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Synthesis and characterization of $BaX_2 \cdot$18-crown-6 complexes. Barium bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionate) · 18-crown-6, a non-hygroscopic, thermally stable, volatile barium compound

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Abstract

The synthesis of a series of $BaX_2 \cdot$18-crown-6 complexes (X = hfac, tclac, tfac, thd, acac, O_2CCF_3, O_3SCF_3, O_2CCH_3, Cl, Br, I, NO_3, OH and SCN) and BaX_2 compounds (X = tclac, tfac, O_2CCF_3 and O_3SCF_3) is described. The $BaX_2 \cdot$18-crown-6 complexes have been characterized by melting point determinations, elemental analysis and NMR spectroscopy. Their thermal stability and volatility at reduced pressure have been investigated. Barium bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato) · 18-crown-6, $Ba(hfac)_2 \cdot$18-crown-6, appears to be a non-hygroscopic, thermally stable, sublimable solid. This compound has also been characterized by mass spectrometry. The 18-crown-6 complexes of BaI_2, $Ba(SCN)_2$, $Ba(O_2CCF_3)_2$ and $Ba(O_3SCF_3)_2$ are involatile and thermally stable up to 200 °C. The 18-crown-6 complexes of BaX_2 with X = Cl, Br, OH, NO_3, O_2CCH_3, acac, tclac, tfac and thd dissociate upon heating between 80 and 200 °C. In the complexes, with X = Cl, Br, NO_3, OH and tfac, loss of 18-crown-6 is accompanied by some co-evaporation of the barium compound.

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 for a sufficient mass transport is prohibitive for a further development of a practical MOCVD (metal-organic chemical vapour deposition) process.

In this laboratory, investigations into the development of volatile alkaline-earth metal complexes have recently resulted in the isolation of a series of solid, thermally stable, volatile, fluorine-substituted Ca–, Sr– and Ba–β-diketonate complexes with neutral (poly)-oxygen and -nitrogen donor ligands [10–14]. Amongst these, the barium complexes are the least volatile. The volatile barium complex, bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)barium · 2,5,8,11,14-pentaoxapentadecane has been found to be suitable as a precursor for MOCVD of Y–Ba–Cu oxides [12] and of Tl–Ba–Ca–Cu oxides [15]. The molecular structure of this compound has been determined by X-ray crystallography [13]. The corresponding barium complex with 18-crown-6, bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)barium · 1,4,7,10,13,16-hexaoxacyclooctadecane ($Ba(hfac)_2 \cdot$18-crown-6) now has been found to possess a similar high thermal stability and volatility. This has prompted us to study the thermal stability and volatility of a series of complexes of various barium compounds with 18-crown-6.

Experimental

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

Reagents such as trifluoroacetic acid, trifluoromethanesulfonic acid, 1,1,1-trifluoropentane-2,4-dione, 18-crown-6, $BaCO_3$ and BaF_2 (Aldrich), $Ba(OH)_2 \cdot 8H_2O$ (Janssen), $BaCl_2 \cdot 2H_2O$ and $Ba(OAc)_2$ (Merck), $BaBr_2$ (Ventron), $Ba(NO_3)_2$ (Baker), $Ba(acac)_2$ (CFZ), $Ba(SCN)_2$, $BaSO_4$ and

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$Ba(Oi\text{-}Pr)_2$ (Alfa), BaI_2, $Ba(thd)_2$ and $Ba(hfac)_2$ (Strem) were commercially obtained and used as received. Elemental analysis of $Ba(hfac)_2$, stored under nitrogen, points to the presence of one mol of H_2O. *Anal.* Calc. for $C_{10}H_2O_4F_{12}Ba.H_2O$: C, 21.08; H, 0.70; F, 40.05. Found: C, 21.09; H, 0.82; F, 40.15%.

1,1,1-Trichloropentane-2,4-dione was synthesized according to literature procedures [16].

Elemental analyses 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. ^1H NMR shifts are given in units of δ, relative to TMS.

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 on 100 °c. For all experiments the direct insertion probe was heated from 40–250 °C at a rate of 30 °C/min.

The thermal stability and volatility of the $BaX_2 \cdot 18$-crown-6 complexes were determined in a classical sublimation apparatus.

$Ba(O_2CCF_3)_2$ (1)

Trifluoroacetic acid, 12.58 g (110.35 mmol), was added dropwise in 0.5 h to a stirred suspension of 15.77 g (50 mmol) of $Ba(OH)_2 \cdot 8H_2O$ in 100 ml of THF. After 1 h the slightly turbid solution was filtered and evaporated to give a colourless solid which after 4 h *in vacuo* at 80 °C analysed for $Ba(O_2CCF_3)_2 \cdot 0.3THF$, m.p. > 360 °C. *Anal.* Calc. for $C_4O_4F_6Ba$: C, 13.21; H, 0.00. Found: C, 15.71; H, 1.16%. Yield 19.23 g (99.9%). Residual THF (±0.3 equivalent) was determined by ^1H NMR. $Ba(O_2CCF_3)_2$ is very hygroscopic and should be stored in a dry atmosphere.

