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Thermal behaviour of hydrated and anhydrous Cucurbituril

A DSC, T.G. and calorimetric study in temperature range from 100 to 800 K

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Abstract

Thermal behaviour of differently hydrated Cucurbituril samples was studied using Differential Scanning Calorimetry and Thermogravimetry in the temperature range from 100 to 800 K. The enthalpy of reaction with water was measured by isothermal calorimetry at 298 K for anhydrous Cucurbituril and Cucurbituril$\cdot$8H_2O. Two or three water molecules appear to be bonded stronger than the others. For these two subgroups of hydration water molecules, the respective bond energies were calculated as: (-22.5 ± 2.5) kJ mol^{-1} H_2O and (-9.4 ± 1.0) kJ mol^{-1} H_2O. © 1998 Elsevier Science B.V.

Keywords: Cucurbituril; Water; Bond energy; Calorimetry

1. Introduction

Cucurbituril is a molecular container compound with an exceptional capacity to encapsulate alkaline cations [1]. The synthesis of this compound has been known since 1905 [2]. The structure readily self assemblies from acidic condensation between urea, glyoxol and formaldehyde [3]. This molecule is rather rigid with an internal cavity of ca. 5.5 Å diameter, which is accessible by two portals with 4 Å diameter.

The trivial name Cucurbituril was proposed by Freemann et al. [3] because of a general resemblance to a gourd or a pumpkin. Recently, a review concerning host-design and molecular recognition devoted to Cucurbituril has been published [4].

Due to the strong interactions of the carbonyl oxygen donners atoms with cations, stable complexes will be obtained. Form a large number of results of elementary analysis, it has been proved that Cucurbituril hydrates with more than eight water molecules exist. The present work was done to get some quantitative data for the hydration and thermal behaviour of this interesting molecule.

2. Experimental

2.1. Materials

The macrocyclic compound Cucurbituril was synthesised according to procedure given in the lit-

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erature [2–5]. After several recrystallizations from acidic solution, the pure ligand is obtained. Anhydrous Cucurbituril was prepared by dehydration under vacuum, at 130°C, during 24 h. The anhydrous state was confirmed by Thermogravimetry (TG) analysis. The product is then stored in a glove box under dry argon.

2.2. Apparatus

The thermal behaviour of Cucurbituril was studied by means of:

a Mettler TA 8000 equipped with a Differential Scanning Calorimetry (DSC) 820 cell and usable from −150 to +500°C.
a simultaneous DSC–TG analyser Setaram Labsys, which can operate in the temperature 25–1600°C range.

They were standardised for temperature and heat flow rate using the temperature and enthalpies of melting of high-purity metals and compounds according to the procedure recommended by the manufacturers. Experiments were performed under inert atmosphere (argon).

A Cucurbituril sample was transferred into an aluminium pan (40 µl) which was sealed and weighed. Masses were in the 15–25 mg range. For the study of dehydration and complexation processes, the crucible covers had calibrated orifices in order to remove volatile species.

Evaluation of TG and DSC events were performed by means of Mettler Star and Setaram softwares.

The enthalpies of interaction were measured in water at 25°C using a home-made isoperibol calorimeter built after the model of Sunner and Wadsö [6]. The calorimeter was chemically calibrated using the enthalpy of dissolution of tris-hydroxyaminomethane in HCl 0.1 mol l^{-1}. The experiment gave an average value of (-29.63 ± 0.8) kJ mol^{-1} in good agreement with the IUPAC value (-29.77) kJ mol^{-1} [7]. During these experiments, the interactions between the solid sample of Cucurbituril and water are measured using the variation of temperature in the measurement cell. Then, the enthalpies of interaction were calculated comparatively to an electric calibration. For each experiment, we used about 100 mg of solid Cucurbituril and 90 ml of distilled water.

3. Results and discussion

3.1. Thermal behaviour of hydrated Cucurbituril

3.1.1. Low temperature

Cucurbituril with different hydration ratios (from anhydrous up to saturated product) is studied by DSC between −100 and +30°C. Unlike ß-Cyclodextrin [8], the thermal behaviour of Cucurbituril does not exhibit a transition in this range of temperature.

