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Review

Combinations of Cyclodextrins with Synthetic and Natural Compounds

ANNA SOPKOVÁ* and PETER MÉZEŠ
Faculty of Sciences, P.J. Šafarik's University, Košice, Slovakia

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Abstract. Host–guest compounds formed by cyclodextrins with synthetic and natural compounds are reviewed with regard to their properties, characterisation (using experimental and computational methods) and applications.

Key words: combinations, cyclodextrins, zeolites, clays, natural, synthetic compounds, host- guest complexes

1. Introduction

Inclusion compounds are formed by very different molecules being of at least two types: the host (H) and the guest (G). Every inclusion compound may be described by the formulation H.G, H1.H2.G1, H.G1.G2 etc. [1–15]. In this manner one may combine the advantageous properties of the individual host or guest components in the newly formed inclusion compound combinations.

The combinations may be utilised in practice in many processes, where an enlarged space inside the host component has to be formed or where the guest component may be stabilised. This is very convenient in the case of the encapsulation and stabilisation of different compounds, inorganic or organic, and also in separation processes. During the formation of inclusion compounds the functions of the host and guest may be changed. In some cases the same compound may be simultaneously in the role of the host and guest, e.g., in the case of the combination of zeolite and cyclodextrin (CD) [16–18], where the CD is enclosed in the zeolite and simultaneously the CD is enclosing a futher compound. In that case the starting materials are two real inclusion compounds.

In a similar way the products of zeolite with sorbed cyclodextrins or tetracyanonickelates were prepared in our Department [4, 5, 16]. Both the zeolites [1, 18, 20–23] and the tetracyanocomplexes $M(Bm)M(CN)_4.nG$ can give inclu-

* Author for correspondence: Vihorlatská 80.04001 Košice, Slovakia.

sion compounds; they both originally contain guest water molecules and different organic molecules replacing the water.

The idea of preparing combinations of CDs with zeolites originated in the papers of Kijima [9–13], where the combinations of montmorillonites and CDs are described. The cyclodextrins have been extensively reviewed elsewhere [24–34].

In some cases of inclusion compounds only a rather spacious, even also often polymeric guest component, G2 or G3 substitutes the original smaller G1 (often a water molecule) in the polymeric host H or in their combination of the H1.H2 type. Some of such new products and some heteromolecular complexes will be treated in this review because they represent some combinations of the single component hosts or guests.

In all the examples reviewed weak supramolecular interactions may be found and utilized [26, 27]. The principles governing these interactions are important in making possible predictions and how they affect the thermal behaviour and properties of new products. Supramolecular compounds may be described as multimolecular assemblies possessing a great deal of structural, three-dimensional information.

2. Combinations with Clays

Montmorillonite, being a layered swelling clay mineral, can accommodate various types of compounds in its interlayer space to give an intercalation type of inclusion compound. As its layer surface has a variable negative charge which is compensated by interlayer exchangeable cations and may have some silanol groups, it can accommodate a large range of both cationic and polar substances e.g., metallic compounds, organic cations, polymers, surfactants, organogels etc. Non-polar compounds such as poorly soluble drugs (e.g., cyclodextrins) [9–13] can also be intercalated by interaction with polar molecules already present in the interlayer space.

Zeolites are inclusion compounds either in their synthetic or natural forms, enclosing in their alumino-silicate lattice molecules of water as sorbate [2, 14, 23, 35–45]. Their empirical formula can be represented as $M_{2/n}O.Al_2O_3.ySiO_2.wH_2O$. Structurally [11, 35, 36, 40, 41] the zeolites are inorganic polymers [46] with extended three dimensional lattices, formed by AlO_4 and SiO_4 tetrahedra, linked together by common oxygen atoms and forming inter-se constructed channels. The negative charge of the framework is compensated by cations in channels, i.e., intrazeolitic cations [37, 38]. The exchange of different molecules is possible in different ways, the interaction between clays, minerals and drugs, especially antibiotics has been reported [47].