$Ba(O_3SCF_3)_2$ (2)

$Ba(O_3SCF_3)_2$, a colourless solid with m.p. > 360 °C, was obtained by essentially the same procedure from 10.00 g (66.62 mmol) of trifluoromethanesulfonic acid and 9.36 g (29.70 mmol) of $Ba(OH)_2 \cdot 8H_2O$ in 100 ml of THF. Yield 12.83 g (99.2%). *Anal.* Calc. for $C_2O_6S_2F_6Ba$; C, 5.51; H, 0.00; S, 14.74. Found: C, 5.48; H, 0.23; S, 14.49%. $Ba(O_3SCF_3)_2$ is very hygroscopic and should be stored in a dry atmosphere.

$Ba(Cl_3CC(O)CHC(O)CH_3)_2 \cdot 0.5H_2O$ $\{Ba(tclac)_2 \cdot 0.5H_2O\}$ (3)

1,1,1-Trichloropentane-2,4-dione, 8.13 g (40 mmol), was added to a stirred suspension of 6.31 g (20 mmol) of $Ba(OH)_2 \cdot 8H_2O$ in 50 ml of ethanol. After 1 h the slightly turbid solution was filtered and evaporated to dryness. The residue was dissolved in 50 ml of THF to give a very light-sensitive solution which rapidly turned yellow. After evaporation to dryness, the residue was washed with hexane and dried *in vacuo* at 50 °C for 4 h to give 5.24 g (48.3%) of **3**; off-white solid; m.p. 110–112 °C (dec.); ^1H NMR (CD_3COCD_3): δ 1.97 (s, CH_3) and 5.83 (s, CH). *Anal.* Calc. for $C_{10}H_8O_4Cl_6Ba \cdot 0.5H_2O$: C, 21.78; H, 1.63; Cl, 38.60. Found: C, 22.16; H, 1.96; Cl, 37.81%. The compound is light-sensitive and has to be stored in the dark.

$Ba\{F_3CC(O)CHC(O)CH_3\}_2 \cdot 0.5H_2O$ $\{Ba(tfac)_2 \cdot 0.5H_2O\}$ (4)

1,1,1-Trifluoropentane-2,4-dione, 12.71 g (82.5 mmol), was added to a stirred suspension of 7.40 g (37.5 mmol) of $BaCO_3$ in 75 ml of ethanol. After 8 h reflux, the solvent was evaporated and the residue was extracted with THF. The combined THF solutions (200 ml) were evaporated. The remaining solid was dissolved in 50 ml of diethyl ether to give **4** after 1 week at −20 °C as colourless crystals. Yield 3.55 g (21.3%); m.p. 168–230 °C (dec.); ^1H NMR (CD_3COCD_3): δ 1.91 (s, CH_3) and 5.39 (s, CH). *Anal.* Calc. for $C_{10}H_8O_4F_6Ba \cdot 0.5H_2O$: C, 26.53; H, 1.99. Found: C, 26.48; H, 2.23%.

$Ba\{F_3CC(O)CHC(O)CF_3\}_2 \cdot 18$-crown-6 $\{Ba(hfac)_2 \cdot 18$-crown-6$\}$ (5)

A mixture of 1.13 g (4.30 mmol) of 18-crown-6 and 2.37 g (4.30 mmol) of $Ba(hfac)_2 \cdot H_2O$ in toluene (75 ml) was stirred for 2 h. The slightly turbid solution was filtered and evaporated and the remaining solid was washed with pentane (50 ml) and dried *in vacuo* at 50 °C for 4 h. Yield 3.08 g (88.0%) of **5**; colourless crystalline solid; m.p. 185–188 °C. *Anal.* Calc. for $C_{22}H_{26}O_{10}F_{12}Ba$: C, 32.38; H, 3.19; F, 27.96. Found: C, 32.45; H, 3.36; F, 27.81%. The compound is non-hygroscopic. After exposure to air for two months, the elemental composition had not changed. The complex rapidly and almost quantitatively sublimes at 165 °C/0.03 mm Hg. *Anal.* Found for the sublimate: C, 32.48; H, 3.22%.