3.1.2. High temperature

A typical DSC curve of hydrated Cucurbituril sample is shown in Fig. 1. A simultaneous TG analysis is performed with the same heating rate of 5°C min^{-1}. In the temperature 25–500°C range, three endothermic effects can be easily detected:

The effect 1 is broad (from 30 to 150°C) and corresponds to the dehydration of Cucurbituril. The corresponding enthalpy and loss of mass obviously depend on the initial water content of the samples.

The effect 2 with a maximum around 250°C is weak and probably corresponds to the beginning of the Cucurbituril decomposition. The average values of enthalpy and loss of mass are respectively of 15 J g^{-1} and 2.1%. These values are independent from the initial hydration ratios.

The effect 3 just begins after the effect 2, with a maximum at 425°C. It is the main step of the Cucurbituril decomposition with a loss of mass of 50% and an important enthalpy value of 760 J g^{-1}.

So, we can conclude that the thermal degradation of Cucurbituril starts at 230°C with two different steps. At the final temperature of 500°C a black powder is obtained.

3.2. Dehydration study: DSC–TG results

The thermal effect 1 corresponding to the dehydration of differently hydrated samples has been measured. The experimental procedure is as follows. After cooling down to −30°C and stabilization during 120 s, the run is performed up to 225°C with a heating rate of 5°C min^{-1}. A broad endothermic effect corresponding to the dehydration of Cucurbituril is observed. DSC curves obtained with various water content are given in Fig. 2. Simultaneously, a DSC–TG experiment was carried out in order to evaluate the water content using

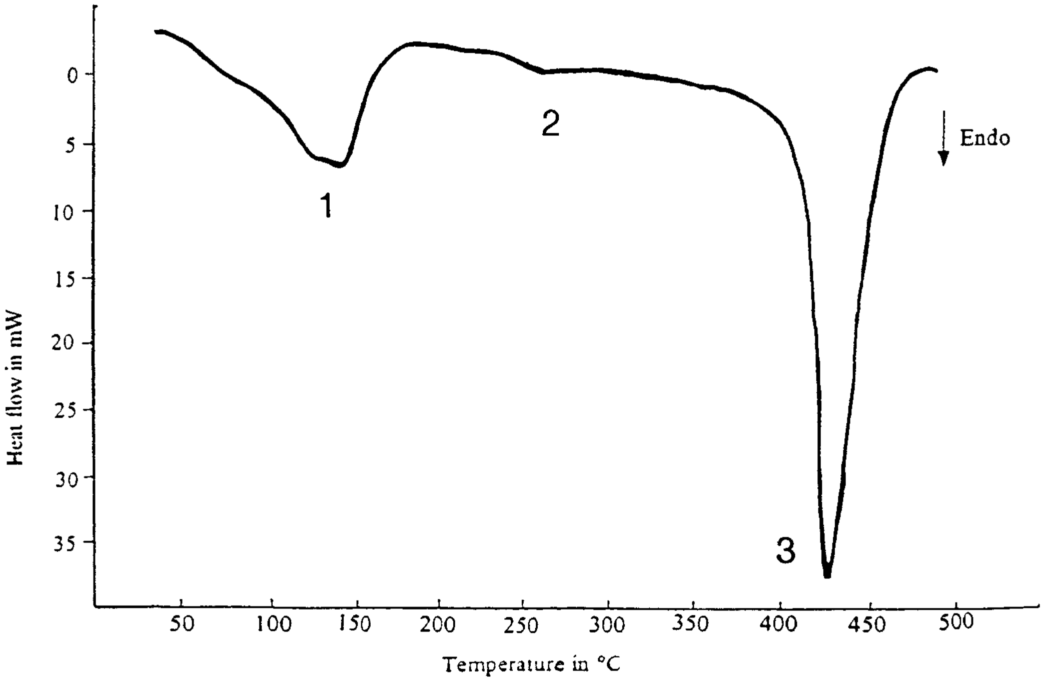

Fig. 1. DSC typical curve of hydrated Cucurbituril (Cucurbituril·8H_2O), effect 1: dehydration; effect 2 and 3: partial decomposition of Cucurbituril.

