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Thermoanalytical studies on crown ether–alkali complexes[1]

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Abstract

Solid samples prepared from benzo-15-crown-5, its nitro, acetylamino and decanoylamino derivatives (Group I), and chloro-dibenzo-aza-crown ethers (Group II) with alkali metal salts were studied. The existence of solid adducts between LiBr, NaSCN, KSCN and crown ethers of group I was proved by DSC. The melting points of adducts of the same ligand were found to increase in KSCN<NaSCN<LiBr order. DSC and TG results suggested a ligand scission mechanism of thermal decomposition for all the complexes except that of benzo-15-crown-5 and KSCN where a dissociation and evaporation process took place. The samples prepared from crown ethers belonging to group II were found to be mechanical mixtures of the alkali salts and crown compounds. © 1998 Elsevier Science B.V.

1. Introduction

The ability of dibenzo-18-crown-6 to form complexes with the alkali ions was first observed by Pedersen, right after the discovery of crown compounds [1,2]. Crown ethers have been applied as selective complexing and adduct forming agents in a number of areas, for example in phase transfer catalysis or as ionophores in alkali ion-selective electrodes.

Thermoanalytical methods have been used in studies on phase transitions and thermal decompositions of solid complexes between crown ethers and different metals. Formation of potassium complexes of dibenzo-18-crown-6 and its nitro derivatives in mixtures of the crown compound and excess KI was detected by DTA by De Souza and Firemand [3]. DSC was applied by Bianchi et al. in the description of the solid–liquid phase diagram in the KCNS–dibenzo-18-crown-6 system. In the same work, complex formation was reported in an equimolar mixture of the reactants after melting of the crown ether [4]. Korber and Jansen recently investigated the thermal decomposition of the complex between rubidium ozonide and dibenzo-18-crown-6 by TG and DTA [5].

Rare earth metal complexes of crown ethers have also attracted attention. The differences between the thermal decomposition of $LnL(NCS)_3$ and $LnL(NO_3)_3$ type (L=dibenzo-18-crown-6) were demonstrated by Gurrieri et al. [6]. In a series of articles, Buenzli and coworkers studied lanthanoid complexes of 12-crown-4, 15-crown-5 and 18-crown-6. TG and DSC were applied to describe the stoichiometry, water content and thermal stability [7–11]. The 1:1 complexes of the heavier lanthanides (Ln=Gd–Lu) with 15-crown-5 and 18-crown-6 usually transformed to 4:3 complexes during thermal decomposition [7–9,11]. This transformation was influenced by the inorganic anion, as well.

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[1] Dedicated to Professor A. Kettrup on the occasion of his 60th birthday.

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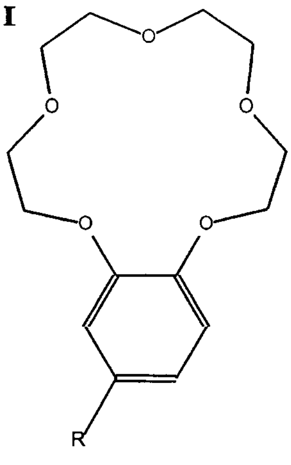
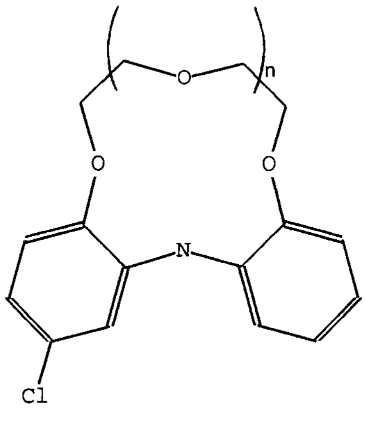
Quasi-isothermal thermogravimetry and mass spectrometry were applied in the characterization of the thermal stability of complexes formed by rare earth β-diketonates and 18-crown-6 by Martynova et al. [12]. Other authors confirmed the existence of 18-crown-6 sulfonamide complexes [13], and described the thermal behavior of crown containing polymers [14] and crown complexes of oligopeptides [15] by DSC.