$Ba\{Cl_3CC(O)CHC(O)CH_3\}_2 \cdot 18$-crown-6 $(Ba(tclac)_2 \cdot 18$-crown-6$)$ (6)

Prepared as described for **5** from $Ba(tclac)_2$, 0.54 g (1.0 mmol), and 0.26 g (1.0 mmol) of 18-crown-6 in toluene (15 ml)/ethanol (5 ml). Yield 0.75 g (93.0%) of **6**; off-white solid; m.p. 158–160 °C (dec.). *Anal.* Calc. for $C_{22}H_{32}O_{10}Cl_6Ba$: C, 32.75; H, 3.97; Cl, 26.39. Found: C, 32.57; H, 4.05; Cl, 25.69%. The complex does not sublime. At 140–160 °C/0.01 mm

Hg, dissociation with evaporation of 18-crown-6 takes place, with concomitant thermal decomposition of Ba(tclac)$_2$.

$Ba\{F_3CC(O)CHC(O)CH_3\}_2\cdot$*18-crown-6* *(Ba(tfac)*$_2\cdot$*18-crown-6) (7)*

Prepared as described for **6** from 0.44 g (1.0 mmol) of Ba(tfac)$_2$ and 0.26 g (1.0 mmol) of 18-crown-6. Yield 0.66 g (94.0%) of **7**; off-white solid; m.p. 190–192 °C (dec.). *Anal.* Calc. for $C_{22}H_{32}O_{10}F_6Ba$: C, 37.32; H, 4.52. Found: C, 37.04; H, 4.53%. The complex partly sublimes at 150–170 °C/0.01–0.5 mm Hg (about 16% in one hour). Simultaneously complex dissociation and evaporation of free 18-crown-6 takes place.

$Ba\{(CH_3)_3CC(O)CHC(O)C(CH_3)_3\}_2\cdot$*18-crown-6*$\cdot H_2O$ *(Ba(thd)*$_2\cdot$*18-crown-6*$\cdot H_2O$*) (8)*

Ba(thd)$_2$, 0.50 g (1.0 mmol), and 0.26 g (1.0 mmol) of 18-crown-6 were dissolved in 25 ml of toluene. After stirring for 0.5 h, the solution was evaporated to dryness and the residue was dried *in vacuo* at 25 °C for 4 h. Yield 0.74 g (96.5%) of **8**; off-white solid; m.p. 130–135 °C. *Anal.* Calc. for $C_{34}H_{62}O_{10}Ba\cdot H_2O$: C, 51.95; H, 8.15. Found: C, 51.90; H, 7.68%. The complex does not sublime. At 110–130 °C/0.01–0.5 mm Hg, dissociation of the complex with evaporation of free 18-crown-6 takes place.

$Ba\{H_3CC(O)CHC(O)CH_3\}_2\cdot$*18-crown-6*$\cdot 0.5H_2O$ *(Ba(acac)*$_2\cdot$*18-crown-6*$\cdot 0.5H_2O$*) (9)*

Ba(acac)$_2$, 1.01 g (3.0 mmol), and 0.79 g (3.0 mmol) of 18-crown-6 were stirred in 20 ml of 96% ethanol for 0.5 h. The slightly turbid solution was filtered and evaporated to dryness. The residue was washed with pentane and dried *in vacuo* above concentrated H_2SO_4 for 4 days. Yield 1.42 g (79.3%) of **9**; off-white solid; m.p. softens at 135 °C, dec. > 140 °C. *Anal.* Calc. for $C_{22}H_{38}O_{10}Ba\cdot 0.5H_2O$: C, 43.40; H, 6.41. Found: C, 43.33; H, 6.43%. The complex does not sublime. At 120–140 °C/0.01–0.5 mm Hg, dissociation of the complex with evaporation of 18-crown-6 takes place.

$Ba(O_2CCF_3)_2\cdot$*18-crown-6*$\cdot H_2O$ *(10)*

A reaction mixture of 1.19 g (4.51 mmol) of 18-crown-6 in 25 ml of THF and of 1.57 g (4.09 mmol) of $Ba(O_2CCF_3)_2\cdot 0.3$THF in 25 ml of THF, was stirred for 1 h. The formed precipitate was filtered off, washed with THF and dried *in vacuo* at 25 °C for 4 h. Yield 2.07 g (91.6%) of **10**; colourless solid; m.p. 285–295 °C (dec.) *Anal.* Calc. for $C_{16}H_{24}O_{10}F_6Ba\cdot H_2O$: C, 29.75; H, 4.03; F, 17.67. Found: C, 30.04; H, 4.13; F, 17.79%. The complex is non-volatile and thermally stable for 1 h at 200 ° C/0.02 mm Hg. *Anal.* Found: C, 29.95; H, 4.03%.