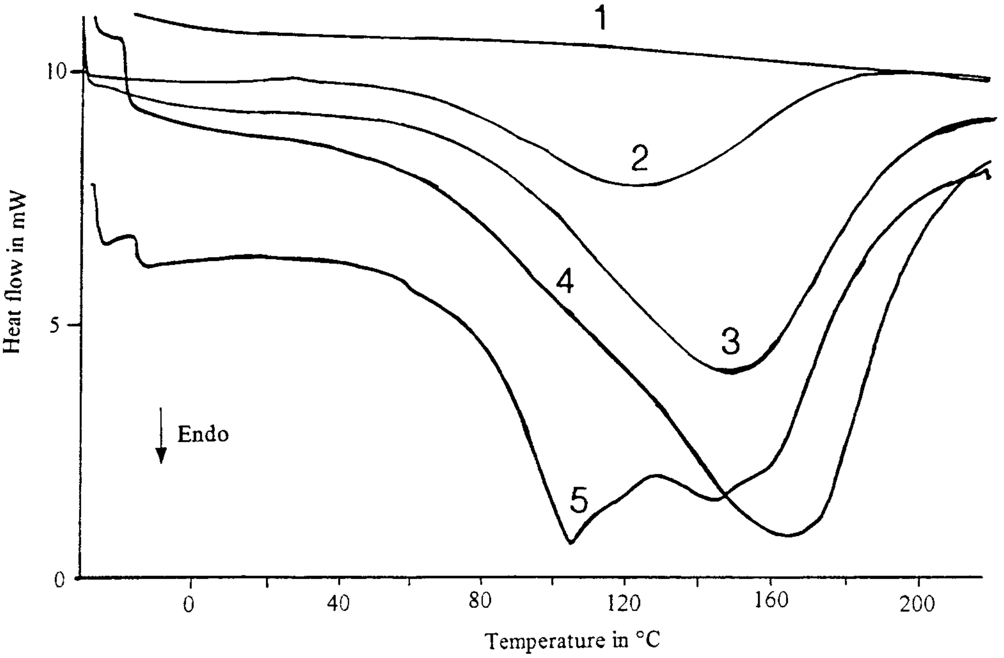

Fig. 2. DSC curves of five hydrated samples of Cucurbituril in the temperature range 0–200°C (effect 1 on Fig. 1): 1. anhydrous Cucurbituril; 2. Cucurbituril·1.8H_2O; 3. Cucurbituril·5.6H_2O; 4. Cucurbituril·8.0H_2O; 5. Cucurbituril·11.0H_2O.

the same heating rate and in the same range of temperature.

Considering the value of enthalpy of vaporization of pure water and the total measured enthalpy, we can calculate the enthalpy of bonding of water molecules on the Cucurbituril macrocycle. From a thermodynamic point of view, the measured thermal effect corresponds to the reaction

$$(\text{Cucurbituril} \cdot n\text{H}_2\text{O})(\text{s}) \xrightarrow{\Delta H_{\text{mes}}} (\text{Cucurbituril})(\text{s}) + n(\text{H}_2\text{O})(\text{g})$$

This reaction can be considered as two steps:

1. dehydration

$$(\text{Cucurbituril} \cdot n\text{H}_2\text{O})(\text{s}) \xrightarrow{\Delta_{\text{dehydr}}H} (\text{Cucurbituril})(\text{s}) + n(\text{H}_2\text{O})(\text{l})$$

2. vaporization of water

$$n(\text{H}_2\text{O})(\text{l}) \xrightarrow{\Delta_{\text{vap}}H} n(\text{H}_2\text{O})(\text{g})$$

So, it is obvious that

$$\Delta H_{\text{mes}} = \Delta_{\text{dehydr}}H + \Delta_{\text{vap}}H \quad \text{(a)}$$

