Mixed ligand complexes of AEE hexafluoroacetylacetonates with diglyme: Synthesis, crystal structure and thermal behavior

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ABSTRACT

The novel mixed ligand complexes $[Ca(hfa)_2(diglyme)(H_2O)]$ (**I**), $[Sr(hfa)_2(diglyme)(H_2O)]$ (**II**) and $[Ba(hfa)_2(diglyme)_2]$ (**III**) (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione, diglyme = 2,5,8-trioxanonane) were synthesized by the reactions of the alkaline earth element (AEE) carbonates in *n*-hexane with a mixture of Hhfa and diglyme, and they were characterized by elemental analysis, ^{1}H and ^{13}C NMR, and FTIR spectroscopy. The crystal structures of **I–III**, consisting of mononuclear isolated molecules, have been determined. The thermal behavior and composition of the vapor phase have been studied for **I–III** by thermal analysis at low pressure and mass spectrometry using a Knudsen cell. The stability of the mixed ligand complexes $[M(hfa)_2(diglyme)_n]$ to the removal of diglyme molecules under heating decreases in the row **I > II ≈ III**, and only **I** evaporates as the mixed ligand complex after water removal.

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1. Introduction

Interest in the coordination chemistry of volatile β-diketonates of alkaline earth elements (AEE) has increased in the last 20 years because they have been used as promising metal organic chemical vapor deposition (MOCVD) precursors for perovskite metal oxides and superconductors [1–3]. A suitable MOCVD precursor must not only have the appropriate reactivity for the desired film growth process but also high volatility and stable vapor pressure characteristics [4]. Monomeric complexes are expected to exhibit enhanced volatility in comparison to oligomeric complexes because of the minimized intermolecular solid-state interactions. AEE bis(β-diketonate) complexes usually exist as oligomeric species $[M(dik)_2]_n$ (M = Ca, Sr, Ba, Hdik = β-diketone) in the solid state, melts and vapor phase [1,5]. They have relatively low volatility, demonstrate unstable vapor pressure and undergo severe deterioration during storage. These undesirable features are caused by the coordination unsaturation of the mononuclear species with composition $M(dik)_2$. Two β-diketonate ligands cannot saturate the inner coordination sphere of M^{2+} ions, which leads to easy

oligomerization or reaction with either donor solvents or nucleophilic impurities (such as water or carbon dioxide), with the formation of low volatile polynuclear clusters or involatile hydroxo- or carbonato-complexes. The synthesis of coordinatively saturated AEE precursors by introducing ancillary Lewis base ligands is well-known as an effective approach to this problem.

Many mononuclear saturated heteroligand complexes $[M(dik)_2Q_n]$ (Q = neutral donor ligand, *n* = 1, 2) have been synthesized [1]. However, for practical application as MOCVD precursors these complexes $[M(dik)_2Q_n]$ must sublime intact, that is to say the ancillary ligands Q must not split off under heating, with the formation of the unsaturated $[M(dik)_2]$. The stability of $[M(dik)_2Q_n]$ to Q removal depends on the Lewis acidity–basicity (electronic effect), the volatility of both $M(dik)_2$ and Q, as well as on steric effects [1,2,6].

Fluorinated β-diketonates demonstrate the most significant Lewis acidity and many of their mixed ligand complexes sublime intact and have been successfully used as MOCVD precursors [e.g., [7–9]]. So, AEE mixed ligand complexes of the general formula $[M(hfa)_2(CH_3O(CH_2CH_2O)_nCH_3)]$ (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione, $n \geqslant 3$) have been recognized as the most popular precursors, especially $[M(hfa)_2(tetraglyme)]$ (M = Ba, Sr, *n* = 4 – tetraglyme) [8–10]. These compounds sublime intact in the

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temperature range 100–200 °C at low pressure, and exhibit rather good stability during storage and use [8,10], which is rather rare for barium and strontium volatile compounds. Nevertheless, [Ba(hfa)$_2$(tetraglyme)] demonstrates a relatively high melting point of 150 °C, so it must be sublimed into the reactor feed stream. Meanwhile, MOCVD techniques with precursor liquid delivery are well-known and applied for deposition of AEE-containing thin films [10]. Therefore, the development of low-melting AEE precursors, which should be liquid and provide constant surface areas for evaporation and transport during deposition experiments is of interest, especially for barium.

