

# Study of thermal stability of $\beta$ -cyclodextrin/metal complexes in the aspect of their future applications

Wojciech Ciesielski · Tomasz Girek

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**Abstract** The interaction of cyclodextrins with transition metal ions, mostly due to the presence of similar complexes in biological systems. Metal polysaccharide chemistry plays a crucial role in crosslinking of many biomolecules, and the formed polysaccharide/metal complexes are promising for pharmaceutical applications, as well as for heavy metal collectors and material for production of various substances i.e. drilling muds. In the study of  $\beta$ -CD/metal complexes made in order to explain the influence of  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoSO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MnSO}_4$  on thermal decomposition of  $\beta$ -cyclodextrin. The theoretical AM1 (Austin Model 1) studies confirm the experimental results. Moreover the studies show that  $\beta$ -cyclodextrin can be a convenient model of starch, which may be useful for examination of starch–metal interactions.

**Keywords** Cyclodextrin · Complex · Metal · Polysaccharides

## Introduction

There exist an abundant number of reports describing Werner-type complexes of mono- and di-saccharides as oxygen donor ligands [1–5]. Polysaccharides also are able to O-ligate metal ions [6–10]. Particular attention has been

paid to starch as a ligand of metal ions. Studies involved coordination of granular as well as pregelatinized starches of various botanical origin with numerous metal salts [11, 12]. The structure of inner coordination spheres of these complexes depends on cations and anions nature of used salts. However, the coordination capacity of starches only in random cases is influenced by their botanical origin. Because of the complex nature of starch thermolysis, a precise measurement of the accompanying weight loss and heat changes process cannot be made, therefore the usefulness of the cyclodextrin as a model of starch was discussed.

Cyclodextrins (CDs) are multicomponent systems that decompose on exposure to a heat source forming a protective blown char layer on the surface of the polymer. This knowledge is relevant for understanding the mechanism of thermal degradation of cellulose which is importance, for example in wood combustion, chemical production from cellulosic waste and maintenance of electrical transformers [13–15].

Besides pharmaceutical applications for drug release [16, 17], cyclodextrins can be employed in environmental protection, since they effectively immobilize toxic or harmful compounds inside their cavities [18]. Cyclodextrins are excellent models of enzymes. These properties have led to their use as catalysts, both in enzymatic and nonenzymatic reactions. For instance, the cyclodextrin complex with two imidazole units is a convenient model of ribonucleases [19].

In this respect, cyclodextrins are ideal low molecular weight model compounds promising elucidation of the mechanism of starch degradation because they are crystalline oligomers of similar structure as amylopectin and can be accurately purified and characterized throughout the degradation process.

W. Ciesielski (✉) · T. Girek  
Institute of Chemistry and Environmental Protection,  
Jan Długosz University, Armii Krajowej Ave. 13/15,  
42-201 Częstochowa, Poland  
e-mail: w.ciesielski@interia.pl

In the present work, the  $\beta$ -cyclodextrin/metal ion complexes (denoted as  $\beta$ -CD/metal complexes) have been studied to establish a relationship between their chemical structure and thermal behavior with particular reference to char yield.

## Experimental

### Synthesis of $\beta$ -CD/metal complexes

The  $\beta$ -CD/metal complexes with  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoSO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MnSO}_4$  were prepared according to [16]. In this procedure CD was mixed with any of the metal salts (10% w/w) with addition of ethanol, and ground in an agate mortar for 1 h.

Thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) of  $\beta$ -CD/metal complexes

The DSC–TG–DTG analysis was carried out with the NETZSCH STA-409 simultaneous thermal analyzer calibrated with standard indium, tin, zinc, and aluminium of 99.99% purity. Samples of approximately 0.020 g were heated in corundum crucibles with non-hermetic lids. Corundum (SINGLE \*R) was the standard. The heating was performed under static conditions in air in a range of 20–500 °C at the 5 K min<sup>-1</sup> temperature rate. The measurements were duplicated. The measurements were duplicated with a  $\pm 0.5$  °C precision. Recorded thermograms were analyzed with the NETZSCH-TA-ANALYSIS and NETZSCH SEPARATION OF PEAKS programs.

### Computation of $\beta$ -CD/metal complexes

The models of transition metal complexes with  $\beta$ -CD were designed based on previous work [20] (Fig. 1). The geometry of the  $\alpha$ -D-glucose molecule is presented in Fig. 2 and Table 1. Computations of complexes were made with CChE version 7.5.0.85 and structures were obtained using Cambridge Data Base [21].

