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Note

A novel route to the second-generation alkaline-earth metal precursors for metal-organic chemical vapour deposition: one-step synthesis of $M(hfa)_2 \cdot$tetraglyme ($M = Ba$, Sr, Ca and $Hhfa = 1,1,1,5,5,5$-hexafluoro-2,4-pentanedione)

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Abstract

A one-pot reaction for the synthesis of better performing alkaline-earth precursors for metal-organic chemical vapour deposition (MOCVD) applications, is reported. The reaction of metal hydroxides ($Ba(OH)_2 \cdot 8H_2O$, $Sr(OH)_2 \cdot 8H_2O$) or oxide (CaO) with Hhfa and tetraglyme in air yields quantitatively monomeric, water-free, highly stable and volatile $M(hfa)_2 \cdot$tetraglyme adducts. All the adducts have been characterized by TGA and DSC. MOCVD capabilities have been tested through depositions of metal fluoride for buffer layer applications and of BaCaCu matrices for HT_c TlBaCaCu superconductor thin films.

Keywords: MOCVD application; Alkaline earth metal complexes; β-diketonate complexes

1. Introduction

Metal-organic chemical vapour deposition (MOCVD) techniques have been successfully applied to a large variety of thin film deposition processes [1,2]. Recently, MOCVD has become an established technology for the deposition of thin films of high temperature superconductors [3] such as $YBa_2Cu_3O_x$ [3,4], $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ [3,5,6] and $Tl_mBa_2Ca_{n-1}Cu_nO_x$ [3,7,8]. Nevertheless, these synthetic strategies require highly volatile and, even more importantly, thermally stable metal precursors since both prerequisites are of major relevance for an adequate stoichiometric control and, hence, for better performing materials.

To date, a large variety of metal β-diketonates has been generally applied [3]. However, the low volatility and thermal instability of alkaline-earth (A.E.) metal β-diketonates, has caused a renewed interest for monomeric, anhydrous, volatile and stable A.E. metal precursors. So far some of the best performing A.E. precursors, in terms of thermal stability and volatility, are the monomeric β-diketonate adducts with multidentate Lewis bases (e.g. glymes) [4b, 6–8]. The presence of the polyether stabilizes the A.E. ion by saturating the metal coordination sphere thus avoiding oligomerization [9–13] and water coordination [12–14].

Recently a large number of monomeric species [M(β-diket)$_2 \cdot$glyme] [15–19] (with $M = Ba$, Sr, Ca; β-diket = Htfa (1,1,1-trifluoro-2,4-pentanedione), Hhfa (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), Hdpm (2,2,6,6-tetramethyl-3,5-heptanedione), Htdf (1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedione) and glyme = triglyme (2,5,8,11-tetraoxadodecane), tetraglyme (2,5,8,11,14-pentaoxapentadecane) and sometimes hexaglymes (2,5,8,11,14,17,20-heptaoxaheneicosane)) have been synthesized. The reported synthetic procedures for the adducts require preliminary syntheses of the parent metal β-diketonate [15] or of the reactant metal alkoxides [17,18]. In addition, all these steps require controlled anaerobic conditions. Moreover, the use of metal hydrides as metal reactants [16] precludes any accurate stoichiometric control because of different reactivities from batch to batch [18].

In this paper we report a general, single-step synthetic strategy to monomeric $Ba(hfa)_2 \cdot$tetraglyme (**1**),

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Sr(hfa)$_2$·tetraglyme (2) and Ca(hfa)$_2$·tetraglyme (3). Our one-pot synthetic route requires neither anaerobic conditions nor the preliminary syntheses of alkoxides or of parent β-diketonates. The single step reaction of commercially available products, yields monomeric, water-free, highly stable and volatile precursors. Their thermal properties have been checked by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and by MOCVD transport experiments.

2. Experimental

2.1. Reagents

Ba(OH)$_2$·8H$_2$O, CaO, Hhfa and tetraglyme were purchased from Aldrich and used without further purification. Sr(OH)$_2$·8H$_2$O was obtained from STREM Chemicals Inc.