In the present work, thermoanalytical methods have been applied to prove or exclude the presence of alkali metal–crown complexes in solid samples. Benzo-15-crown-5 and derivatives (**I**), and dibenzo-aza-crown ethers (**II**) were used as ligands.

I



II



	I		**II**
B15	R = -H	A1	n = 1
NO_2-B15	R = -NO_2	A2	n = 2
ACA-B15	R = -NH-CO-CH_3	A3	n = 3
DA-B15	R = -NH-CO-C_9H_{19}	A4	n = 4

The thermal behavior has been characterized on the basis of DSC and TG measurements. The stoichiometry of the complexes and the effect of complex formation on the thermal decomposition of the ligand have been described, as well.

2. Experimental

Crown-alkali adducts were prepared with the ligands listed above from lithium bromide, sodium thiocyanate and potassium thiocyanate. The total list of adducts (or intended adducts) is shown in Table 1. In the following, the prepared materials are denoted by the short code of the ligand (see the structural formulae of **I** and **II**) and the metal, for example, the adduct obtained from potassium thiocyanate and 4′-nitrobenzo-15-crown-5 is abbreviated as NO_2–B15–K.

The benzo-15-crown-5 complexes were obtained by the crystallization from acetonic (Li and Na complexes) and ethanolic (K complexes) solutions. In the case of the dibenzo-aza-crown ethers, an equimolar mixture of the ligand and the metal salt was processed in boiling acetone. Dibenzo-aza-crown adducts usually did not crystallize from the applied solutions. Therefore, with the exception of A3–Li (which separated from the solution on cooling), the solid samples were prepared by the total evaporation or by the addition of ethyl ether to the solution. The first procedure was applied in the case of A1–Li, A2–Li, A1–Na and A2–Na, the second for A4–Li, A1–K, A2–K, A3–K and A3–Na.

Table 1
Solid samples prepared from crown ethers and alkali salts

	LiBr	NaSCN	KSCN
I and derivatives			
B15	+		+
NO_2–B15	+	+	+
ACA–B15	+		+
DA–B15	+		
II			
A1	+	+	+
A2	+	+	+
A3	+	+	+
A4	+		

Thermoanalytical investigations were carried out on a DuPont 1090 thermal analysis system. TG curves were recorded in flowing air with a heating rate of 10°C/min. The DSC cell was purged by nitrogen, and the heating rate was 5°C/min. In some cases EGA curves were measured in nitrogen with 8°C/min (DuPont 916 TEA detecting the organic volatiles by means of a hydrogen FID). Phase changes were also observed on a hot stage microscope.

In order to obtain comparative data on the stoichiometry of the complexes, emission spectrometry was used. The samples were dissolved in 10 ml cc. HNO_3:H_2O_2 solution (volume ratio 3:1), the analysis was carried out in a Labtest Plasmalab ICP–AES.

3. Results and discussion

DSC curves of benzo-15-crown-5 and its adducts with LiBr and KSCN are presented in Fig. 1. Melting peaks are marked on the basis of thermomicroscopic observation. The free ligand exhibited a sharp melting peak, then, starting at about 130°C a second, broad endotherm. Both adducts show endothermic effects