The geometry optimizations of  $\beta$ -CD/metal complexes were performed for the ground state using the density-functional theory (DFT) method with Becke's three-parameter hybrid exchange functional [22] using the Lee–Yang–Parr gradient-corrected correlation functional [23] B3LYP and basis set 6-31G. No constraints to bonds/angles/dihedral angles were applied in calculations. The DGauss engine in the Cache Pro Version 7.5.0.85 [24] was employed.

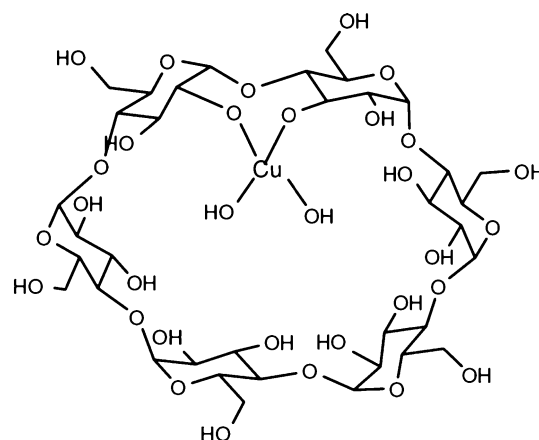


Fig. 1 Model structure of  $\beta$ -CD/Cu(II) complex [20]

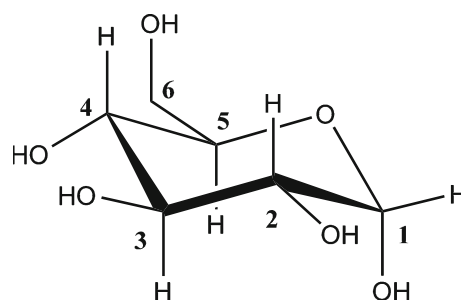


Fig. 2 Structure of  $\alpha$ -D-glucose

## Results

Coordination of  $\beta$ -CD with metal salts results in differences in thermal decomposition processes of  $\beta$ -CD/metal complexes. In no case the thermogravimetric, differential thermogravimetric and differential scanning calorimetric diagrams could be considered as a superposition of relevant diagrams for  $\beta$ -CD and admixed salt. Figure 3 shows the TG/DTG/DSC curves of  $\beta$ -CD, which was prepared in an analogous way to its complexes with metal ions. The first endothermic peak between 70 and 125 °C with 15% weight loss corresponds to the dehydration of CD. The second small endothermic peak represents a process corresponding to a molecular reorganisation of CD [25]. The third step is related to the decomposition of the CD structure.

