ^1H NMR of the sublimate showed that the composition of the complex had not changed.

Results

The alkaline-earth metal complexes $M(hfac)_2\cdot$polyether, **1**–**4**, are easily prepared by the reaction of a suspension of $M(hfac)_2$ in toluene with one equivalent of polyether. The complexes thus formed are soluble in toluene and can be isolated in almost quantitative yield as colourless thermally stable, crystalline solids. They are non-hygroscopic, in contrast to the starting $M(hfac)_2$ compounds. Consequently, they can be handled and even stored in air. The complexes are soluble in common organic solvents such as benzene, chloroform, acetone and ethanol and slightly soluble in pentane. $Ba(hfac)_2\cdot$hexaglyme (**2**) is even well-soluble in pentane. The complexes have been readily sublimed without decomposition, **1** and **2** at 145–150 °C/0.02–0.03 mm Hg, **3** at 115 °C/0.01 mm Hg and **4** at 100 °C/0.02 mm Hg. The sublimation temperatures are considerably lower than for the parent $M(hfac)_2$ compounds, which sublime under partial decomposition, at 205–220 °C (Ba), 180–190 °C (Sr) and 130–150 °C (Ca), respectively [15].

The $M(hfac)_2\cdot$polyether complexes, presented in this paper, form a new class of volatile alkaline-earth metal compounds. They have been characterized by elemental analysis, molecular weight determinations, ^1H NMR, IR and mass spectrometry and TG-DTA analysis. $Ba(hfac)_2\cdot$tetraglyme (**1**) has also been characterized by an X-ray structure determination [13].

Molecular weight determinations (osmometry in benzene)

These showed all complexes to be monomeric in benzene solution. On the contrary, the parent $M(hfac)_2$ compounds have oligomeric structures [15].

^1H NMR spectra

The data are presented in Table 1. In $CDCl_3$ solution the ^1H NMR spectra of the $M(hfac)_2\cdot$polyether complexes **1**–**4** show the absence of free polyether ligands. The assignment and interpretation of the polyether ligand signals is as follows. Generally a downfield shift of the various CH_2 signals in coordinated tri-, tetra- and hexaglyme is expected as compared to the free ligands, due to electron transfer from oxygen to the alkaline-earth ion. However, it should be kept in mind that the conformation of the coordinated ligands is determined by wrapping around the metal ion (Ca, Sr or Ba), while the free ligands may be stretched. In $CDCl_3$, for triglyme, for instance the central CH_2 groups (d) and the CH_3 groups (a) appear at δ 3.67 and 3.38 ppm, respectively, while in **4** they are at 3.91 and 3.29 ppm. Tetraglyme has CH_2 resonances at δ 3.66 (d,e: singlet: central CH_2) and 3.55 and 3.64 ppm (b,c; multiplets) and its CH_3 resonance at 3.38 ppm (singlet). The corresponding tetraglyme resonances in **1** are at 3.75 and 3.81 (d,e); 3.48 and 3.58 (b,c); and 3.36 ppm (CH_3). The ^1H NMR spectrum of **3** very closely resembles that of the Ba analogue. For hexaglyme, two singlets are present at δ 3.65 and 3.66, in 8/8 ratio (assignment: d,e,f,g: central CH_2 groups). In the complex **2** these resonances appear as multiplets at δ 3.63, 3.68 and 3.72 ppm in 4/8/4 ratio.

To obtain more information about the coordination of the ether oxygens to barium, a solution of **2** in toluene-d_8 was cooled to −75 °C. All hexaglyme resonances were broadened and had shifted upfield. This suggests the existence of an aromatic solvent induced shift (ASIS) as discussed by Laszlo and others [16–19].