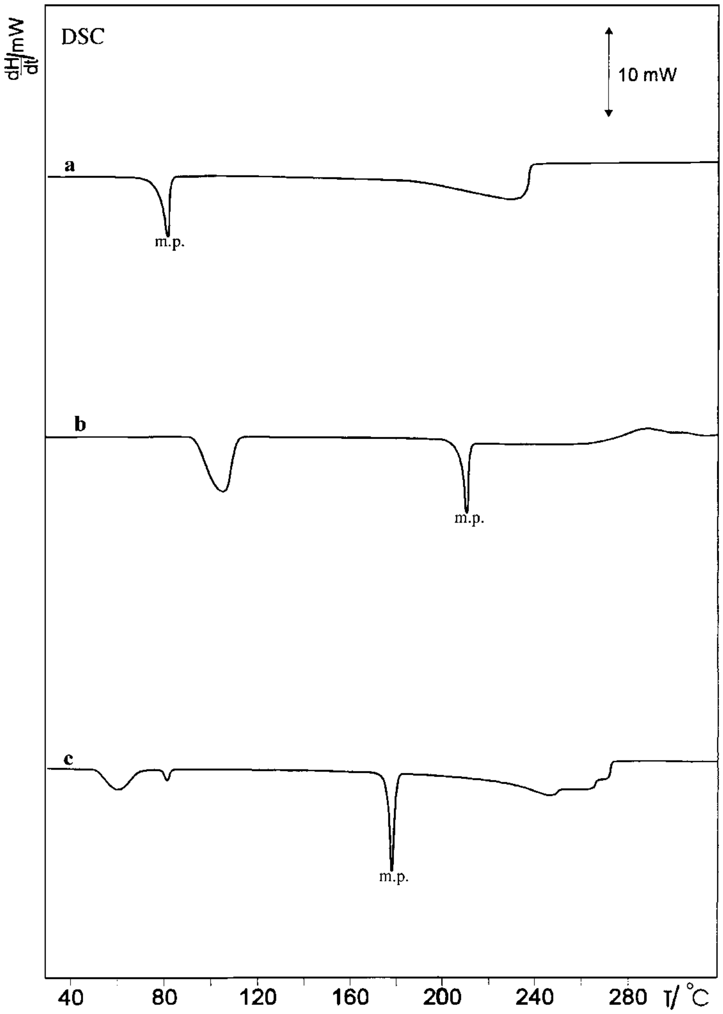


Fig. 1. DSC curves of benzo-15-crown-5 and its complexes. (a) B15; (b) B15–Li; (c) B15–K.

before melting. The melting peaks of B15–Li and B15–K are sharp and appear at much higher temperatures than that of the free ligand. Note that the melting peak of the ligand is totally missing from the pattern of the adducts. Besides, potassium thiocyanate itself has an endothermic structural transformation at 145°C and melts at 173°C, whose effects are also absent from the curve of the potassium complex. These facts prove that both samples were real adducts (compounds) containing complexes of the metal ion and the crown ether. The melting peak of both the lithium and the potassium adducts are superposed on a broad effect, which is endothermic for B15–K and consists of endothermic and exothermic parts for B15–Li. These broad effects are due to the decomposition of the complexes, which will be discussed on the basis of thermogravimetric results.

The TG curves of benzo-15-crown-5 and its adducts with lithium bromide and potassium thiocyanate are shown in Fig. 2. The scale belonging to the low temperature fractions of the curves is larger (see the left-hand side) in order to show the small mass changes below 200°C. The weight loss of the crown ether itself started near 200°C, and became complete at 250°C under the conditions of the experiment. Considering the shape of the curve, a simple evaporation may be assumed. A similar conclusion was drawn by Souza [3] about the behavior of 18-crown-6. This is supported by the shape of the corresponding DSC endotherm, as well (see Fig. 1). Both adducts exhibited a mass loss step at low temperatures, explaining the small endothermic peaks in the DSC below the melting points. According to the EGA measurements, organic volatiles (solvent residue) are only responsible for a small fraction of this mass loss. So the TG steps in question may be assigned to the evolution of water (taken up from the solvent during preparation or from the air afterwards), and the height of the steps may be used in a rough calculation of the stoichiometric ratio of water in the samples.