$Ba(O_3SCF_3)_2\cdot$*18-crown-6*$\cdot H_2O$ *(11)*

Prepared as described for **10** from 0.98 g (2.25 mmol) of $Ba(O_3SCF_3)_2$ and 0.74 g (2.81 mmol) of 18-crown-6. Yield 1.36 g (86.6%) of **11**; colourless solid; m.p. > 360 °C. *Anal.* Calc. for $C_{14}H_{24}S_2O_{12}F_6Ba\cdot H_2O$: C, 23.41; H, 3.62; S, 8.95. Found: C, 23.45; H, 3.71; S, 8.42%. The complex is non-volatile and thermally stable for 1 h at 200 °C/0.02 mm Hg. *Anal.* Found: C, 23.59; H, 3.67%.

$Ba(O_2CCH_3)_2\cdot$*18-crown-6*$\cdot 1.5H_2O$ *(12)*

Prepared as described for **9** from 1.02 g (4.0 mmol) of $Ba(O_2CCH_3)_2$ and 1.06 g (4.0 mmol) of 18-crown-6. Yield 1.7 g (82.1%) of **12**; colourless solid; m.p. softens at 90 °C, dec. > 250 °C. *Anal.* Calc. for $C_{16}H_{30}O_{10}Ba\cdot 1.5H_2O$: C, 35.14; H, 6.04. Found: C, 35.09; H, 5.97%. The complex does not sublime. Already at 80–100 °C/0.01–0.5 mm Hg rapid dissociation occurs.

$BaCl_2\cdot$*18-crown-6*$\cdot H_2O$ *(13)*

Prepared as described for **9** from 0.98 g (4.0 mmol) of $BaCl_2\cdot 2H_2O$ and 1.06 g (4.0 mmol) of 18-crown-6. Yield 1.74 g (92.6%) of **13**; colourless solid; m.p. dec. > 250 °C. *Anal.* Calc. for $C_{12}H_{24}O_6Cl_2Ba\cdot H_2O$: C, 29.37; H, 5.30; Cl, 14.46. Found: C, 29.72; H, 5.22; Cl, 13.74%. The complex does not sublime. At 160–180 °C/0.01–0.5 mm Hg, dissociation with evaporation of 18-crown-6 occurs, accompanied by some evaporation of $BaCl_2$.

$BaBr_2\cdot$*18-crown-6*$\cdot H_2O$ *(14)*

Prepared as described for **9** from 1.19 g (4.0 mmol) of $BaBr_2$ and 1.06 g (4.0 mmol) of 18-crown-6. Yield 2.15 g (96.0%) of **14**; colourless solid; m.p. dec. > 300 °C. *Anal.* Calc. for $C_{12}H_{24}O_6Br_2Ba\cdot H_2O$: C, 24.86; H, 4.49; Br, 27.59. Found: C, 24.92; H, 4.71; Br, 27.63%. The complex does not sublime. At 160–180 °C/0.01-0.5 mm Hg, dissociation with evaporation of 18-crown-6 takes place, accompanied by some evaporation of $BaBr_2$.

$BaI_2\cdot$*18-crown-6*$\cdot H_2O$ *(15)*

Prepared as described for **9** from 1.36 g (3.48 mmol) of BaI_2 and 0.92 g (3.48 mmol) of 18-crown-6. Yield 2.26 g (99.6%) of **15**; yellow solid; m.p. > 360 °C. *Anal.* Calc. for $C_{12}H_{24}O_6I_2Ba\cdot H_2O$: C, 21.39; H, 3.86. Found: C, 21.14; H, 4.09%. The complex is non-volatile and thermally stable for 1 h at 200 °C/0.02 mm Hg. *Anal.* Found: C, 21.72; H, 3.97%.

$Ba(NO_3)_2 \cdot$ 18-crown-6 (16)

Prepared as described for **9** from 1.05 g (4.0 mmol) of $Ba(NO_3)_2$ and 1.06 g (4.0 mmol) of 18-crown-6 in a mixture of 25 ml of ethanol and 6 ml of water. Yield 2.0 g (95.2%) of **16**; colourless solid; m.p. dec. > 250 °C. *Anal.* Calc. for $C_{12}H_{24}N_2O_{12}Ba$: C, 27.41; H, 4.57; N, 5.33. Found: C, 27.63; H, 4.69; N, 5.19%. The complex does not sublime. Dissociation with evaporation of 18-crown-6 occurs at 160–180 °C/0.01-0.5 mm Hg, accompanied by some evaporation of $Ba(NO_3)_2$.