Further information on the ASIS effect was obtained by comparing the ^1H NMR spectra of the free polyether ligands and the corresponding alkaline-earth complexes in this study, in chloroform-d as the 'inert' solvent and benzene-d_6 as the aromatic solvent. The observed solvent effect for the polyethers is quite different between free and coordinated polyethers (see Table 1 and Fig. 1). In the free polyethers a small decrease in upfield ASIS is observed from the methyl hydrogens (*c*. 0.25 ppm) to the central CH_2 hydrogens (*c*. 0.17 ppm), in agreement with the methyl groups being more easily accessible for association with the aromatic molecules. The influence of coordination to the alkaline earth ions on the ASIS effect of the polyether is large. For instance for $Ba(hfac)_2\cdot$tetraglyme (**1**), high ASISs are observed for the tetraglyme ligand, between 0.17 and 1.00 ppm (Fig. 1).

In particular the ^1H signals of the central CH_2 groups (d,e) move upfield by 0.92–1.00 ppm, suggesting that these hydrogens form the positively charged and sterically accessible part of the complex molecule. This is compatible with an average structure for the weak association between the Ba complex and benzene, which may be represented by a tangential approach of the solvent molecules to the central part of the tetraglyme ligand. The upfield shift arises by the magnetic field from the aromatic ring current effect on the chemical shift, when solute hydrogens are placed inside the shielding cone of the aromatic compound. Similar high ASISs are

TABLE 1. ^{1}H NMR data of the M(hfac)$_2$·polyether complexes and the free polyether ligands

Compound[a]		$CDCl_3$	C_6D_6	ASIS ($\Delta\delta(C_6D_6-CDCl_3)$)
Tetraglyme:	a:	3.38 (s; 6H)	3.13	−0.25
$(CH_3OCH_2CH_2OCH_2CH_2)_2O$	b,c:	3.55 (m: 4H)	3.35	−0.20
a b c d e		3.64 (m; 4H)	3.47	−0.17
	d,e:	3.66 (s; 8H)	3.48	−0.18
1	a:	3.36 (s; 6H)	3.19	−0.17
	b,c:	3.48 (m; 4H)	3.22	−0.26
		3.58 (m: 4H)	3.07	−0.51
	d,e:	3.75 (m; 4H)	2.83	−0.92
		3.81 (m; 4H)	2.81	−1.00
	f[b]:	5.84 (s; 2H)	6.25	+0.41
3	a:	3.34 (s; 6H)	3.20	−0.14
	b,c:	3.46 (m; 4H)	3.18	−0.28
		3.57 (m; 4H)	3.07	−0.50
	d,e:	3.76 (m; 4H)	2.89	−0.87
		3.79 (m; 4H)	2.87	−0.92
	f[b]:	5.88 (s; 2H)	6.28	+0.40
Hexaglyme:	a:	3.38 (s; 6H)	3.15	−0.23
$(CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2)O$	b,c:	3.54 (m; 4H)	3.37	−0.17
a b c d e f g		3.64 (m; 4H)	3.48	−0.16
	d,e:	3.65 (s; 8H)	3.49	−0.16
	f,g:	3.66 (s; 8H)	3.50	−0.16
2	a:	3.30 (s; 6H)	3.11	−0.19
	b,c:	3.50 (m; 4H)	3.39	−0.11
		3.68 (m; 4H)	3.16	−0.52
	d,e:	3.63 (m: 4H)	3.27	−0.36
		3.72 (m; 4H)	3.32	−0.40
	f,g:	3.68 (m; 8H)	3.16	−0.52
			3.20	−0.48
	h[b]:	5.80 (s; 2H)	6.25	+0.45
Triglyme: $(CH_3OCH_2CH_2OCH_2)_2$	a:	3.38 (s; 6H)	3.13	−0.25
a b c d	b,c:	3.55 (m; 4H)	3.34	−0.21
		3.65 (m; 4H)	3.47	−0.18
	d:	3.67 (s; 4H)	3.49	−0.18
4	a:	3.29 (s; 6H)	2.97	−0.32
	b,c:	3.53 (m; 4H)	2.92	−0.61
		3.65 (m; 4H)	2.70	−0.95
	d:	3.91 (s; 4H)	3.23	−0.68
	e[b]:	5.94 (s; 2H)	6.30	+0.36

[a] **1** = Ba(hfac)$_2$·tetraglyme; **2** = Ba(hfac)$_2$·hexaglyme; **3** = Sr(hfac)$_2$·tetraglyme; **4** = Ca(hfac)$_2$·triglyme. [b] Hydrogen of the hfac ligand $CF_3C(O)CHC(O)CF_3$.

observed for the central CH_2 groups (d,e; 0.87–0.92 ppm) of the Sr analogue **3**. In **4** the largest upfield ASISs (0.95 ppm) are observed for two hydrogens belonging to the b,c positions. In Ba(hfac)$_2$·hexaglyme (**2**) the differences are less pronounced (0.11–0.52 ppm). This may be due to less specific association and/or a more flexible structure.