In the case of natural zeolites, different types of zeolitic minerals and cations are present. If one type of zeolitic mineral prevails ($>50\%$) the zeolitic material is called after that mineral. Therefore the east Slovakian zeolite from the deposit at Nižný Hrabovec is designated as Clinoptilolite (CT) type. According to Horváth

[48] its mineralogical formula is $Ca_{1.55–2.0}Mg_{0.1–0.4}Na_{0.6–0.8}K_{6.4–6.7}Si_{29}O_{78}$. Because of the diverse atoms, different forms of water and of OH groups are present, the best fitting formula is according to Meier [39]: $M_x M'_y N_z[T_m T'_n \ldots O_2(m+n\cdots-\epsilon)(OH)_{2\epsilon}](OH)_{br}(aq)_p \cdot qQ$.

The zeolite of Slovak origin was used for the preparation of different compounds useful in agrochemistry, perfumery and separation; electrochemical [43, 44, 54] and catalysis processes have also been studied [55]. Complexes with NPK fertilizers [2, 49, 50, 53] and insecticides [49, 51, 52] were prepared and separation [5, 16] and electrochemical process [43, 44, 54] were studied. In the electrochemical testing iodine, iodides, and silver chloride [45] were used for ammelioration of the electrochemical behaviour of the original zeolites.

Cyclodextrins (CDs) are compounds formed by joining six, seven or eight molecules of glucose, giving cyclic voids [28–32, 56, 57]. According to the number of glucose molecules they are designated as α-, β- or γ-cyclodextrins. It is possible to substitute the originally present H_2O sorbate [G] by other neutral molecules or ions. The effective guest component (e.g.c.) may be thus be stabilised or solubilised. Therefore CDs are currently used e.g., in pharmacy and alimentation, in the cosmetics, chemical and agricultural industries [27, 29, 31, 59].

Different derivatives of CDs are frequently used due to their increased solubility. For example the solubilities of α-CD, β-CD, γ-CD, hydroxypropyl-β-CD and diglucosyl-β-CD are 57.0, 1.85, 31.0, 50.0 and 140.0 g/100 g H_2O respectively [58].

3. Combinations of Cyclodextrins

Combinations of cyclodextrins with compounds such as montmorillonites, phosphates, and synthetic or natural zeolites are thermally stable [18].

The complexation of vegetable oils containing triglycerides of polyunsaturated fatty acids with γ-cyclodextrin was found to be useful in obtaining stable dispersions of these oils in aqueous media [60]. Extensive molecular dynamic simulations were carried out to elucidate the mechanism of the acceleration by β-CD of the hydrolysis rate of triolein by pancreatic lipase[61]. The mechanism could involve either of the two cyclodextrin inclusion complexes, β-CD/triolein or β-CD/oleic acid. The MD simulations clearly show that β-CD can accommodate only the liberated fatty acid thus accelerating lipolysis by decreasing product inhibition.

A series of water soluble CD polymers were prepared by the reaction with epichlorhydrin in NaOH solution [62]. In order to obtain water soluble products, the reaction must be stopped before a polymer gel was formed due to the polyfunctionality of CDs. Depending on the experimental conditions polymers having very high molecular weight averages (M_w) can be obtained.

A new class of associating polymer system was obtained by mixing an aqueous solution of CD polymer with an aqueous solution of an amphiphilic polymer [63]. Inclusion compounds are formed by association of the hydrophobic moiety

of the polymers and the β-CD cavities: epichlorhydrin was used for the preparation. Complex formation and viscosity studies were performed and the optimum of thickening properties was achieved with a polyethylene oxide chain length of about 20,000 units.

The inclusion of a complete polymer chain may be obtained by polymerisation of inclusion compounds of monomers or by threading of polymeric chains. The threaded complexes and the interlocking phenomena in crystals were studied in [27]. The polymer inclusion compounds are readily soluble in water. Polyethylene or polypropylene glycols and polyamides were mainly synthesised.

Different architectures of complexes of linear polymers (polyalkylene oxides) and of CDs represent nanostructures [64]. In the case of di- and triblock polymers of ethylene and propylene oxides a self organisation by selective interactions was observed. The complexes exhibit a strong interaction with water. The stoichiometry effect on the location of the interacting block causes morphological changes. If CD interacts with the internal block of the triblock polymer, the stoichiometry is the same as for the diblock polymer.

Various water soluble polymers have a synergistic effect and give an increase of the stability of CD drug complexes [65]. Polyvinylpyrrolidine [PVP] and hydroxypropylmethyl cellulose [HPMC] resulted in an increase of the stability constants of the hydrocortisone – HPMC – CD complex (1:1). Ten different drugs together with other CD polymers were studied.