Marks and co-workers [11] have proposed to reduce the melting points of [Ba(hfa)$_2$(CH$_3$O(CH$_2$CH$_2$O)$_n$CH$_3$)] by increasing the number of ether fragments ($n > 4$) and by the introduction of bulky R^1 and R^2 substituents in the polyglyme ligands. In this way, the complexes [Ba(hfa)$_2$(R^{1}O(CH$_2$CH$_2$O)$_n$R^2)] with melting points down to 50 °C were obtained, but decomposition and low volatility of some such complexes were observed under heating. This is caused by impossibility of coordination of all the polyglyme oxygen atoms to the barium ion, which leads to additional intermolecular interactions and complicates evaporation.

In contrast to Marks and co-workers [11], Fragala and co-workers [12] suggested the use of glyme ligands with short chains ($n = 1$ or 2, corresponding to monoglyme or diglyme) for the synthesis of low-melting precursors, and such volatile, low-melting mixed ligand complexes with diglyme were obtained for hexafluoroacetylacetonates of lanthanides [12], lead(II) [13] and cobalt(II) [14].

However, the complexes of AEE hexafluoroacetylacetonates with diglyme have not been described yet. Here we report the synthesis, X-ray structures, thermal behavior and mass spectrometric study of [Ca(hfa)$_2$(diglyme)(H$_2$O)] (**I**), [Sr(hfa)$_2$(diglyme)(H$_2$O)] (**II**) and [Ba(hfa)$_2$(diglyme)$_2$] (**III**).

2. Experimental

Analytically pure hexane, metallic Ba, CaCO$_3$, SrCO$_3$ and BaCO$_3$ from Reakhim (Russia) were used without further purification. Hhfa (P&M Invest, Russia, 98%) and diglyme (Fluka, 99%) were preliminary distilled under reduced pressure.

The C, H and N contents were determined by conventional elemental analysis. The calcium and strontium contents were determined titrimetrically. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer as Nujol and hexachlorobutadiene mulls between KBr plates in the region 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance-400 (400 MHz, CDCl$_3$/TMS). TG curves at low pressure (0.01 torr) were recorded on a ULVAC SINKU-RIKO TA-7000 analyzer with a 10 °C min^{-1} heating rate.

2.1. Synthesis of [Ca(hfa)$_2$(diglyme)(H$_2$O)] (**I**), [Sr(hfa)$_2$(diglyme)(H$_2$O)] (**II**), [Ba(hfa)$_2$(diglyme)$_2$] (**III**)

MCO$_3$ (4 mmol, M = Ca, Sr, Ba) was added to a Hhfa and diglyme mixture (molar ratio 1:2:1 or 1:2:2) in hexane (40 ml) followed by continuous stirring for 2 h at 50 °C, until full dissolution of MCO$_3$. White crystalline precipitates were obtained after slow solvent evaporation in air. Yield: ∼90–95%.

Anal. Calc. for C$_{16}$H$_{18}$F$_{12}$O$_8$Ca: C, 31.69; H, 2.99; Ca, 6.61. Found: C, 32.63; H, 3.07; Ca, 6.45. IR, cm^{-1}: 3640–3340 ν(O–H); 2960–2840 ν(C–H); 1661 ν(C=O); 1527, 1510 ν(C=C); 1248, 1187, 1132 ν(C–F); 1472 δ(CH$_2$); 1455 δ(CH$_3$); 1067 ν(C–O–C). ^{1}H NMR (CDCl$_3$), ppm: δ 6.01 (s, 2H, CH), 3.81 (tr, 4H, CH$_2$), 3.73 (tr, 4H, CH$_2$), 3.41 (s, broad, 6H, OCH$_3$ + 2H, H$_2$O); ^{13}C (CDCl$_3$), ppm: δ 177.1 (quartet, CO), 122.1, 119.3, 115.9 (s, CF$_3$), 86.8 (s, CH), 71.1, 69.4 (s, CH$_2$CH$_2$), 59.7 (s, OCH$_3$). M.p. 109 °C.