For **1**, where the crystal structure is known, one may compare the NMR results with the molecular structure (see Fig. 2), assuming similarity in the crystalline phase and in solution. It is clear that for steric and inductive reasons the benzene solvent tends to associate in particular with the central part of the tetraglyme ligand and not with the electron-withdrawing hfac end of the complexes, in agreement with the hfac–CH resonance showing downfield ASIS in all cases.

Infrared spectra

The IR spectra of the M(hfac)$_2$·polyether complexes **1**–**4** are virtually identical. In agreement with a monomeric structure of these complexes, only two strong absorption bands are found in the C=O/C=C region at 1678–1660 and 1538–1530 cm^{-1},

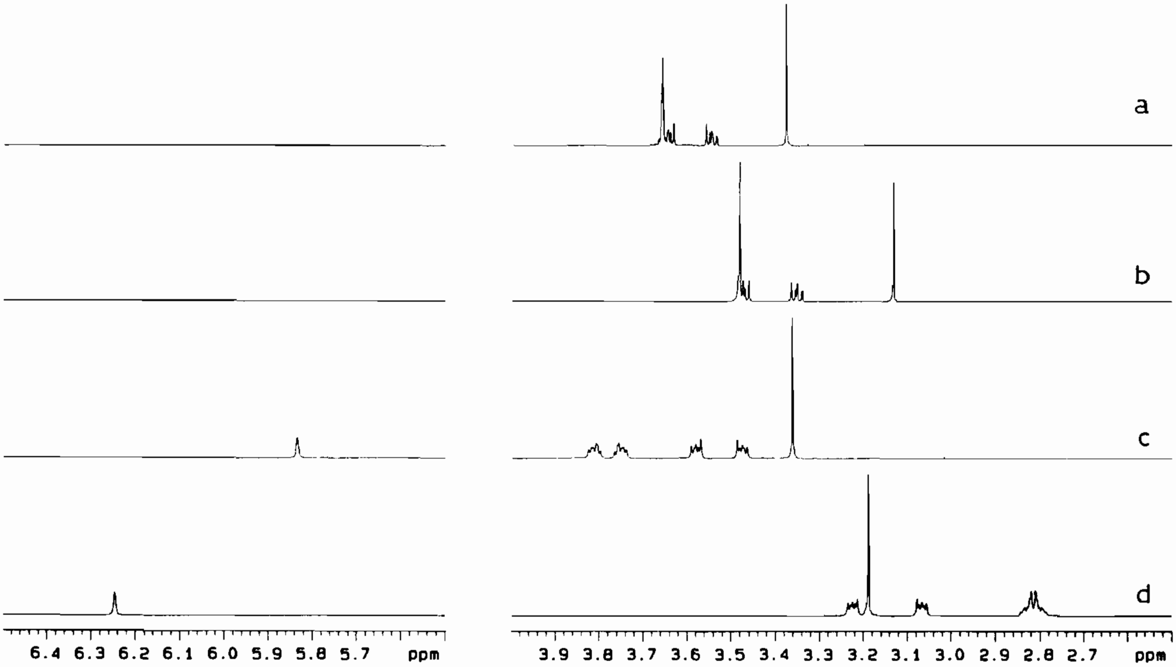

Fig. 1. ^1H NMR spectra of tetraglyme and Ba(hfac)$_2$·tetraglyme (1) in $CDCl_3$ (a, c) and C_6D_6 (b, d), illustrating the ASIS phenomenon.