$Ba(OH)_2 \cdot$ 18-crown-6 (17)

$Ba(OH)_2 \cdot 8H_2O$, 0.32 g (1.0 mmol), and 0.26 g (1.0 mmol) of 18-crown-6 were stirred in 25 ml of ethanol for 1 h. The slightly turbid solution was filtered and evaporated to dryness. The syrupy residue was dried *in vacuo* above conc. H_2SO_4 for 4 days. Yield 0.42 g (96.5%) of **17**; colourless solid; m.p. softens at 130 °C, dec. > 180 °C. *Anal.* Calc. for $C_{12}H_{26}O_8Ba$: C, 33.08; H, 5.97. Found: C, 33.50; H, 5.83%. The complex does not sublime. Dissociation with evaporation of 18-crown-6 takes place at 105–125 °C/0.01–0.5 mm Hg, accompanied by some evaporation of $Ba(OH)_2$.

$Ba(SCN)_2 \cdot$ 18-crown-6 (18)

Prepared according to ref. 17. Yield: 86.8% of **18**; colourless solid; m.p. 265–300 °C (dec.) (lit.: 270–300 °C, dec). *Anal.* Calc. for $C_{14}H_{24}N_2S_2O_6Ba$: C, 32.44; H, 4.63; N, 5.41. Found: C, 32.67; H, 4.93; N, 5.03%. The complex is non-volatile and thermally stable for 1 h at 200 °C/0.02 mm Hg. *Anal.* Found: C, 32.27; H, 4.78; N, 5.42%.

Attempted preparations of $BaF_2 \cdot$, $BaSO_4 \cdot$ and $Ba(Oi\text{-}Pr)_2 \cdot$ 18-crown-6 complexes

Various attempts have been made to prepare 18-crown-6 adducts of BaF_2, $BaSO_4$ and $Ba(Oi\text{-}Pr)_2$ by treatment of one equivalent of barium compound with one equivalent of 18-crown-6. Experimental conditions varied from reactions in toluene or ethanol solution at reflux temperatures to heating of both reactants together without solvent. No distinct adducts could be isolated.

Thermal stability and volatility of the $BaX_2 \cdot$ 18-crown-6 complexes

A 100 mg sample was heated at 0.01–0.05 mm Hg. The temperature was raised until sublimation of the complex or release of 18-crown-6 was observed. Subsequently, that temperature was maintained for 1 h. Ultimately, the temperature was raised to a maximum of 200 °C. After cooling, the composition of the sublimate and of the residue was determined by ^1H NMR and/or elemental analysis.

Results and discussion

Since Pedersen's first report on the coordination of metal ions with synthetic macrocyclic polyethers [18], the so-called crown ethers, the kinetics and mechanism of such a coordination have been extensively studied [19, 20]. Much attention has been given to the coordination of the divalent barium ion with 18-crown-6 ethers in solution [21–25], but only a few complexes of the type $BaX_2 \cdot$ 18-crown-6 have been isolated and characterized in the solid state ($X = SCN$ [17, 26], $\frac{1}{2}CH_2(SO_3)_2$ [27] and $(C_4H_9O)_2PO_2$ [28]). No data on volatility have been reported.

Aiming at the synthesis of volatile barium compounds a series of $BaX_2 \cdot$ 18-crown-6 complexes has now been synthesized and characterized.

Besides commercially available BaX_2 compounds, the new fluorine-containing barium compounds $Ba(O_2CCF_3)_2$ (**1**) and $Ba(O_3SCF_3)_2$ (**2**) and the chlorine-substituted barium–β-diketonate $Ba(tclac)_2$ (**3**) have been synthesized and applied as starting materials. These compounds have been prepared from $Ba(OH)_2$ and two equivalents of the appropriate acid (**1, 2**) or β-diketone (**3**). Compounds **1** and **2** were isolated in almost quantitative yield as colourless hygroscopic solids, which have to be stored in a dry atmosphere. Compound **3** appears to be light-sensitive, especially in solution. It was isolated in 48% yield as an off-white solid, which has to be stored in the dark. The corresponding fluorine-substituted barium–β-diketonate, $Ba(tfac)_2$ (**4**), recently prepared from Ba metal and 1,1,1-trifluoropentane-2,4-dione [29], has been prepared from $BaCO_3$ and the diketone in 21% yield. Within the series of BaX_2 compounds, compounds **1–4** possess high Lewis acid characteristics and hence exert a strong tendency to complex formation with Lewis bases.

The $BaX_2 \cdot$ 18-crown-6 complexes, **5–18**, have been synthesized by an equimolar reaction of BaX_2 with 18-crown-6 at room temperature in toluene, THF or ethanol (see 'Experimental'). Initially, slightly turbid solutions were obtained, due to the presence of insoluble impurities. The complexes **10** ($X = O_2CCF_3$) and **11** ($X = O_3SCF_3$) appeared to be insoluble in the solvent used (THF) and precipitated from the reaction mixture. $Ba(SCN)_2 \cdot$ 18-crown-6 (**18**) has been prepared according to ref. 17.