The main decomposition step of the metal complexes took place at temperatures about 50°C higher

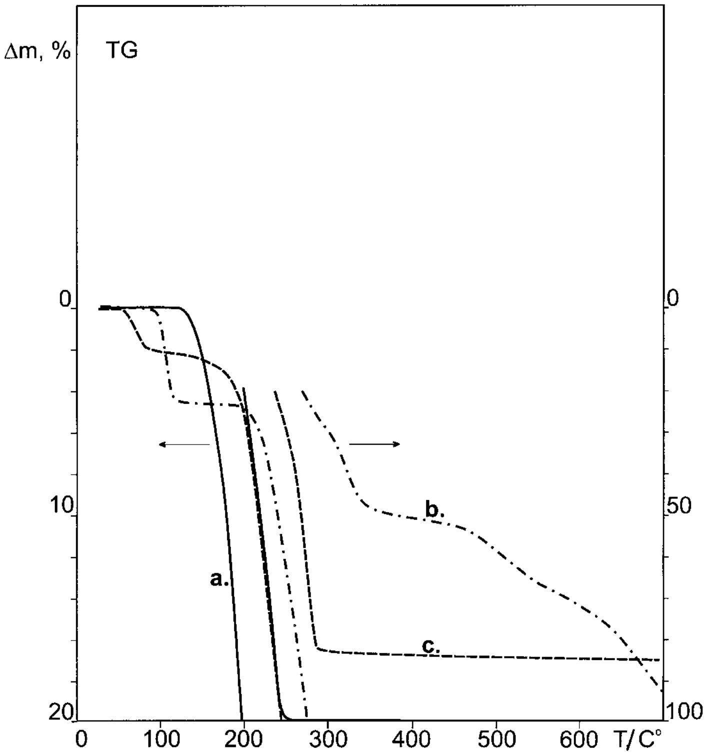


Fig. 2. TG curves of benzo-15-crown-5 and its complexes. (a) B15; (b) B15–Li; (c) B15–K.

than that of B15 itself. The potassium complex, similar to the free ligand, decomposed in a single step ending at 290°C. This reaction may be regarded as a simple dissociation and evaporation process, corresponding to the broad endotherm in the DSC curve (see Fig. 1). The amount of residue at 700°C is the inorganic component and can be used in the calculation of the salt:crown ether stoichiometric ratio.

Note that the TG runs were carried out in air in order to remove the entire organic matter, while an inert gas was applied in the DSC investigations. Yet, a qualitative comparison of the DSC and TG results is possible. The oxidative character of the processes in air only dominates at higher temperatures (above 300–400°C).

The lithium complex decomposed in a different way: the shape of the TG curve above 200°C shows a multi-step process, which may be explained by the decomposition of the ligand. This process corresponds to the broad effect detected by DSC, consisting of endothermic and exothermic parts. So in this case, in contrast to B15–K, the metal– ligand bond is strong and the scission of covalent bonds inside the ligand and the dissociation of the complex probably compete. A similar phenomenon, i.e., an endothermic and a subsequent exothermic part of metal–crown complex decomposition was reported earlier by Gurrieri et al. [6] for the heavier lanthanides.

In the case of the lithium complex, TG data are not suitable for the calculation of the stoichiometry as an overlap occurs between the oxidative decomposition of the organic residue and the evaporation of LiBr starting below 700°C.

The DSC and TG curves of the nitro derivative and its adducts are shown in Figs. 3–4. The results may be interpreted similarly to the B15 series discussed earlier. Melting temperatures of the adducts are much higher than that of the free ligand, confirming the existence of a solid complex.

The decomposition of free NO_2–B15 is similar to that of benzo-15-crown-5, however, it started at a higher temperature (as shown by the TG curve, Fig. 4). The residue at the end of the decomposition (ca. 300°C) may be attributed to a small carbonized fraction, which decomposed in air at higher temperatures. The lithium and potassium adducts showed a low temperature mass loss corresponding to the endothermic effects on the relevant DSC curves. The adduct of NaSCN was stable up to 250°C.

The shape of the TG curves in the interval belonging to the adduct decomposition resembles the pattern of B15–Li discussed above. Besides, the part of DSC curves corresponding to the decomposition was exothermic for all the three adducts (Fig. 3). So, in the case of NO_2–B15, the bonds between the crown ether and the metal ion were very strong, and ligand decomposition dominated in the entire temperature interval of the reaction.