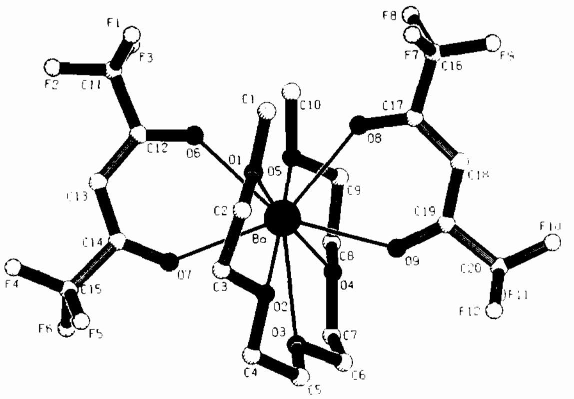

Fig. 2. Structure of Ba(hfac)$_2$·tetraglyme (1). Hydrogen atoms are omitted for clarity.

respectively. This is in contrast with the spectra of the parent M(hfac)$_2$ compounds, where several absorption bands are observed, due to the oligomeric character of these compounds [15].

Mass spectra

Selected mass spectral data of the M(hfac)$_2$·polyether complexes are presented in Table 2. In the electron impact mass spectra, peaks arising from loss and fragmentation of the hfac ligand are not as predominant as they are with the parent M(hfac)$_2$ compounds [15]. In all complexes, prominent signals correspond to the fragments $(P-\text{hfac})^+$, $(P-2\text{hfac}+\text{F})^+$, $(P-\text{hfac}-\text{polyether})^+$ and $(P-2\text{hfac})^{2+}$. Molecular ion (parent P^+) peaks are not observed. Fragments like $(P-2\text{hfac}+\text{F})^+$ result from fluorine transfer that occurs upon the loss of CF_3 fragments, as has been observed before with barium·bis(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate), Ba(hfod)$_2$ [20]. Fragments $(P-2\text{hfac})^{2+}$ are found at $\frac{1}{2}$ m/z. Another intense peak, observed with all complexes, is at m/z 59, corresponding to the polyether fragment $(CH_2CH_2OCH_3)^+$. Intense peaks for the (metal + F)$^+$ fragments are found, i.e. at m/z 157 in the spectra of the barium complexes $(^{138}BaF)^+$, at m/z 107 in the spectrum of the strontium complex $(^{88}SrF)^+$ and at m/z 59 in the spectrum of the calcium complex $(^{40}CaF)^+$. The latter peak coincides with the peak of $(CH_2CH_2OCH_3)^+$, but exact mass determination confirmed the presence of both peaks. The observation of (metal + F) fragments in the mass spectra is in agreement with the observation that the M(hfac)$_2$·polyether complexes ultimately decompose to the corresponding alkaline-earth metal fluorides. Thermal decomposition to the corresponding metal fluorides is observed in MO-CVD experiments [12] and by thermogravic analysis (*vide infra*). In this respect, these M(hfac)$_2$·polyether complexes behave similar to the parent M(hfac)$_2$ compounds [15].

The positive chemical ionization spectra (with methane as the reagent gas) of **1**–**4** show, under loss

TABLE 2. Selected mass spectral data (*m/z*; % intensity) of the $M(hfac)_2 \cdot$polyether complexes