Skirt-shaped amphiphilic cyclodextrins were obtained by grafting alkyl chains onto the secondary hydroxyl groups of β- and γ-CDs. They have the remarkable characteristic of being able to form nanoparticles easily, either nanocapsules or nanospheres. Nanoparticles can be loaded with either hydrophilic or lipophilic drugs and, in the latter case, they are capable of a fast release of the drug with a possible increase in bioavailability [66].

Dimeric β-CD inclusion compounds with porphyrinoid drugs shield the body organs from the unwanted excess of drugs used in chemotherapy [67].

Thermodynamic studies of the binding of a series of *p*-nitrophenyl glycosides, with α-CD were performed using a microcalorimetric technique [67a] whilst the complex formation with pyridoxine was studied using ^{1}H NMR and UV spectroscopy [68].

Aminoacids and peptides may not be trapped fully in cyclodextrins. The interactions of the side chain of aminoacids are responsible for their specific binding with CDs.

Chloramphenicol palmitate (CPP) was converted to an amorphous complex when spray dried with hydroxypropyl-β-CD, and no crystallisation of CPP was observed for at least 2 months under the storage condition of 50 °C and 50% relative humidity [69].

Structural and thermal analysis data of new cyclodextrin-drug inclusion complexes (with diclofenac sodium, meclofenamic acid and (*L*)-menthol) were studied in order to reconcile X-ray packing features with behaviour on heating [70].

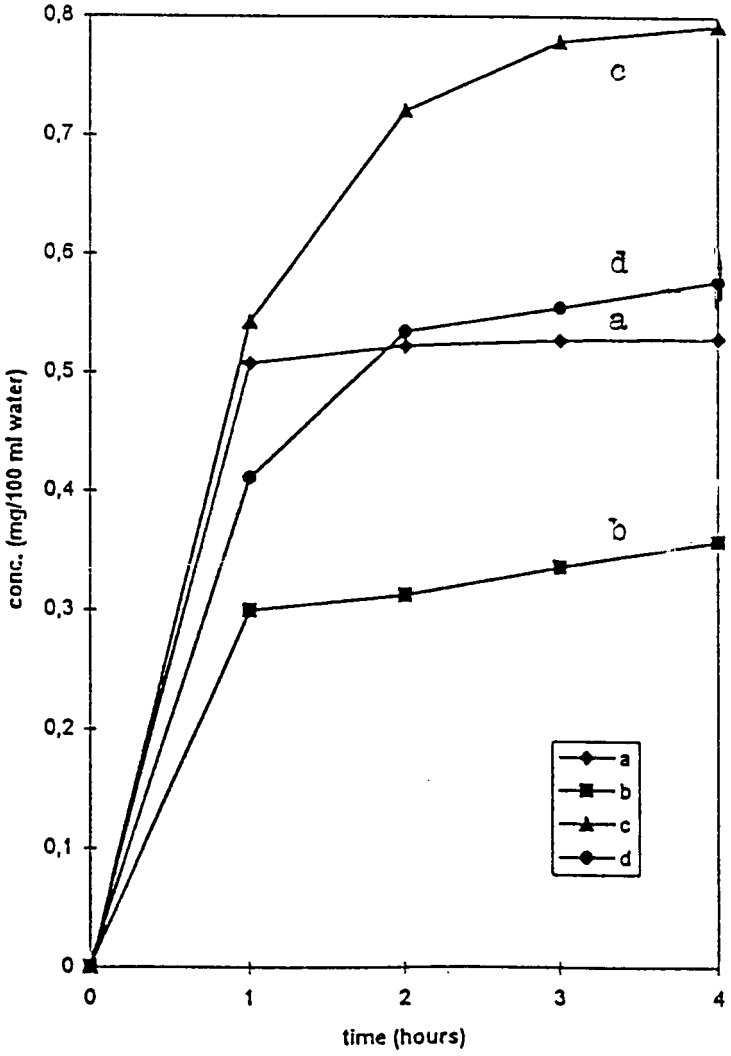

Figure 1. Desorption curves obtained [16, 20] at room temperature of (a) the Cu-Clinoptilolite-salicylic acid [CTCu-sal] complex, (b) CTCu-[DM-β-CD-sal], (c) the CTCu-spironolactone [CTCu-SP] complex and (d) CTCu-[β-CD-SP].