The thermal behavior of ACA–B15 and DA–B15 as well as that of their adducts was qualitatively similar to the nitro derivative. The decomposition of the free acetylamino and decanoylamino derivative resembled that of NO_2–B15. The amount of the carbon-rich residue at the end of the main decomposition step showed an increasing trend in B15<NO_2–B15<ACA–B15<DA–B15 order. The approximate values in the same order were 0%, 3%, 5% and 13%. The existence of solid adducts was proved by the DSC curves; the decomposition of the metal complexes showed an exothermic character. ACA–B15–Li lost water below 150°C. In the case of DA–B15–Li a sample measured immediately after preparation did not show any mass change below decomposition, while another batch, stored and handled under normal circumstances for days, contained a significant amount of water. This points to a highly hygroscopic character of the lithium bromide adducts. Lithium bromide itself is hygroscopic, too.

The most important characteristics and data of the DSC curves of samples containing benzo-15-crown-5 and derivatives are summarized in Table 2. Formation of adducts resulted in much higher melting points for all the ligands. The available data suggest a trend in this respect: the effect of the alkali metal salts on the melting points decreased in LiBr>NaSCN>KSCN order.

The free ligands and B15–K decomposed in an endothermic process. For all the adducts of NO_2–B15, ACA–B15 and DA–B15, the decomposition of the complexes was exothermic. Taking into account the information from the TG curves discussed before, evaporation of the free ligand is involved in the endothermic reactions (after complex dissociation in the case of B15–K). The exothermic decompositions are dominated by ligand scission. B15–Li exhibited an

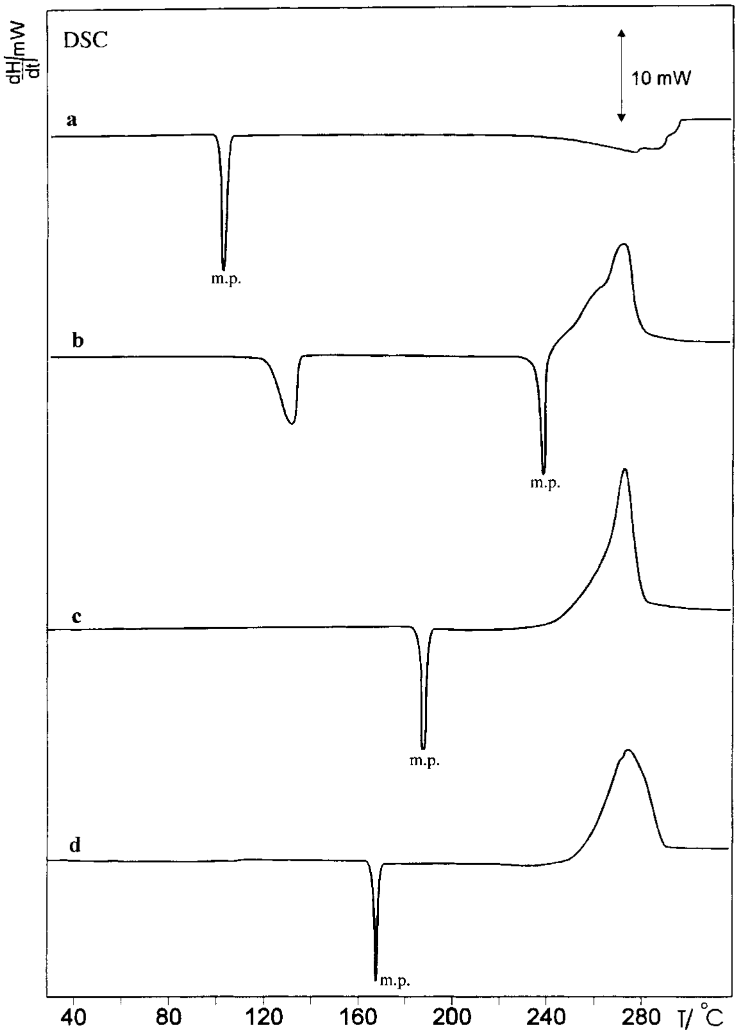


Fig. 3. DSC curves of the nitro derivative and its complexes. (a) NO_2–B15; (b) NO_2–B15–Li; (c) NO_2–B15–Na; (d) NO_2–B15–K.

intermediate behavior with the two mechanisms probably competing.