Fragment[b]	Method[c]	Compound[a]			
		1	**2**	**3**	**4**
$(P)^-$	1	774; 10.3	862; 22.1	724; 58.6	632; 3.6
$(P\text{–polyether})^-$	1	552; 85.3	552; 73.4	502; 100.0	454; 100.0
$(\text{Hfac}+\text{H})^-$	1	208; 70.1	208; 73.0	208; 65.9	208; 9.3
$(\text{Hfac–F})^-$	1	188; 100.0	188; 100.0	188; 88.7	188; 13.0
$(\text{Hfac–CF3})^-$	1	138; 40.2	138; 32.4	138; 35.4	138; 5.1
$(P\text{–H})^+$	2	773; <0.5	861; <0.5	723; 0.5	631; <0.5
$(P\text{–F})^+$	2	755; 0.9	843; 1.2	705; 6.7	613; 7.1
$(P\text{–hfac})^+$	2	567; 28.9	655; 30.0	517; 75.1	425; 100.0
$(\text{Polyether}+\text{H})^+$	2	223; 47.3	311; 47.6	223; 42.7	179; 14.5
$(\text{Hfac}+2\text{H})^+$	2	209; 100.0	209; 100.0	209; 100.0	209; 78.1
$(P\text{–hfac})^+$	3	567; 93.1	655; 36.9	517; 92.1	425; 100.0
$(P\text{–2hfac}+\text{F})^+$	3	379; 17.8	467; 5.8	329; 19.9	237; 20.5
$(P\text{–hfac–polyether})^+$	3	345; 34.0	345; 18.3	295; 20.1	247; 14.0
$(P\text{–2hfac})^{2+}$	3	180; 100.0	224; 100.0	155; 100.0	109; 20.5
$(\text{Metal}+\text{F})^+$	3	157; 34.3	157; 19.9	107; 14.3	59; 45.9[d]
$(CH_3OCH_2CH_2)^+$	3	59; 67.9	59; 62.9	59; 48.5	59; 45.9[d]

[a] **1** = $Ba(hfac)_2 \cdot$tetraglyme; **2** = $Ba(hfac)_2 \cdot$hexaglyme; **3** = $Sr(hfac)_2 \cdot$tetraglyme; **4** = $Ca(hfac)_2 \cdot$triglyme. [b] P = parent or molecular ion. [c] 1 = negative chemical ionization; 2 = positive chemical ionization; 3 = electron impact. [d] = Sum of intensities of both peaks.

of a hydrogen atom, molecular ion peaks $(P-\text{H})^+$ at *m/z* 773, 861, 723 and 631, respectively, albeit with very low intensities. $(P-\text{F})^+$ fragments are found with somewhat (Ba) to much (Sr, Ca) higher intensities. With all complexes, the major fragments are $(P-\text{hfac})^+$, $(\text{polyether}+\text{H})^+$ and $(\text{hfac}+2\text{H})^+$ (see Table 2).

The negative chemical ionization spectra of **1**–**4** show the molecular ions $(P)^-$ at *m/z* 774, 862, 724 and 632, respectively. High-intensity peaks are observed for the fragments $(P-\text{polyether})^-$ and $(\text{hfac}+\text{H})^-$, together with signals due to further fragmentation of the hfac ligand.

The isotope patterns of the metal-containing peaks are fairly consistent with those computed from natural abundances. The given *m/z* ratios relate to the isotopes with the highest natural abundance, i.e. ^{138}Ba, ^{88}Sr and ^{40}Ca.

Scale expansions of the high-mass regions in the spectra of the $M(hfac)_2 \cdot$polyether complexes (M = Ba, Sr) did not show any peak beyond the molecular ions, in accordance with the monomeric nature of these complexes. For $Ca(hfac)_2 \cdot$triglyme (**4**), a minor peak of a $\{Ca_2(hfac)_4\}^-$ fragment (at *m/z* 908) is observed in the negative ionization spectrum only, likely formed by a dimerization reaction under the electron capture conditions used. On the contrary, in the mass spectra of the parent $M(hfac)_2$ compounds, high mass peaks corresponding to $M_x(hfac)_y$ fragments ($x \leqslant 7, y \leqslant 8$) are found and molecular ions could not be observed [15].

Thermogravic data

The thermogravic behaviour of the $M(hfac)_2 \cdot$polyether complexes has been investigated by thermogravimetry (TG) and differential thermal analysis (DTA). In the experiments, carried out in ambient air at atmospheric pressure, partial evaporation of the complexes is observed. At reduced pressures, i.e. 15–30 mm Hg, a complete evaporation of the complexes occurs under the conditions applied. Selected results from the TG and DTA experiments at atmospheric pressure are presented in Table 3. The peaks due to melting, observed in the DTA spectra, are in good agreement with the actual melting points. In the DTA spectra of **3** and **4**, an irreversible phase transition peak is observed at 120 and 63 °C, respectively.