2.2. General procedures

Elemental microanalyses were performed in the Analytical Laboratories of the University of Catania. ^{1}H NMR spectra were recorded on an F.T. Bruker 200 spectrometer. IR data were collected on a 684 Perkin-Elmer spectrometer either as nujol or hexachlorobutadiene mulls between KBr plates. Thermal measurements were made using a Mettler 3000 system equipped with a TG 50 thermobalance, a TC 10 processor and DSC 30 calorimeter. The weight of the samples investigated was between 15 and 20 mg (TGA) and 4 and 10 mg (DSC). Analyses were made under prepurified nitrogen using a 5 °C/min heating rate. Electron impact mass spectra were obtained using a Kratos MS 50 spectrometer.

2.3. Synthesis of Ba(hfa)$_2$·tetraglyme (1)

Ba(OH)$_2$·8H$_2$O (4.284 g, 13.58 mmol) was first suspended in toluene (60 ml). Tetraglyme (2.67 g, 12.01 mmol) was added to the suspension. Hhfa (5.002 g, 24.04 mmol) was added under vigorous stirring after 5 min and the mixture was refluxed for 1 h. After cooling, the excess of barium hydroxide was filtered off and the water phase was separated from the organic layer containing the adduct. The resulting clear solution was evaporated in vacuo and the remaining white solid was stirred with 80 ml of pentane for 60 min. White solid crystals were collected by filtration and dried under vacuum. The yield was 94%. The melting point of the crude product was 152–155 °C/760 mmHg. *Anal.* Calc. for BaC$_{20}$H$_{24}$F$_{12}$O$_9$: C, 31.03; H, 3.13; F, 29.47. Found: C, 31.15; H, 3.08; F, 29.30%. The adduct quantitatively sublimes at 145 °C/10^{-2} mmHg. The NMR, MS and IR data of the sublimed adduct and even of the raw product are in very good agreement with those previously reported [15].

2.4. Synthesis of Sr(hfa)$_2$·tetraglyme (2)

Prepared as described for the barium adduct from 2.0741 g (7.80 mmol) of Sr(OH)$_2$·8H$_2$O, 2.94 g (14.13 mmol) of Hhfa and 1.57 g (7.06 mmol) of tetraglyme. Yield 91%. Melting point of the crude product 138–140 °C/760 mmHg. *Anal.* Calc. for SrC$_{20}$H$_{24}$F$_{12}$O$_9$: C, 33.16; H, 3.34; F, 31.50. Found: C, 33.29; H, 3.48; F, 31.38%. The adduct quantitatively sublimes at 130 °C/10^{-2} mmHg. The NMR, MS and IR data of the raw and sublimed adduct are in very good agreement with the previously reported [15] characterisation.

2.5. Synthesis of Ca(hfa)$_2$·tetraglyme (3)

CaO (1.104 g, 19.69 mmol) was first suspended in toluene (60 ml). Tetraglyme (4.264 g, 19.18 mmol) was added to the suspension. Hhfa (7.981 g, 38.37 mmol) was added under vigorous stirring after 5 min and the mixture was refluxed for 1 h. After cooling, the excess of calcium oxide was filtered off. The solvent was removed in vacuo and the resulting colourless oil yielded a white crystalline solid on addition of pentane (50 ml). After stirring the suspension for 60 min, the white crystals were collected by filtration and dried in vacuo. Yield 92%. Melting point of the crude product 94–97 °C/760 mmHg. *Anal.* Calc. for CaC$_{20}$H$_{24}$F$_{12}$O$_9$: C, 35.49; H, 3.58; F, 33.71. Found: C, 35.31; H, 3.45; F, 33.60%. MS (EI, 70 eV, m/e; (fragment); $M=$Ca(hfa)$_2$·tetraglyme): 469 $(M-\text{hfa})^+$ 100%, 281 $(M-2\text{hfa}+\text{F})^+$ 16%, 247 $(M-\text{hfa}-\text{tetraglyme})^+$ 15%, 131 $(M-2\text{hfa})^{2+}$ 5%. IR (hexachlorobutadiene; ν, cm^{-1}): 2930(s), 1660(s), 1525(s), 1455(s), 1350(w), 1245(s), 1200(s), 1180(s), 1135(s), 1080(s), 1060(s), 1010(w), 960(w), 945(m), 870(w), 850(w), 830(vw), 790(m), 755(w), 730(w), 650(m), 580(w). ^{1}H NMR (CDCl$_3$): δ 3.33 (s,6H), 3.45 (m, 4H), 3.56 (m, 4H), 3.7 (m, 8H), 5.85 (s, 2H). The adduct quantitatively sublimes at 90 °C/10^{-2} mmHg.