TG data are evaluated in Table 3 from the aspect of complex stoichiometry. This was only possible for adducts of sodium and potassium thiocyanates. The evaporation of lithium bromide, as has been mentioned, is not negligible below 700°C. The metal content of the adducts measured by ICP–AES allowed the calculation of the stoichiometry for all the samples. The results are summarized in Table 4.

The data in Tables 3 and 4 demonstrate the existence of 1:1 complexes for lithium and sodium and that of 2:1 complexes for potassium.

Since water removal appeared as a clear step on the TG curves of several adducts, the existence of stoichiometric hydrates seemed possible. The water:adduct molar ratios calculated from the height of the TG steps and the proposed compositions are listed in Table 5. Comparing the measured mass loss to the theoretical amount of water, the existence of some hydrate phases may be assumed. Further investigations are needed to verify these assumptions and to describe the characteristics of the hydrates.

Dibenzo-aza-crown adducts, as has been mentioned in Section 2, usually did not crystallize from the applied solutions, therefore complex formation

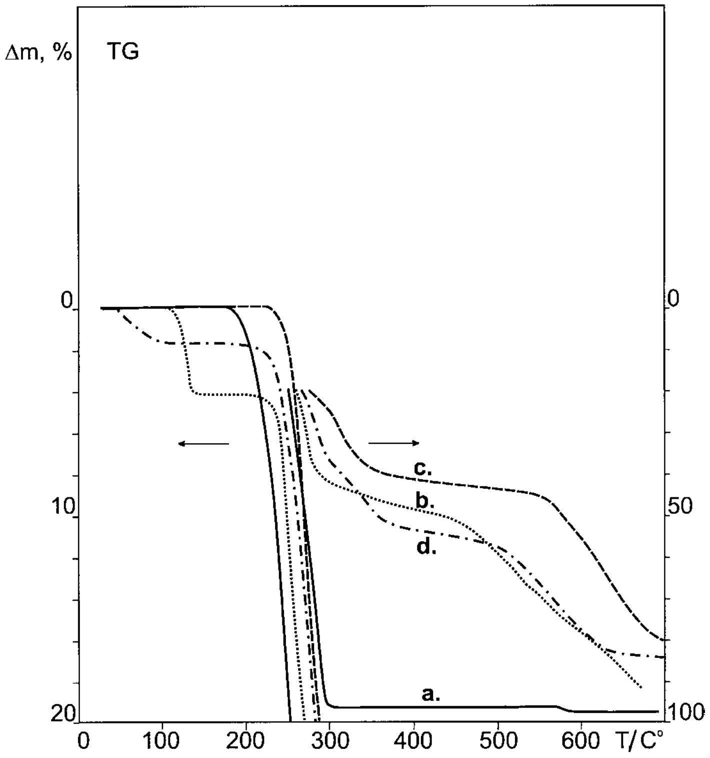


Fig. 4. TG curves of the nitro derivative and its complexes. (a) NO_2–B15; (b) NO_2–B15–Li; (c) NO_2–B15–Na; (d) NO_2–B15–K.