Distinct complexes of BaF_2, $BaSO_4$ and $Ba(Oi\text{-}Pr)_2$ with 18-crown-6 could not be isolated. Apparently, the high crystal lattice energies of the uncoordinated barium compounds prevent complex formation with 18-crown-6 to occur as has been noticed by Pedersen for instance for other metal fluorides [18]. For metal alkoxides, the intermolecular coordination via alkoxide bridges is sufficiently strong to preclude the occurrence of complex formation with additional free oxygen donor ligands [30].

The $BaX_2\cdot$18-crown-6 complexes have been isolated, generally in high yields, as off-white to colourless solids which have been characterized by melting point, elemental analysis and ^1H NMR. The melting points are sizably higher than that of 18-crown-6 (42–45 °C), indicating that real complexes are present, not mixtures of BaX_2 and 18-crown-6.

The elemental analyses of most complexes point to the presence of 0.5–1.5 equivalents of H_2O. The presence of water in metal–crown ether complexes has been discussed by various authors [31–37]. A H_2O molecule bonded to the metal ion provides hydrogen bonding to the crown ether ligand, which adds stability to the complex [28]. In general, X-ray structure determinations have shown hydrogen bonding to be a significant phenomenon in the crystal structures of many crown ether complexes [38–44].

NMR data of the $BaX_2\cdot$18-crown-6 complexes, together with those of 18-crown-6 in various solvents, are presented in Table 1.

Coordination of 18-crown-6 to the various BaX_2 compounds appears to result in downfield shifts of the crown ether proton signals from 0.07–0.27 ppm in non-aromatic solvents. These shifts are in the same order as those reported in the literature to occur upon coordination of alkali metal cations to 18-crown-6 [17]. The largest downfield shifts do not necessarily imply the strongest coordinating power as also solvent effects are involved. Downfield shifts are generally larger in CD_3COCD_3 than in $CDCl_3$ or CD_3OD. In C_6D_6, upfield shifts are observed due to aromatic solvent-induced shift (ASIS) effects. This is best demonstrated with complex **5**, $Ba(hfac)_2\cdot$18-crown-6. In C_6D_6, as compared with $CDCl_3$, a large upfield ASIS of about 0.6 ppm is observed for the crown ether protons. This points to a non-specific tangential approach by benzene molecules to these sites of the complex (see refs. 45 and 46 and refs. therein). For the CH signal of the hfac ligand, a downfield ASIS of 0.56 ppm is observed. This is explained by the nearby presence of large, electron-rich CF_3 groups. At this site, the interaction with benzene will be with the positive sites of the molecule, thus causing a negative ASIS. The same phenomena have been observed in the NMR spectra of the related complex of $Ba(hfac)_2$ with 2,5,8,11,14-pentaoxapentadecane [14] in $CDCl_3$ and C_6D_6.

The thermal stability and volatility of the various $BaX_2\cdot$18-crown-6 complexes have been investigated. In general, stability constants of complexes with the cyclic ligand 18-crown-6 are 3–4 orders of magnitude larger than those with the corresponding open-chain compound tetra-ethylene glycol dimethylether (pentaglyme) [47, 48], the so-called macrocyclic effect. Moreover, the better the metal ion fits into the 18-crown-6 cavity (cavity radius: 1.38 Å), the more stable the 18-crown-6–metal ion complex will be [49, 50]. With the Ba^{2+} ion radius being 1.36 Å, $BaX_2\cdot$18-crown-6 complexes are expected to be very stable.

The thermal stability and possible volatility of the various $BaX_2\cdot$18-crown-6 complexes have been studied by heating the complexes *in vacuo* (0.01–0.5 mm Hg) with concomitant condensation of volatile products. The temperature was raised until sublimation and/or release of 18-crown-6 ligand was observed. The maximum temperature applied was 200 °C.

The complexes **10**, **11**, **15** and **18** are stable and non-volatile up to 200 °C at 0.01–0.5 mm Hg for 1 h. Elemental analysis showed that no decomposition had taken place. Apart from complex **5**, all the other complexes decompose with loss of the 18-crown-6 ligand, as shown by ^1H NMR of the condensate. Complex **12** is the weakest of the series and loss of 18-crown-6 ligand already occurs at 80 °C. The more stable complexes **13**, **14** and **16** dissociate *in vacuo* at temperatures between 160–200 °C. Small amounts of barium salts have been found to be present in the 18-crown-6 condensate from compounds **13**, **14**, **16** and **17**. However, the overall volatility of these complexes is low.