CD polymers modified with ionic groups are used as a sustained release wound powder, as well as in chewing gum formulations [71]. The salt formation effectively improved the host-guest interactions. Natural colorants such as carotenoids and curcuminoids are also stabilised by CD [71a].

The complexation of bile acids with HP-CD was studied by ^{13}NMR spectroscopy. The alkyl chain of the bile acids enters the CD cavity, the interactions differed between individual derivatives of bile acids [72].

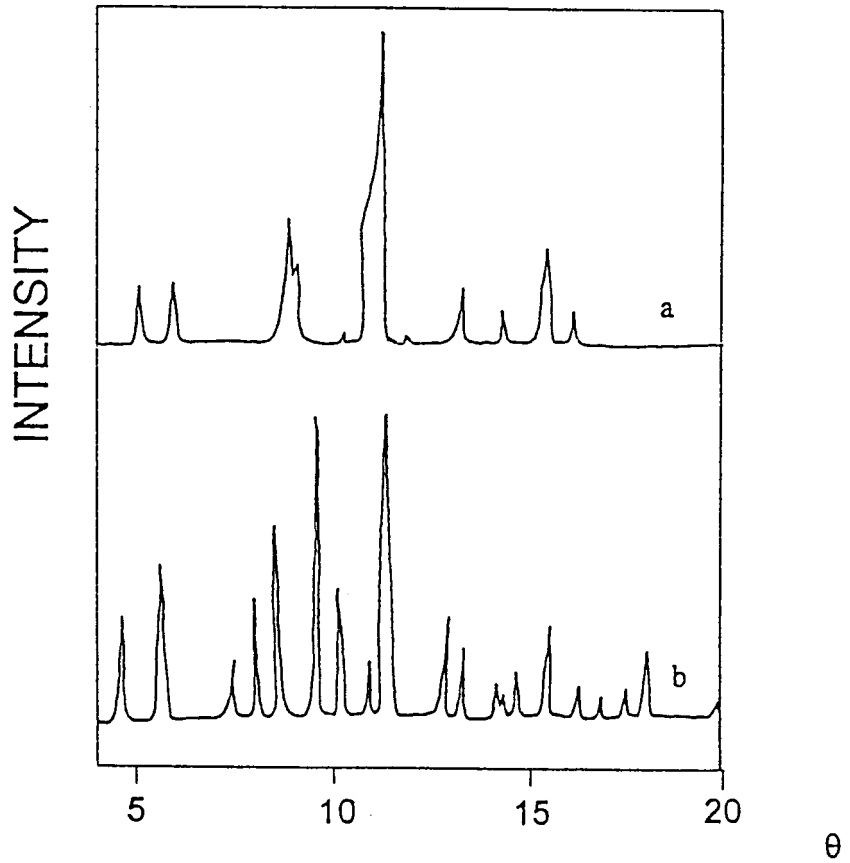

Figure 2. X-ray diffraction patterns of (a) CTCu-[β-CD-SP] and (b) the physical mixture.

CD complexes with compounds such as free perfumes, waxy fabric softeners and bactericides [73] are used in laundry operations.

Ternary cyclodextrin complexes are known [20–22, 72]. The formation of three component inclusion compounds where different organic compounds are present as coguests in β-CD, were studied. The β-CD acetophenone complex was prepared in the presence of triethylamine [74].

Drug solubility may be improved by using hydroxyacids for multicomponent complex formation. The acids serve as a third component [75].

Interesting three component complexes are represented by polyiodides and nitrophenyl maltose [76]. Complex formation of CD polymers with I_2^-, I_3^-, I_2 and Br_2 was also studied [77].

The solubility of disperse dyes in aqueous solutions increases in the presence of CDs due to complex formation. The use of these CD complexes in dyeing processes has some advantages compared with the standard procedure. More dye molecules

are used in the dyeing process thus reducing the concentration of the remaining dyes in the waste water [79].

CDs may be used as sensing molecules by modifications with two naphthalene or pyrene units [80].

Induced circular dichroism (ICD) spectra of ferrocene in CDs showed that the inclusion is axial in β-CD but equatorial in γ-CD [81].