2.6. MOCVD experiments

Low pressure (6 torr) MOCVD depositions were performed, under Ar/O$_2$ (100/400 sccm) flow, using a horizontal cold-wall reactor. The source temperatures were controlled in the 90–130 °C range. Silicon (111) substrates were used for the deposition of MF$_2$ and yttria stabilized zirconia (YSZ) substrates for the deposition of BaCaCu matrices. The substrates were held on a heated (450–550 °C) boron nitride susceptor.

3. Results and discussion

3.1. Synthesis

The single-step reaction of the A.E. oxide or hydroxide with hexafluoroacetiylacetone and tetraglyme in toluene has been found to yield reproducible monomeric air stable adducts in 1 h in air. Our synthetic strategy has some notable features.

Firstly, it yields reproducible oxo- and water-free products even using alkaline-earth hydroxide. The hard Lewis base tetraglyme encapsulates the metal ion thus competing with the H_2O molecules in saturating the coordination sphere. Entropic advantages which are due to the chelate effect help in the displacement of the H_2O ligand.

Secondly, the present procedure quantitatively yields non-hygroscopic adducts through a viable low cost route, since it uses simple, commercially available chemicals. This represents an important aspect for materials used for CVD applications where low-cost chemicals that may be manipulated on open benches are an important objective [20].

Thirdly, the raw materials obtained through the present route represent pure, final products since no foreign species are introduced in the one-pot synthesis. Even more importantly, the polyether adducts are soluble in the same reaction medium and, therefore, they can be easily separated from unreacted oxides or hydroxides. No sublimation steps are thus required to obtain pure material.

Finally, the advantages of the presently described synthetic strategy may be contrasted with previously published routes to second generation A.E. precursors [15–18]. The use of BaH_2 as the barium reactant and tetraglyme as reaction solvent results in a low yield (42%) of product with unusually low melting point [16]. The ethoxide route, proposed by Drake et al., requires the preliminary synthesis of calcium ethoxide and results in a 64% yield of $Ca(hfa)_2 \cdot$tetraglyme adduct [17]. Other proposed [15] synthetic procedures require the preliminary syntheses of the parent β-diketonates.

Our alternative route produces pure crystalline solids with very high yields (>90%) in a single-step synthesis.

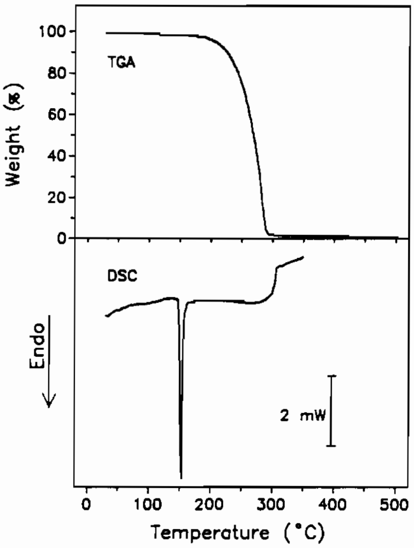

Fig. 1. TGA–DSC curve of the raw adduct $Ba(hfa)_2 \cdot$tetraglyme.

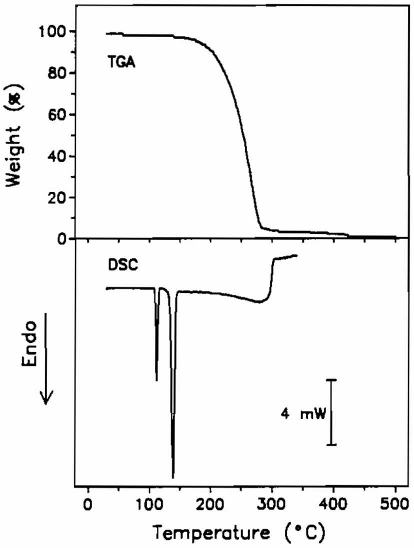

Fig. 2. TGA–DSC curve of the raw adduct $Sr(hfa)_2 \cdot$tetraglyme.

