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Thermal transformations of the supramolecular compound of cucurbit[8]uril with cobalt(III) complex {*trans*-[Co(en)$_2$Cl$_2$]@CB[8]}Cl·17 H$_2$O

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Abstract The thermal decomposition of hydrated cucurbit[8]uril $C_{48}H_{48}N_{32}O_{16}\cdot 20H_2O$ (CB[8]) and the inclusion compound of cucurbit[8]uril with cobalt(III) complex {*trans*-[Co(en)$_2$Cl$_2$]@CB[8]}Cl·17 H$_2$O was studied in the inert atmosphere by TG, TM, and DSC methods. The dehydration of $(C_{48}H_{48}N_{32}O_{16})\cdot 20H_2O$ (at 320–390 K), and the decomposition of cucurbituril itself (at 620–720 K) are accompanied by a decrease in the sample volume. The inclusion compound loses water molecules at 320–380 K; dehydration is accompanied by an increase in the sample volume. The decomposition (pyrolisis) of the anhydrous compound takes place at 620–720 K; the decomposition is forestalled by a continued increase in the sample volume with an endothermic peak (490–600 K), and only the mass loss (620–720 K) is accompanied by a decrease in the sample volume. The included guest complex does not lose amines until the decomposition process is complete; the previously observed increase in the sample volume is explained by the expansion of cavitand molecules due to a distortion of the included $[Co(en)_2Cl_2]^+$ complex on heating.

Keywords Coordination compounds · Dilatometry · Inclusion compounds · Supramolecular chemistry · Thermogravimetry

Introduction

The cavitand cucurbit[8]uril $C_{48}H_{48}N_{32}O_{16}$ (CB[8]) [1] (Fig. 1) was used as a molecular container for different complexes of transition metals with various organic amines [2]. Specifically, [Co(en)$_2$Cl$_2$]Cl, [Ni(en)$_2$Cl$_2$], and [Cu(en)$_2$(H$_2$O)$_2$]Cl$_2$ trans-complexes are encapsulated with the formation of stable supramolecular inclusion compounds. In compliance with the structural investigations [2], the compound compositions are: {*trans*-[Co(en)$_2$Cl$_2$]@CB[8]}Cl·17H$_2$O (Fig. 2), {*trans*-[Ni(en)$_2$(H$_2$O)$_2$]@CB[8]Cl$_2$}·23.5H$_2$O, {*trans*-[Cu(en)$_2$(H$_2$O)$_2$]@CB[8]}Cl$_2$·17H$_2$O. These inclusion compounds under heating lose water molecules at 320-390 K and are stable up to 620 K [2].

Individual ethylenediamine complexes decompose on heating with the amine removal at 490–510 K [2], however, these coordinated amines are not removed from the mentioned inclusion compounds until the pyrolysis of the cucurbit[8]uril matrix is complete at 620 K [2].

It has previously been shown that supramolecular compounds with different structures (such as intercalates, clathrates, and inclusion compounds based on microporous coordination polymers) undergo a complex transformation during heating; the decomposition processes with the removal of volatile guest molecules are accompanied by the structural transformations not only during but also before the decomposition process [3–5].

Experimental

Synthesis and properties [2]

Cucurbit[8]uril and the ethylenediamine complex were synthesized according to the published procedures [2].

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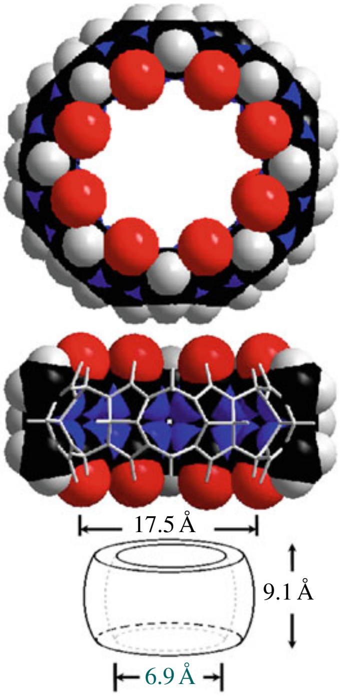

Fig. 1 The structure of the Cucurbit[8]uril $C_{48}H_{48}N_{32}O_{16}$ (CB[8]) [1, 2]

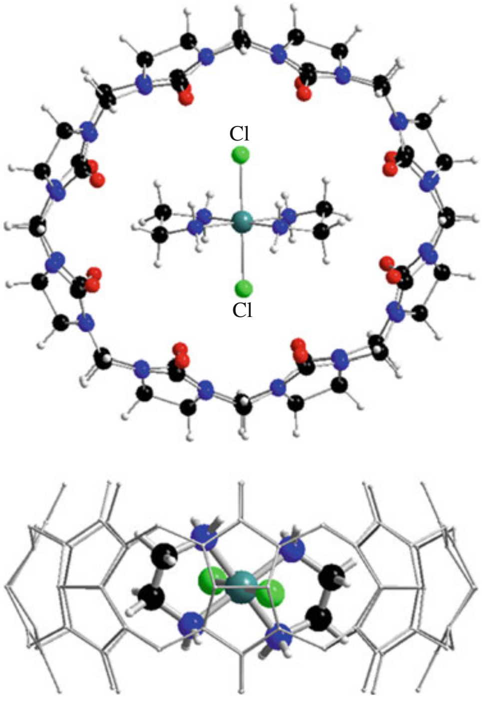

Fig. 2 The structure of the {trans-$[Co(en)_2Cl_2]$@CB[8]}$^+$ [2]