Table 1
Enthalpy of the endothermic effect measured in the temperature range 30–150°C by DSC during the dehydration of Cucurbituril

%H_2O (weight)	nH_2O	$\Delta_{\text{mes}}H$ in kJ mol^{-1}
1.7	0.96	55.8
2.2	1.25	88.7
3.0	1.71	104.7
3.3	1.89	123.7
3.8	2.19	142.0
4.0	2.31	141.2
5.0	2.92	149.0
7.0	4.17	214.4
7.5	4.49	235.1
7.8	4.69	239.7
7.9	4.75	243.5
10.5	6.50	332.0
10.8	6.71	342.0
13.2	8.42	430.0
13.4	8.57	426.0
13.7	8.79	455.2
14.3	9.24	458.0
15.2	9.93	498.0

The values of ΔH_{mes} for eighteen samples with various hydrated states are given in Table 1.

Evaluation of ΔH_{mes} in kJ mol^{-1} (Cucurbituril $\cdot nH_2O$) is plotted vs. n (Fig. 3). There is an obvious

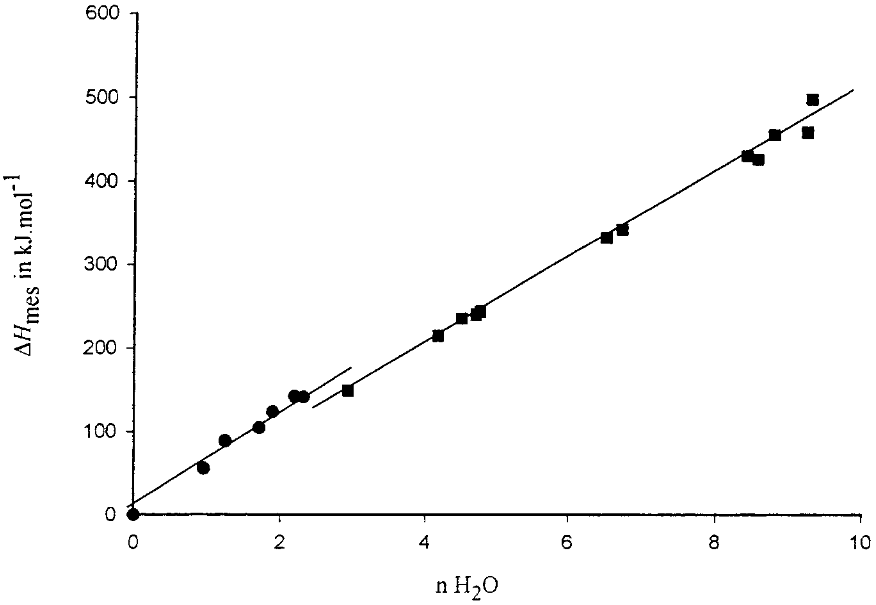

Fig. 3. DSC results: total measured enthalpy of dehydration (+vaporization of water) for (Cucurbituril$\cdot nH_2O$) samples vs. n.

discontinuity in the dehydration thermal behaviour of Cucurbituril between n=2 and n=3. Above and below these values, two straight lines can be plotted with a good reliability.

$$\Delta H_{\text{mes}} = (50.0n + 4.6)\ \text{kJ mol}^{-1} \quad 2 \text{ or } 3 < n < 10$$

$$\Delta H_{\text{mes}} = (63.1n + 0.8)\ \text{kJ mol}^{-1} \quad 0 < n < 2 \text{ or } 3$$

The slope of each relationship directly corresponds to the average value of ΔH_{mes} in kJ mol^{-1} H_2O. According to the relation (a) and taking into account $\Delta_{\text{vap}}H$ mol^{-1} H_2O=40.6 kJ mol^{-1} (at 373 K) [9], it comes

for 2 or 3 < n < 10

$$\Delta_{\text{dehydr}}H\ \text{mol}^{-1}H_2O = (9.4 \pm 1.0)\ \text{kJ mol}^{-1}$$

for 0 < n < 2 or 3

$$\Delta_{\text{dehydr}}H\ \text{mol}^{-1}H_2O = (22.5 \pm 2.5)\ \text{kJ mol}^{-1}$$

The given relative uncertainties include the experimental accuracy concerning DSC measurements and water content evaluations. Form these results, we assume that two types of hydration water molecules exist in Cucurbituril hydrates. The bond energies are rather different but the number of water molecules being part of each subgroup (2 and 6 or 3 and 5) cannot be evaluated by means of DSC experiments. In order to precise this point, other experiments have been performed as follows.