Thermal analysis [82, 83], computer simulation [84] and spectroscopic [85] techniques have been used to study CD inclusion complexes. e.g., the study of the hydrates of α- and β-CD [82, 83]; a MM study of the electrostatic properties of the cavity and structural features of higher order or nanotube aggregates and of fullerene complexes [84]; an NMR and FT-IR study of water soluble inclusion compounds of nylons [85].

Different metal-CD complexes and the metallo-CD interaction were studied [18, 71]. These kinds of reactions are interesting for catalysis and redox reactions.

4. Zeolite/CD Effective Guest Component

In addition to the different combinations of zeolites and agrochemicals, perfumes and insecticides [2] combinations of cyclodextrins with salicylic acid, iodine [16, 19] or spironolactone [20, 21] have also been prepared in our laboratories [4].

Ternary compounds containing zeolite, CDs and another f guest have also been prepared [20]. In such products all the CD complexes exhibited different properties from the starting materials and from the physical mixtures of the starting compounds [20–22].

The results of two modes of preparation of ternary compounds are of interest [20]. The first method (sorption of the e.g.c. into the previously prepared zeolite-cyclodextrin complex) showed its advantage in a higher quantity of sorbed e.g.c. A disadvantage is the lower quantity of sorbed CD. The second method, sorption of the CD/guest complex into the zeolitic host was advantageous, because more CD is sorbed in the product, but less of the guest.

The desorption of the individual components from the three component CuClinoptilolite(CuCT)/dimethyl-β-CD/salicylic acid and CuCT/β-CD/spironolactone [16, 20] complexes show different sequencies (Figure 1) and phenomena [17, 18, 20, 22].

The X-ray diffraction patterns of CuCT/β-CD/SP and of the physical mixture of the three components are very different (Figure 2) indicating formation of the ternary complex. The CT/β-CD complex was also studied by computer modelling (Figure 3) which was used to clarify the intermolecular interactions between α- and β-cyclodextrin complexes with zeolites as host [16]. The pores in Slovak clinoptilolite (79 $\times$ 35 nm) are too small to accommodate a CD molecule (78 $\times$ 153 nm) [28] completely and it is assumed that the CD is anchored by chemisorption via its functional groups [20]. It was not possible to prepare single crystals of the

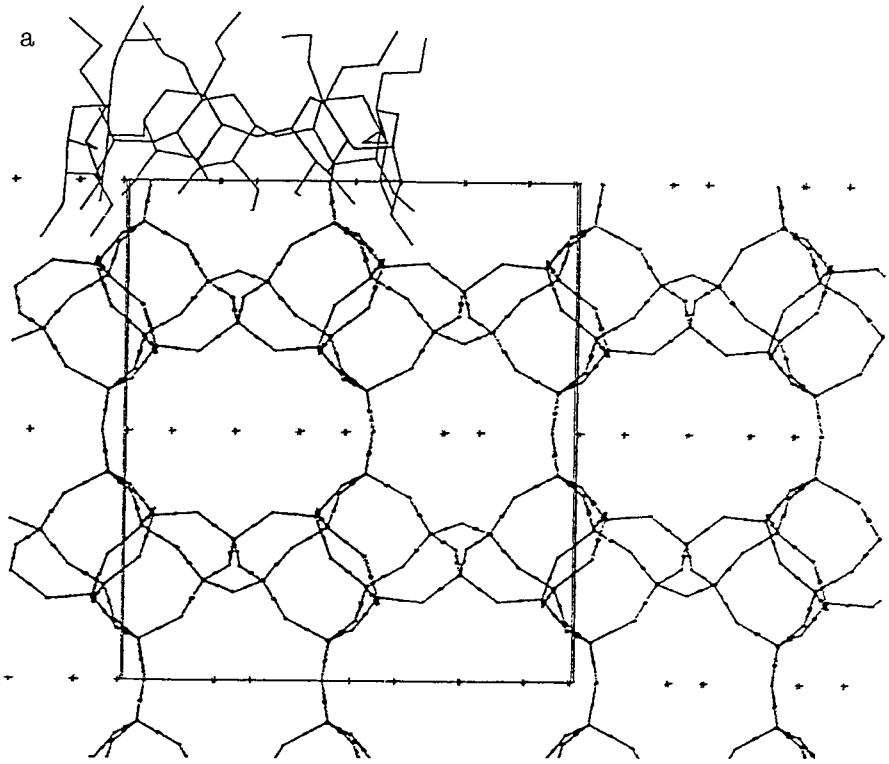

Figure 3. Molecular modelling study of the interaction of β-CD with Slovak clinoptilolite showing possible orientation of the components [16].

above compounds, thus proof that they are host-guest type inclusion compounds is obtained using methods such as thermal analysis and powder XRD.