3.2. TGA–DSC data

Thermal behaviours or the raw adducts **1**–**3** have been studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under N_2 as carrier gas. The TGA curves of $M(hfa)_2 \cdot$tetraglyme (M = Ba, Sr, Ca) are reported in Figs. 1, 2 and 3, respectively. Singular sublimation steps are always observed. The sublimation process takes place in the temperature range 160–350 °C (residue = 6% to 350 °C), 140–300 °C (residue = 7% to 300 °C) and 100–300 °C (residue = 5% to 300 °C) for **1**, **2** and **3**, respectively. No carbonaceous residue has found in any of the adducts. In contrast, the TGA curve of the $Ba(hfa)_2 \cdot H_2O$ parent complex shows [21] two well defined steps due to the loss of the coordinated water (110–130 °C) and to the sublimation of the $[Ba(hfa)_2]$ itself (200–350 °C).

The DSC curves of the $M(hfa)_2 \cdot$tetraglyme adducts are reported in Figs. 1–3. Sharp melting points at 153.6 °C (−11.2 cal/g), 138.8 °C (−10.6 cal/g) and 94.2 °C (−14.4 cal/g) are observed for **1**, **2** and **3**, respectively and are in very close agreement with the actual melting point. Sublimation from melts occurs afterwards. The DSC curve of the Sr adduct shows an interesting feature. A reversible sharp endothermic peak, attributed to a structural phase transition, is observed at 112 °C (−2.9 cal/g). The occurrence of coordinated H_2O loss can be ruled out for several reasons: (i) no weight loss becomes evident in the TGA plot, (ii) no IR bands are observed in the 3300–3600 cm^{-1} range (O–H stretching), (iii) an identical and reproducible sharp peak is observed along with several consecutive heating and cooling DSC experiments in the 30–125 °C temperature range. This

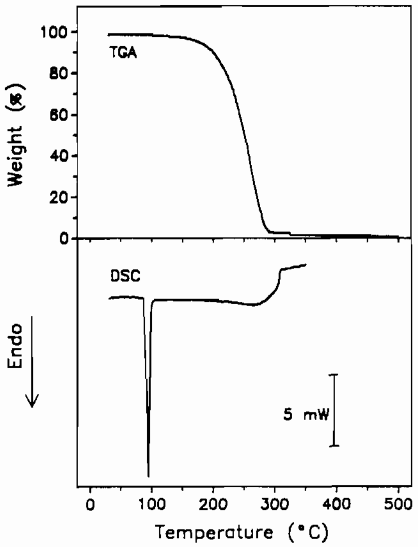

Fig. 3. TGA–DSC curve of the raw adduct $Ca(hfa)_2 \cdot$tetraglyme.

last observation suggests that, at variance with previously reported results [15], a reversible phase transition occurs.

Finally, it is important to note that the NMR, MS and IR spectra, and thermal properties of the present raw materials remain identical after several sublimation cycles in vacuo.

3.3. MOCVD experiments

The X-ray diffraction scans of the metal fluoride CaF_2, SrF_2 and BaF_2 films deposited on Si substrates are reported in Fig. 4. On passing from CaF_2 to BaF_2 the X-ray patterns indicate a preferential (*h*00) orientation. Wavelength dispersive X-ray analyses are indicative of minor (<3%) amounts of carbon contamination. The fluorinating agent is supplied from the source material itself.

The capabilities of the present one-pot adducts for stoichiometric control in MOCVD depositions of BaCaCu matrices have been thoroughly investigated for HT_c superconducting thin films. Copper (II) acetylacetonato ($Cu(acac)_2$) has been used as a CuO precursor. Energy dispersive X-ray analysis (EDX) data (Fig. 5) provide evidence that BaCaCu matrices with 2:2:3 and 2:1:2 stoichiometric ratios can be reproducibly obtained by suitable selections of temperatures in the reactor sublimation sections. Further details of the MOCVD experiments will be reported elsewhere [22].