The volatility of the complexes is in the order **4** > **3** > **1** > **2**. Thermal decomposition starts in the temperature range 247–256 °C. The final decomposition product is the metal fluoride, MF_2 (M = Ba, Sr, Ca). However, when loss of weight in TG has come to an end, a continued change in the DTA spectra is observed which is more pronounced in the order Ca complex > Sr complex > Ba complexes. This may be due to so called second-order transitions, like for instance a glass transition [21].

Discussion

In recent years, alkaline-earth metal *β*-diketonates, e.g. metal · bis(2,2,6,6-tetramethylheptane-3,5-dion-

TABLE 3. Characteristic results from the TG and DTA spectra of the M(hfac)$_2$·polyether complexes[a]

Compound[b]	ΔH_{ph}[c] (J/g)	Start of evaporation (°C)	Evaporated before decomposition (%)	Start of decomposition (°C)	End of decomposition	
					TG (°C)	DTA (°C)
1	43.0 (146 °C)[d]	209	11	247	427	453
2	33.6 (69 °C)[d]	227	1	256	453	481
3	12.2 (120 °C)[e] 43.9 (147 °C)[d]	197	17	251	420	468
3[f]	43.0 (145 °C)[d]	190	21	254	431	485
4	8.4 (63 °C)[e] 49.5 (127 °C)[d]	181	37	251	381	468
4[f]	47.0 (126 °C)[d]	156	33	247	405	481

[a] Experiments in ambient air and at atmospheric pressure; $\Delta T/\Delta t = 5$ °C/min from ambient temperature up to 500 °C. [b] **1** = Ba(hfac)$_2$·tetraglyme; **2** = Ba(hfac)$_2$·hexaglyme; **3** = Sr(hfac)$_2$·tetraglyme; **4** = Ca(hfac)$_2$·triglyme. [c] ΔH_{ph} = calculated enthalpy change from melting or phase transitions. [d] Melting. [e] Phase transition. [f] Samples heated to a temperature above the phase transition temperature and then cooled down before performing the TG-DTA experiment.

ate) (M(thd)$_2$ or M(dpm)$_2$; dpm = dipivaloylmethanate), metal·bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate) [M(hfod)$_2$] and metal·bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionate) [M(hfac)$_2$] have been intensively studied by various groups as alkaline-earth metal precursors in the metal organic chemical vapour deposition (MO-CVD) of thin films of high-Tc superconducting oxides, such as Y–Ba–Cu, Bi–Sr–Ca–Cu and Tl–Ba–Ca–Cu oxides [1–9] and of alkaline-earth metal fluorides [15, 22]. However, the low volatility and thermal instability of particularly the barium and strontium β-diketonates at temperatures ≥ 200 °C, required for a sufficient barium and strontium transport, through the gas phase, still prohibits the application of these compounds in a practical MO-CVD process.

Recently Sievers and coworkers [20] have reported that the low volatility and thermal instability of Ba(thd)$_2$ under MO-CVD process conditions are caused by the occurrence of intermolecular association and/or hydrolysis by coordinated water. This can be overcome by the concomitant evaporation of the barium β-diketonate with free β-diketone. This effect is probably due to adduct formation and, consequently, suppression of the formation of intermolecularly associated oligomeric complexes. Furthermore, the formation of non-volatile products by hydrolysis is prevented.