Table 2
DSC data for the alkali complexes of benzo-15-crown-5 and derivatives

Substance	Temperature of the melting peak (°C)	Endothermic or exothermic decomposition	Temperature of the decomposition peak (°C)
B15	82	Endo	229
B15–Li	210	Endo+exo	250 and 286
B15–K	178	Endo	250
NO_2–B15	99	Endo	273
NO_2–B15–Li	238	Exo	272
NO_2–B15–Na	188	Exo	273
NO_2–B15–K	168	Exo	273
ACA–B15	155	Endo	315
ACA–B15–Li	268	Exo	298
ACA–B15–K	161	Exo	325
DA–B15	110	Endo	330
DA–B15–Li	188	Exo	302

between the two components in the solid material was also questionable. The thermal measurements proved that these samples were no real adducts. The DSC curves of all but one of the alkali salt: dibenzo-aza-crown ether preparates (obtained by evaporation or ethyl ether addition) showed the thermal effects belonging to melting and other transitions of the free ligands and pure alkali salts, proving the presence of mechanical mixtures. In the case of A3–Li, the melting process detected by the DSC and observed in the

Table 3
Stoichiometry of the anhydrous adducts on the basis of thermogravimetric data

Sample	Inorganic residue (%)	Assumed composition	Theoretical residue (%)
B15–K	15.0	L_2KSCN	13.1
NO_2–B15–Na	18.5	LNaSCN	19.0
NO_2–B15–K	14.0	L_2KSCN	11.8

In the column of assumed stoichiometry, L denotes the relevant ligand. The decomposition of ACA–B15–K was not complete at 700°C.

Table 4
Stoichiometry of the anhydrous adducts on the basis of metal content determined by ICP–AES

Sample	Determined metal content (mg/g)	Proposed composition	Theoretical metal content (mg/g)
B15–Li	18.5	LLiBr	19.7
B15–K	49.2	L_2KSCN	61.6
NO_2–B15–Li	17.0	LLiBr	17.4
NO_2–B15–Na	59.5	LNaSCN	58.0
NO_2–B15–K	48.6	L_2KSCN	53.6
ACA–B15–Li	16.6	LLiBr	17.0
ACA–B15–K	49.8	L_2KSCN	52.2
DA–B15–Li	14.0	LLiBr	13.4

In the column of proposed compositions, L denotes the relevant ligand.

Table 5
Stoichiometry of water containing adducts on the basis of TG measurements

Sample	Mass loss below decomposition (%)	Proposed composition of the hydrate	Theoretical amount of water (%)
B15–Li	5	$LLiBr \cdot H_2O$	4.8
B15–K	2.5	$L_2KSCN \cdot H_2O$	2.8
NO_2–B15–Li	4.5	[a]	
NO_2–B15–K	1.5	[b]	
ACA–B15–Li	4	$LLiBr \cdot H_2O$	4.2
DA–B15–Li	6.5[c]	$LLiBr \cdot 2H_2O$	6.6

[a] Uncertain; the amounts of water and volatile organic material were comparable.
[b] Uncertain; 2.4% and 1.2% corresponds to the monohydrate and the hemihydrate, respectively.
[c] Mass loss value relates to a sample stored for some days.
In the column of proposed compositions, L denotes the relevant ligand.

microscope was very broad and incorporated the melting point of the free crown ether; thus the existence of an adduct in the solid phase could not be proven or entirely excluded.

4. Conclusions

The existence of solid adducts was proved by DSC in the systems containing benzo-15-crown-5 and its derivatives. The formation of the alkali metal crown ether complexes resulted in an increase of the melting temperature (as compared to that of the free ligand). The intensity of this effect showed a trend depending on the alkali metal salt (LiBr>NaSCN>KSCN) or on the alkali ion itself. Some adducts, firstly those of LiBr, most likely form stoichiometric hydrates.

In case of some potassium and sodium complexes, TG curves recorded in air were suitable to describe the ligand:metal molar ratio.

Complex formation brought about a change in the temperature range and the mechanism of thermal decomposition. In most complexes, the decomposition was dominated by the scission of the ligand; in the case of the free crown ethers evaporation took place. Among the adducts studied, B15–K was found the only one whose decomposition consists of complex dissociation and ligand evaporation.

The samples prepared from the alkali salts and dibenzo-aza-crown ethers were not real adducts, rather mechanical mixtures of the solid components. In one case, the existence of a real complex could neither be proved nor excluded by thermal analysis.

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