Within the series of barium–β-diketonate·18-crown-6 complexes **5**–**9**, only in the presence of the highly fluorinated β-diketonate, hfac, is a stable and volatile complex formed which can be sublimed without decomposition, as has been demonstrated with **5**. This complex rapidly and almost quantitatively sublimes at 165 °C and 0.03 mm Hg. Lowering the degree of fluorination in the β-diketone, as in $Ba(tfac)_2\cdot$18-crown-6 (**7**), results in a less stable complex which cannot be sublimed without substantial dissociation. At 150–170 °C/0.01–0.5 mm Hg, only 16% of **7** had sublimed after 1 h. The corresponding complexes, containing the fluorine-free β-diketones thd (**8**) and acac (**9**), are even less stable, resulting in complex dissociation at 110–140 °C. Upon comparison of the fluorine- and chlorine-substituted β-diketonate ligand containing complexes **6** and **7**, it has become apparent that thermal degradation of the chlorinated β-diketonate system occurs at 150°C. This is consistent with the findings of Morris and Koob [51] who, in mass spectroscopic studies of metal tclac complexes, observed C–Cl bond cleavages which had no analogues in the corresponding fluorinated or non-halogen-containing β-diketonates.

TABLE 1. ^1H NMR data of 18-crown-6 and the $BaX_2 \cdot$18-crown-6 complexes

Compound	Solvent	18-crown-6 δ CH_2	Δ[f]	Other groups δ	
				CH_3	CH
18-crown-6	CD_3COCD_3	3.59			
18-crown-6	$CDCl_3$	3.68			
18-crown-6	CD_3OD	3.67			
18-crown-6	D_2O	3.69			
18-crown-6	C_6D_6	3.54			
$Ba(hfac)_2 \cdot$18-crown-6[a] (**5**)	$CDCl_3$	3.75	−0.07		5.78
$Ba(hfac)_2 \cdot$18-crown-6	CD_3OD	3.77	−0.10		5.66
$Ba(hfac)_2 \cdot$18-crown-6	C_6D_6	3.19	+0.35		6.25
$Ba(tclac)_2 \cdot$18-crown-6[b] (**6**)	CD_3COCD_3	3.84	−0.25	2.02	5.72
$Ba(tclac)_2 \cdot$18-crown-6	$CDCl_3$	3.82	−0.14	2.04	5.86
$Ba(tclac)_2 \cdot$18-crown-6	CD_3OD	3.79	−0.12	2.12	5.81
$Ba(tfac)_2 \cdot$18-crown-6[c] (**7**)	$CDCl_3$	3.78	−0.10	1.99	5.43
$Ba(tfac)_2 \cdot$18-crown-6	CD_3OD	3.82	−0.15	2.13	5.40
$Ba(thd)_2 \cdot$18-crown-6$\cdot H_2O$[d] (**8**)	$CDCl_3$	3.82	−0.14	1.15	5.53
$Ba(thd)_2 \cdot$18-crown-6$\cdot H_2O$	C_6D_6	3.48	+0.06	1.35	5.68
$Ba(acac)_2 \cdot$18-crown-6$\cdot 0.5H_2O$[e] (**9**)	$CDCl_3$	3.77	−0.09	1.83	5.63
$Ba(acac)_2 \cdot$18-crown-6$\cdot 0.5H_2O$	CD_3OD	3.76	−0.09	1.90	5.58
$Ba(O_2CCF_3)_2 \cdot$18-crown-6$\cdot H_2O$ (**10**)	CD_3COCD_3	3.79	−0.20		
$Ba(O_3SCF_3)_2 \cdot$18-crown-6$\cdot H_2O$ (**11**)	CD_3COCD_3	3.86	−0.27		
$Ba(O_2CCH_3)_2 \cdot$18-crown-6$\cdot 1.5H_2O$ (**12**)	$CDCl_3$	3.79	−0.11	1.94	
$BaCl_2 \cdot$18-crown-6$\cdot H_2O$ (**13**)	CD_3OD	3.81	−0.14		
$BaBr_2 \cdot$18-crown-6$\cdot H_2O$ (**14**)	CD_3OD	3.81	−0.14		
$BaBr_2 \cdot$18-crown-6$\cdot H_2O$	D_2O	3.79	−0.10		
$BaI_2 \cdot$18-crown-6$\cdot H_2O$ (**15**)	CD_3OD	3.82	−0.15		
$Ba(NO_3)_2 \cdot$18-crown-6 (**16**)	D_2O	3.78	−0.09		
$Ba(OH)_2 \cdot$18-crown-6 (**17**)	CD_3OD	3.80	−0.13		
$Ba(SCN)_2 \cdot$18-crown-6 (**18**)	CD_3OD	3.83	−0.16		

[a] hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate. [b] tclac = 1,1,1-trichloropentane-2,4-dionate. [c] tfac = 1,1,1-trifluoropentane-2,4-dionate. [d] thd = 2,2,6,6-tetramethylheptane-3,5-dionate. [e] acac = pentane-2,4-dionate. [f] Δ = δ(18-crown-6)−δ($BaX_2 \cdot$18-crown-6).