Complexes of CD with KOH (β-CD$K^+ \cdot OH^- \cdot 8H_2O$) [87] and acetone ($\alpha$-CD.acetone.$9H_2O$) [88] have been reported. The interaction energies were found to be in the order: oxygen (41.8 kJmol^{-1}), carbon (33.4 kJmol^{-1}) and potassium (4.18 kJmol^{-1}) [89]. K^+ may replace a H_2O molecule in the β-CD lattice and the acetone is clearly located within the cavity of α-CD [89].

5. Conclusions

For most of the complexes reviewed here it is not always possible to perform structural analysis. Therefore only individual methods of identification are often available, examples being [26]: solid state NMR (Ripmeester); stability, solvent patterns and molecular recognition studies in cyclodextrins (Tsoucaris); thermodynamic and kinetic aspects (Nassimbeni); the self assembly of molecules (Gotarelli).

The reviewed complexes often occur in amorphous or very finely particulate form. Checking their thermal stability against that of the starting materials and

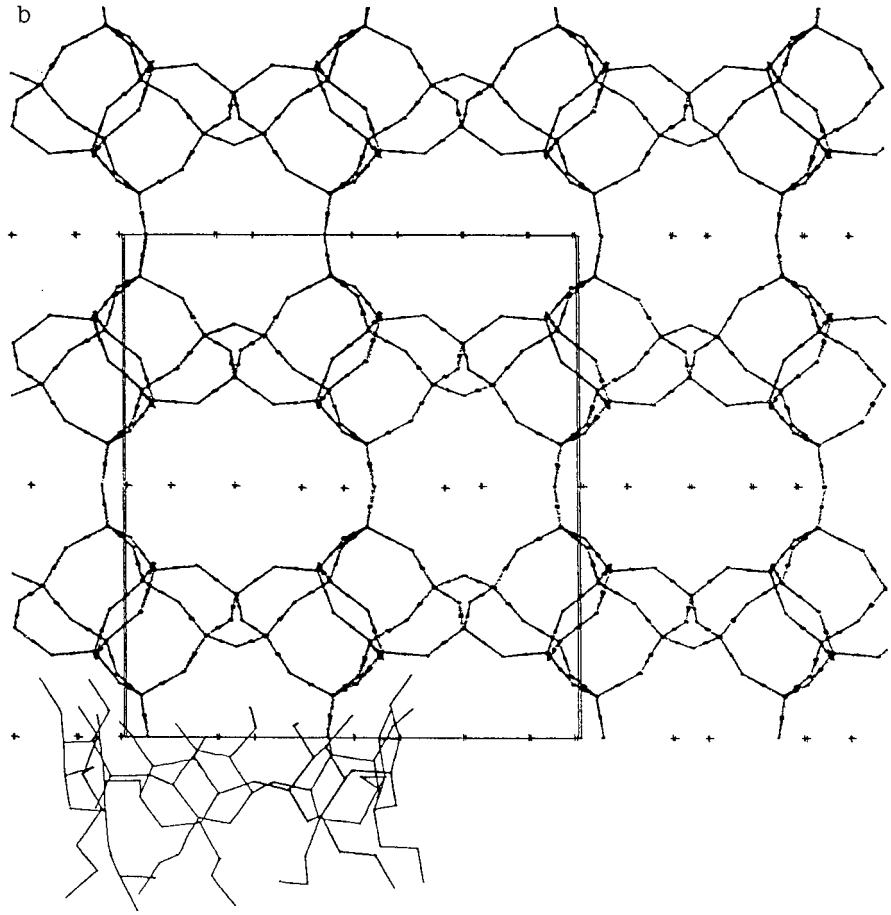

Figure 3.

physical mixtures provides a valuable indirect way of confirming their existence [17]. Electronmicroscopy combined with thermal analysis helped to identify the intermediate and final products of the thermal decomposition [90, 91]. The thermal behaviour of different combinations was used to study CDs and benzoic acid [92].

A very extensive study of the preparation, properties, characterisation and applications of supramolecular compounds can be found in a recent multi-volume publication [93].

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