For the synthesis of the inclusion compound, cucurbit[8]uril (0.012 mol) was added into the boiling solution of *trans*-$[Co(en)_2Cl_2]Cl$ (0.095 mol) in water (6.5 cm^3). The boiling (with the backflow condenser) was in progress for 2 h, after that the solution was cooled. The solution was cured for 12 h; green crystals were filtered and dried in air.

Elemental analysis. Found (%): C, 32.48; H, 4.88; N, 26.24; Cl, 5.75; calculated for $C_{52}H_{98}Cl_3N_{36}O_{33}Co$ (%) : C, 32.52; H, 5.14; N, 26.25; Cl, 5.54 [2].

There are two different crystallographic forms (I and II) of the *trans*–$[Co(en)_2Cl_2]^+$ cation in the crystal structure of the inclusion compound. A definite disparity in the inclination of the CoN_4 plane to the equatorial plate of the cavitand molecule is observed: 85^0(I) and 87^0(II). The structure of the ethylenediamine complex changed after the inclusion into the cavitand cavity: the Co–N and Co–Cl bond lengths changed differently in the two forms (I and II). The inclusion of guest molecules is accompanied by an ellipsoidal distortion of the cavitand molecule itself [2]. The crystal structure consists of the alternating (I) and (II) layers of $\{[Co(en)_2Cl_2]@CB[8]\}^+$ fragments; the space between the fragments inside these layers is filled with the Cl^- anions and the water molecules with a complex system of hydrogen bonds.

Thermal analysis

TG measurements were carried out on a Netzsch TG 209 F1 thermal analyzer. The experiments were performed in the argon flow (40 cm^3 min^{-1}), at heating rates of 10 K min^{-1}; the sample mass was kept ca. 11.0–15.0 mg. Thermomechanical analysis (dilatometry) was carried out on a Netzsch TMA 202 thermal analyzer; the powder layer thickness was 1.02–1.03 mm. DSC measurement were carried out on a Netzsch DSC-204 thermal analyzer.

Results and discussion

Cucurbit[8]uril $(C_{48}H_{48}N_{32}O_{16})\cdot 20H_2O$ loses water molecules on heating at 320–390 K; the subsequent decomposition of the anhydrous compound (the pyrolysis of organic molecules) takes place at 630–720 K. Both dehydration and decomposition reactions are accompanied by a decrease in the sample volume on the TMA curve (Fig. 3). Such a decrease in the sample volume can be due to that the structure changes when the gaseous molecules are removed; it is typical of simple decomposition processes [3, 4].

$\{[Co(en)_2Cl_2]@CB[8]\}Cl\cdot 17H_2O$ loses water molecules on heating at 320–380 K; the dehydration reaction is accompanied by an increase in the sample volume. There is no mass loss up to 620 K, but the heating from 490 to 620 K is accompanied by a continued increase in the sample volume and a new endothermic peak (Fig. 4). The decomposition process (the pyrolisis of the organic matrix)

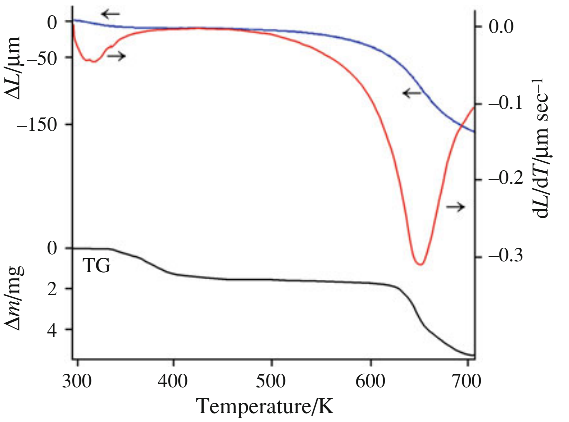

Fig. 3 The thermal decomposition of Cucurbit[8]uril (CB[8])·$20H_2O$. The thermogravimetric and dilatometric curves are obtained at the heating rate 10 K min^{-1}

takes place at 620–720 K and is accompanied by a decrease in the sample volume.

The observed variations in the sample volume must be caused by a change in the compound structure on heating. It is evident (Fig. 4) that water molecules can leave the compound as it expands, because the water molecules deeply packed between the $\{[Co(en)_2Cl_2]@CB[8]\}^+$ fragments in the stack of layers are now released.