3.3. Hydration study

Two series of experiment have been performed by isothermal calorimetry in water at 25°C:

1. anhydrous Cucurbituril+water (6 runs)
2. Cucurbituril·8H_2O+water (4 runs).

The corresponding enthalpies of reaction are ΔH_1 and ΔH_2. The average values are:

$$\Delta H_1 = (-119.6 \pm 5.0)\ \text{kJ mol}^{-1}$$

$$\Delta H_2 = (-5.7 \pm 0.5)\ \text{kJ mol}^{-1}$$

Considering the following thermodynamic cycle based on the obvious final state in the two series of experiments:

$$\begin{tikzcd}
\text{(anhydrous Cucurbituril) (s)} + 8H_2O \arrow[rr, "\Delta_{\text{hydr}}H"] \arrow[dr, "\Delta H_1"'] & & \text{(Cucurbituril } 8H_2O\text{) (s)} \arrow[dl, "\Delta H_2"] \\
& \text{(Cucurbituril) in water} &
\end{tikzcd}$$

$$\Delta_{\text{hydr}}H = \Delta H_1 - \Delta H_2$$

Using the above experimental values, the hydration of one mole of Cucurbituril by 8 moles of water is:

$$\Delta_{\text{hydr}}H = (-113.9 \pm 5.5)\ \text{kJ mol}^{-1}$$

This value represents the sum of the eight bond energies relative to the eight water molecules.

Using the bond energy values previously determined for the first subgroup E_1=−9.4 kJ mol^{-1} H_2O and for the second subgroup E_2=−22.5 kJ mol^{-1} H_2O,the sum $5E_1$+$3E_2$=−114.5 kJ mol^{-1} H_2O is in good agreement with the above value of $\Delta_{\text{hydr}}H$.

From this correlation, it could seem likely that three water molecules are stronger bonded than the five others. But, taking all the uncertainties into account, we cannot totally eliminate the hypothesis of only two water molecules strongly bonded and six more weakly bonded.

4. Conclusion

Considering all our calorimetric results, we assume that the various hydration water molecules are not energetically equivalent in Cucurbituril hydrates. Our macroscopic interpretation can be correlated with previous structural observations [3]. In this crystallographic study, Freeman describes the cavity of Cucurbituril as being occupied by a free water molecule, which is a part of a hydrogen bond chain containing three water units. Some other interesting informations have been given by recent works [1,10] concerning the complex formation of Cucurbituril with alkaline and other metal cations.

At first, the metal ions do not enter the Cucurbituril cavity but coordinate to the carbonyl O atoms at its portals. Then three water molecules reside in the cavity between the two metal ions. So, obviously we can distinguish these three water molecules from the other external water molecules. They probably have an important role in the formation and in the stabilization of the Cucurbituril/cations complexes in aqueous solution. These differences between two subgroups of water molecules are clearly in good agreement with our results of two distinct values of bond energies. A similar study [11] of a comparable compound ß-Cyclodextrin concluded that water molecules in the cavity and interstitial water molecules were equivalently bonded with an energy around (-10 kJ mol^{-1} H_2O). From this work, we propose approximately the same value (-9.4 kJ mol^{-1} H_2O) for the bond energies of interstitial water molecules in hydrated Cucurbituril. From a thermodynamic point of view, the host-guest chemistry by Cucurbituril in aqueous medium is more complicated than by Cyclodextrin. At least, two cases must be considered in relation to the release or not of the three more bonded internal water molecules.

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