Anal. Calc. for C$_{16}$H$_{18}$F$_{12}$O$_8$Sr: C, 29.39; H, 2.77; Sr, 13.40. Found: C, 29.53; H, 2.78; Sr, 13.07. IR, cm^{-1}: 3640–3390 ν(O–H); 2960–2850 ν(C–H); 1676 ν(C=O); 1532, 1514 ν(C=C); 1256, 1194, 1142, ν(C–F); 1470 δ(CH$_2$); 1458 δ(CH$_3$); 1072 ν(C–O–C). ^{1}H NMR (CDCl$_3$), ppm: δ 5.94 (s, 2H, CH), 3.72 (tr, 4H, CH$_2$), 3.67 (tr, 4H, CH$_2$), 3.41 (s, broad, 6H, OCH$_3$ + 2H, H$_2$O); ^{13}C (CDCl$_3$), ppm: δ 175.8 (tr, CO), 122.3, 119.4, 116.6 (s, CF$_3$), 87.9 (s, CH), 71.4, 69.8 (s, CH$_2$CH$_2$), 59.1 (s, OCH$_3$). M.p. 122 °C.

Anal. Calc. for C$_{22}$H$_{30}$F$_{12}$O$_{10}$Ba: C, 32.23; H, 3.69. Found: C, 32.21; H, 3.72; IR, cm^{-1}: 2942–2844 ν(C–H); 1674 ν(C=O); 1532

Table 1
Crystal and refinement data

	[Ca(hfa)$_2$(diglyme)(H$_2$O)] (**I**)	[Sr(hfa)$_2$(diglyme)(H$_2$O)] (**II**)	[Ba(hfa)$_2$(diglyme)$_2$] (**III**)	[Ba(hfa)$_2$(diglyme)$_2$] (**III***)
Formula	C$_{16}$H$_{18}$CaF$_{12}$O$_8$	C$_{16}$H$_{18}$F$_{12}$O$_8$Sr	C$_{22}$H$_{30}$F$_{12}$O$_{10}$Ba	C$_{22}$H$_{30}$F$_{12}$O$_{10}$Ba
Formula weight	606.38	653.92	819.80	819.80
Diffractometer	Bruker APEX II	Bruker APEX II	Bruker Smart 1000	Enraf-Nonius CAD-4
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans	$\omega/1.33\theta$ scans
T (K)	100(2)	100(2)	143(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$
a (Å)	17.0254(7)	17.6449(11)	9.4484(16)	11.5431(9)
b (Å)	18.3627(7)	18.1523(11)	9.6588(17)	15.4702(11)
c (Å)	17.8369(7)	17.7294(11)	18.681(3)	18.969(2)
α (°)	90	90	97.954(9)	90
β (°)	117.063(1)	117.7646(11)	95.743(7)	101.217(8)
γ (°)	90	90	106.915(5)	90
V (Å^3)	4965.8(3)	5024.9(5)	1597.6(5)	3322.7(5)
Z	8	8	2	4
Color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions (mm)	0.63 × 0.40 × 0.35	0.34 × 0.25 × 0.23	0.50 × 0.24 × 0.20	0.52 × 0.25 × 0.28
D_{calc} (g cm^3)	1.622	1.729	1.704	1.639
μ (mm^{-1})	3.81	2.272	1.360	1.308
Unique reflections (R_{int})	13058 (0.0319)	12526 (0.076)	8332 (0.022)	4839 (0.051)
Observed reflections [$I > 2\sigma(I)$]	10010	7377	7400	3307
Parameters	769	671	411	235
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.0436, 0.0914	0.046, 0.109	0.038, 0.094	0.046, 0.127
Goodness-of-fit on F^2	1.001	0.969	1.03	1.15
Absorption correction	multi-scan APEX II [16]	multi-scan APEX II [16]	multi-scan SADABS [17]	GAUSSIAN [18]
T_{max}, T_{min}	0.629, 0.612	0.623, 0.512	0.773, 0.550	0.751, 0.700
ρ_{min}, ρ_{max} (e Å^3)	−1.11, 1.19	−0.66, 0.89	−1.20, 1.73	−0.67, 0.68