The increased sample volume of the anhydrous inclusion compound continues to increase at 490–620 K, and the decomposition reaction itself begins only at 620 K. This can be explained by the previous expansion of the matrix molecular structure because of the presence of the complex $[Co(en)_2Cl_2]^+$ cation. The individual $[Co(en)_2Cl_2]Cl$ complex is known to lose ethylenediamine molecules at 490–510 K [2]; the $[Co(en)_2Cl_2]^+$ coordination sphere, packed inside the cavitand molecule $C_{48}H_{48}N_{32}O_{16}$, cannot break the bonds (N–Co–N), but can distort at these temperature (there is enough space for this distortion with bond elongation without breaking the coordination sphere (Fig. 2). This distortion results in the expansion of cavitand molecules.

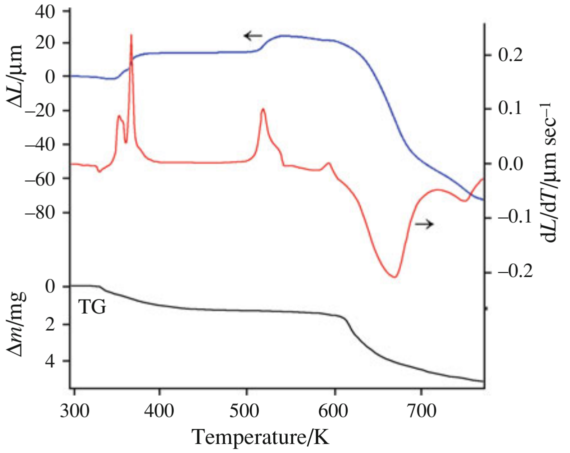

Fig. 4 The thermal decomposition of the inclusion compound {trans-$[Co(en)_2Cl_2]@CB[8]\}Cl\cdot17H_2O$. The thermogravimetric and dilatometric curves are obtained at the heating rate 10 K min^{-1}

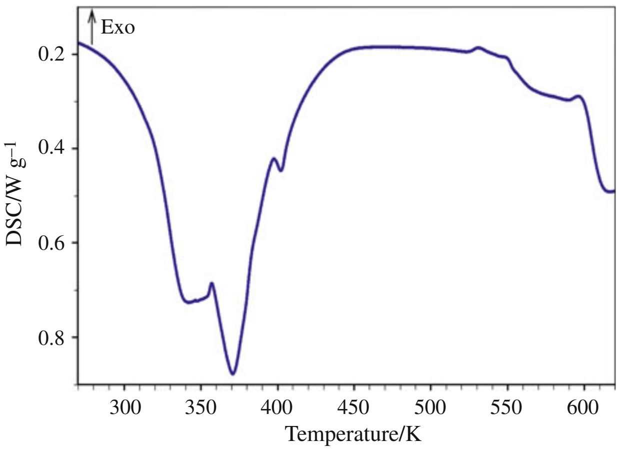

Fig. 5 The thermal decomposition of the inclusion compound {trans-$[Co(en)_2Cl_2]@CB[8]\}Cl\cdot17H_2O$. The DSC curve was obtained at the heating rate 6 K min^{-1}

The DSC curve (Fig. 5) is in full agreement with this explanation. A series of the endothermic peaks at 273–500 K are associated with the dehydration process; the complex endothermic peak at 530–600 K is not associated with mass loss (Fig. 4), but corresponds to the increase in the sample volume.

Conclusions

The supramolecular compounds based on the cavitand cucurbit[8]uril $(C_6H_6N_4O_2)_8$ with the included coordination compounds of transition metals with amines are sufficiently stable. Although simple coordination compounds such as $[Co(en)_2Cl_2]Cl$, $[Ni(en)_2Cl_2]$, $[Cu(en)_2(H_2O)_2]Cl_2$ begin to lose ethylenediamine molecules at $\approx$490 K, the included guests do not detach from the coordinated amines on heating until the complete decomposition (pyrolisis) of the inclusion compound at 620–730 K [2].

The dilatometric and DSC experiments show that the sample volume of the studied inclusion compound increases on heating (at 490–600 K) much earlier than the decomposition reaction is complete (620–720 K). It is explained by the expansion of the $(C_{48}H_{48}N_{32}O_{16})$ molecule because of the distortion of the included $[Co(en)_2Cl_2]^+$ coordination sphere. This distortion occurs instead of the removal of ethylenediamine molecules locked in the limited space inside the cavitand molecule. The structural phase transformation forestalls the decomposition.

The observed distortion seems to be the relief of the primary structural tension (changes in the Co–N and Co–Cl bond lengths generated by the inclusion phenomenon) [2].

It is worth noting that the traditional studies of the thermal properties of the inclusion compounds are limited to the determination of thermal stability and the steps of the decomposition (e.g., [6–8]), while a study of volume transformations in these interesting systems can be quite informative.

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