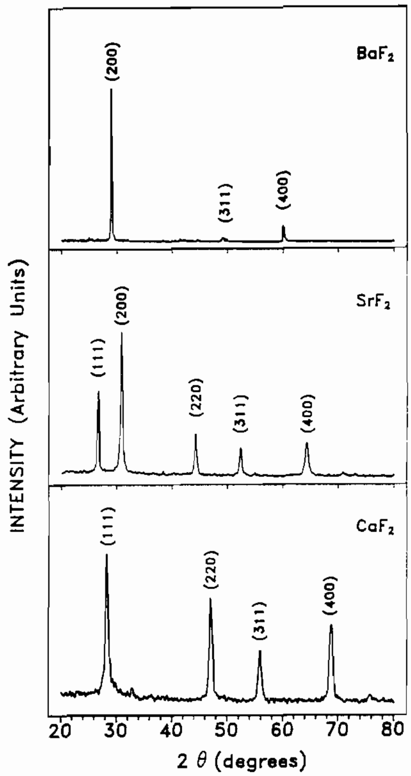

Fig. 4. θ–2θ X-ray diffraction scans for MF_2 films deposited using the adducts $Ca(hfa)_2 \cdot$tetraglyme, $Sr(hfa)_2 \cdot$tetraglyme and $Ba(hfa)_2 \cdot$tetraglyme.

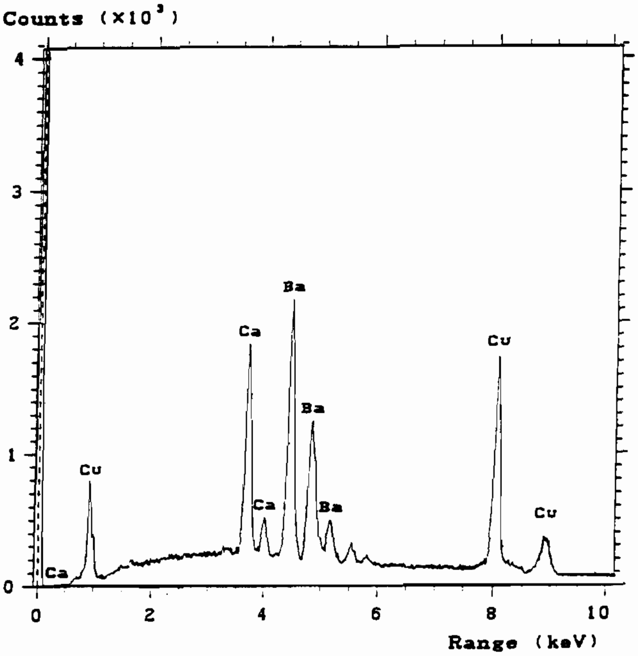

Fig. 5. Energy dispersive X-ray analysis of a BaCaCu film grown by MOCVD using $Ba(hfa)_2 \cdot$tetraglyme, $Ca(hfa)_2 \cdot$tetraglyme and $Cu(acac)_2$.

4. Conclusions

The presently described one-pot synthetic strategy has proven an efficient route for preparation of water-free, thermally stable and volatile $M(hfa)_2 \cdot$tetraglyme ($M = Ca$, Sr, Ba) adducts from commercially available products. There is evidence that the tetraglyme ligand acts as a displacing and partitioning agent which precludes water coordination via a chelate effect even in the presence of H_2O in the reaction mixture.

The TGA and DSC data suggest that the adducts **1–3** have better mass transport properties and thermal behaviour than conventional A.E. metal CVD precursors. Their favourable thermal properties find counterpart in the reproducible stoichiometric control found in MOCVD procedures for deposition of BaCaCu matrices. As a general consideration, it is worthy of note that the present synthetic procedure may represent a general approach for the synthesis of β-diketonate polyether adducts of a large variety of metal ions. Work is in progress in this direction.

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