This study has been actuated by the present need for volatile barium compounds as MOCVD precursors for the deposition of thin films of high-Tc superconducting oxides, such as Y–Ba–Cu and Tl–Ba–Ca–Cu oxides. Barium-β-diketonates are currently applied as MOCVD precursors for the synthesis of thin films of $YBa_2Cu_3O_{7-x}$. A major disadvantage of these precursors is that sufficient volatility is only attained at temperatures in excess of 200 °C. Under these conditions oligomerization and decomposition reactions occur, resulting in the formation of non-volatile barium-containing products. Barium-β-diketonates as such are coordinatively unsaturated and hence they have a strong tendency to form intermolecularly associated clusters [52]. The strategy chosen to enhance the volatility of barium compounds has now been to complete the barium coordination sphere with multidentate Lewis base ligands, in particular the cyclic polyether 18-crown-6. Compared to non-fluorine-containing barium-β-diketonates like $Ba(acac)_2$ and $Ba(thd)_2$, the Lewis acid characteristics of $Ba(hfac)_2$ and hence its tendency to adduct formation is much higher. Strong coordinative bonds are formed between the hard barium cation and the ether oxygen donor atoms. $Ba(hfac)_2 \cdot$18-crown-6 is a colourless, thermally stable, non-hygroscopic, crystalline solid, m.p. 185–188 °C, which readily sublimes at 165 °C and 0.03 mm Hg. It is soluble in common organic solvents such as benzene, chloroform, acetone and methanol and it can be handled and stored in air. This is in contrast to $Ba(hfac)_2$ itself, which is hygroscopic and it sublimes only at a very low rate at 205–220 °C/10^{-5} mm Hg, with simultaneous decomposition [29].

The electron impact mass spectrum of $Ba(hfac)_2 \cdot$18-crown-6 shows peaks at *m/z* ratios 609, 421, 345, 201 and 157, corresponding to $(M\text{–hfac})^+$, $(M\text{–2hfac+F})^+$, $[M\text{–hfac–(18-crown-6)}]^+$, $[M\text{–2hfac}]^{2+}$ and BaF^+, respectively, as well as a number of other small peaks. The fragment $(M\text{–2hfac})^{2+}$ is found at *m/z* 201 instead of 402, due to the presence of a double positive charge. A molecular ion peak was not observed. The positive chemical ionization spectrum shows the molecular ion peak $(M\text{–}H)^+$ at m/z 815. The major other peaks are at m/z 797, 609, 265 and 209, corresponding to $(M\text{–}F)^+$, $(M\text{–hfac})^+$, $[(18\text{-crown-6})+H]^+$ and $(\text{hfac}+2H)^+$, respectively.

The negative chemical ionization spectrum shows the molecular ion M^- at m/z 816. Two other major peaks are found at m/z 552 and 208, corresponding to $[M\text{–}(18\text{-crown-6})]^-$ and $(\text{hfac}+H)^-$, respectively. Scale expansion of the high-mass regions does not show any peak beyond the molecular ion, indicating $Ba(hfac)_2 \cdot 18$-crown-6 to be a stable monomeric complex, this in contrast to $Ba(hfac)_2$ itself, where the dimeric ion $[Ba_2(hfac)_3]^+$ appeared to give the highest mass peak [29].

Attempts to determine the X-ray crystal structure of $Ba(hfac)_2 \cdot 18$-crown-6 have run into difficulties. So far no accurate data set could be obtained, but further work is in progress.

Attempts to apply the same concept to convert other types of barium salts into thermally stable, more volatile barium salt · 18-crown-6 complexes has met with limited success. A few complexes show some volatility (**7**, **13**, **14**, **16** and **17**), but their thermal stability appears to be insufficient. On the other side, the thermally very stable $BaX_2 \cdot 18$-crown-6 complexes (**10**, **11**, **15** and **18**) show no volatility up to 200 °C/0.02 mm Hg. Apparently, in these compounds rather strong intermolecular interactions exist due to intermolecular coordination and/or ionic interactions. Together with the recently reported $Ba(hfac)_2 \cdot 2,5,8,11,14$-pentaoxapentadecane complex [13, 14], $Ba(hfac)_2 \cdot 18$-crown-6 is a representative of a new class of thermally stable volatile barium compounds. The application of these compounds as MOCVD precursors for the deposition of thin films of superconducting $YBa_2Cu_3O_{7-x}$ is currently being investigated [10–14].

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