As compared to non-fluorine containing alkaline-earth metal β-diketonates, like the M(thd)$_2$ compounds, the Lewis acid character of the M(hfac)$_2$ compounds and hence their tendency to adduct formation is much higher. Consequently, in the presence of polyethers, strong coordinative bonds are formed between the hard, coordinatively unsaturated alkaline-earth metal cations and the hard oxygen donor atoms of the neutral polyether ligands. This results in the formation of thermally stable monomolecular 1:1 M(hfac)$_2$·polyether complexes. On the contrary, with the M(thd)$_2$ compounds the tendency towards complex formation is too low to give a well-defined 1:1 complex. The supposed coordination numbers, 8 in Ca(hfac)$_2$·triglyme, 9 in M(hfac)$_2$·tetraglyme (M = Sr, Ba) and 11 in Ba(hfac)$_2$·hexaglyme are not unprecedented, although the latter number has been rarely reported. For instance, whereas a seven-coordinated calcium atom has been found in the related [(triglyme)Ca](SCN)$_2$·H$_2$O complex [23], an eight-fold coordination of the calcium atom is observed in the complex [(tetraglyme)Ca](SCN)$_2$·H$_2$O [24]. The strontium analogue of the latter complex also shows an eight-coordinated strontium atom [24]. A nine fold coordination polyhedron around strontium has been observed in the complex [(tetraethyleneglycol)Sr]{3,5-(NO$_2$)$_2$C$_6$H$_3$CO$_2$}$_2$·H$_2$O [25]. In the tetraglyme–barium complex [(tetraglyme)Ba]-(SCN)$_2$·2H$_2$O, a nine-coordinated barium atom is found [24], as well as in the related complex [(hexaglyme)Ba](SCN)$_2$ [26]. Moreover, ten- and eleven-coordinated barium cations have been observed in heterodinuclear complexes of macrocycles, compiled of a Schiff base and a polyether chain, suitable for coordination to a soft cation (e.g. Ni^{2+}) and a hard cation (e.g. Ba^{2+}) [27].

The coordination of tetraglyme to Ba(hfac)$_2$ leads to the formation of a nine-coordinated, thermally stable monomolecular 1:1 Ba(hfac)$_2$·tetraglyme com-

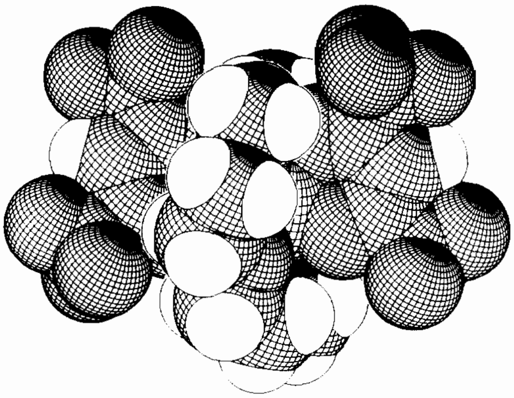

Fig. 3. CPK drawing of Ba(hfac)$_2$·tetraglyme (**1**), illustrating the globular character of the complex and the shielding of the barium atom by the ligands.

plex (**1**). The spacefilling model of this complex, presented in Fig. 3, shows the globular character of the complex and the shielding of the barium atom by the ligands. This explains the markedly increased volatility of this complex, as compared with Ba(hfac)$_2$ itself. The latter compound has an oligomeric structure; it sublimes at a very low rate at 205–220 °C/10^{-5} mm Hg, with simultaneous decomposition [15].

In **1**, Ba is coordinated by nine oxygen atoms with distances in the range of 2.683(2)–2.893(1) Å. The coordination mode and geometry closely resembles that found in the related Ba–tetraglyme complex Ba(SCN)$_2$·tetraglyme·2H$_2$O [24]. There are no significantly short intermolecular contacts.

The M(hfac)$_2$·polyether complexes **1**–**4**, presented in this paper, are representative of a new series of volatile alkaline-earth metal fluorinated β-diketonate·ligand complexes. The application of these compounds as MO-CVD precursors for the deposition of thin films of Bi–Sr–Ca–Cu oxides [28] and of Tl–Ba–Ca–Cu oxides [29] has been proven to be successful. The use of **1** as precursor in the deposition of thin films of superconducting $YBa_2Cu_3O_{7-x}$ and of BaF_2 is currently being investigated [10–12, 30]. Future research will also be focused on the application of the hexaglyme analogue **2**. This complex has a similar volatility, but a lower melting point (59–62 °C), which allows its use as a liquid MO-CVD precursor. This concept, i.e. lengthening of the polyether ligand, will also be applied in the synthesis of strontium– and calcium–M(hfac)$_2$·polyether complexes with low melting points, potentially suitable as liquid MO-CVD precursors.

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