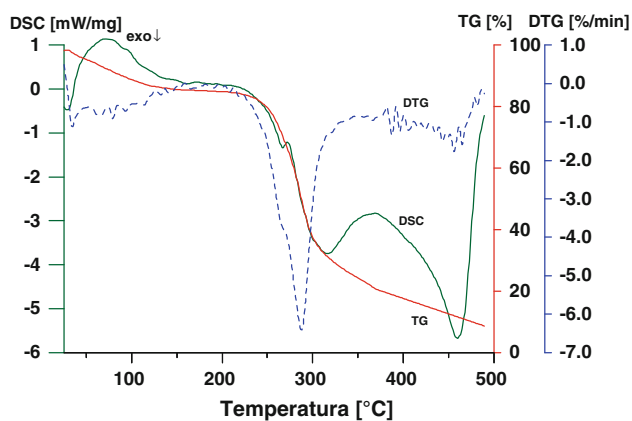
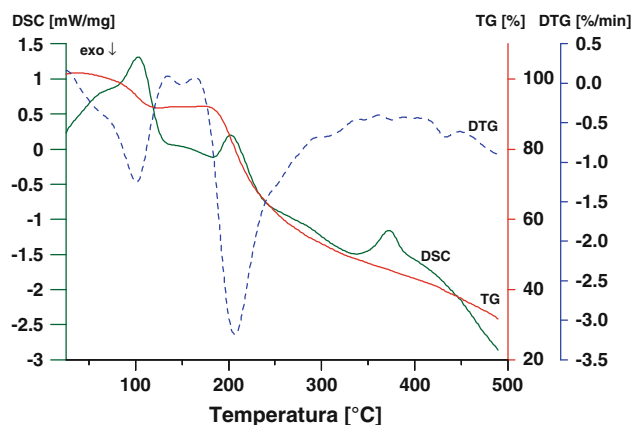
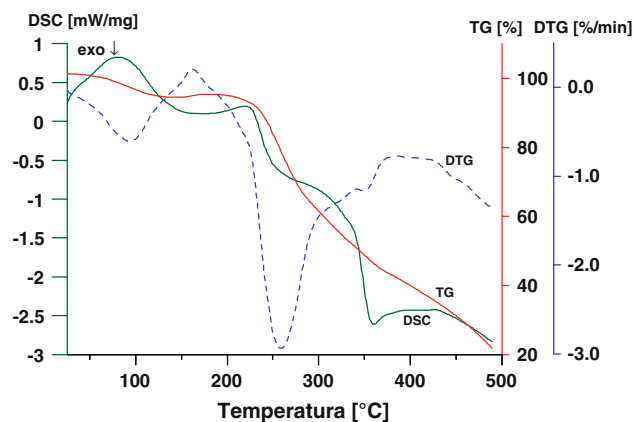
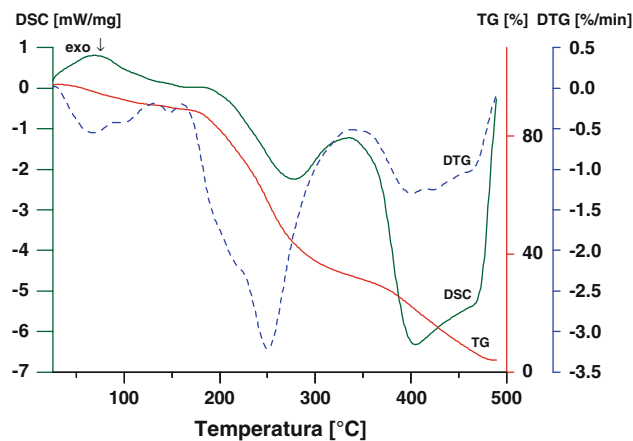
After loss of ca. 14% of water, shown by the DTG peaks and the endothermic effect in the low temperature part of the DSC plot, a plateau appears on the TG curve. Then, from the point of plateau breakdown, a considerable mass loss begins. This point shows the start of the  $\beta$ -CD decomposition. Then the sharp, monotonous lowering of TG line, connected with the fast mass loss occurs, followed by the slower decomposition. The shape of the TG line suggests a one-step decomposition of the sample. The DTG peak is observed in majority of considered complexes.

**Table 1** Bond lengths [Å] and bond angles [°] in  $\alpha$ -D-glucose [21] accepted for calculations

Bond lengths			
C1–C2=C4–C5	1.54	C2–C3	1.56
C3–C4=C5–C6	1.53	C1–O1=C6–O6	1.32
C2–O2	1.41	C3–O3	1.44
C4–O4=C5–O5	1.40	C1–O5	1.42
O–H	0.97	C–H	1.09
Bond angles			
O5C1C2=C2C3C4=O5C5C6=C3C4O4=C–C–H	110.0	C3C4C5=C4C3O3	108.0
C1C2C3	104.0	C5O5C1=O–C–H	111.0
O5C5C4=C4C3O3	109.5	C5C6O6	113.0
C4C5C6=O5C1O1=C5C4O4	112.0	O1C1C2	115.0
C2C3O3	102.0	C–C–O	112.5
C1C2O2=C3C2O2	109.0		
H–C–H	107.0		

Analogous curves may be seen for  $\beta$ -CD complexes with  $\text{CoCl}_2$  (Fig. 4),  $\text{Co}(\text{NO}_3)_2$  (Fig. 5) and  $\text{CuCl}_2$  (Fig. 6), as well as with  $\text{Cu}(\text{NO}_3)_2$  and  $\text{MnCl}_2$  which are not shown. The peaks on their DTG curves are asymmetric and have an inflection either on the low- or on the high-temperature side.

The TG curves for  $\beta$ -CD complexes with all metal acetates and with  $\text{FeCl}_3$ ,  $\text{NiCl}_2$  and  $\text{Ni}(\text{NO}_3)_2$  have a different shape (Figs. 4, 5 and 6) and the diagrams for  $\beta$ -CD complexes with  $\text{Mn}(\text{CH}_3\text{COO})_2$  and with  $\text{FeCl}_3$  are shown in Figs. 7 and 8, respectively. After the loss of adsorbed

**Fig. 3** The TG/DTG/DSC curves of  $\beta$ -CD**Fig. 5** The TG/DTG/DSC curves of  $\beta$ -CD complex with  $\text{Co}(\text{NO}_3)_2$ **Fig. 4** The TG/DTG/DSC curves of  $\beta$ -CD complex with  $\text{CoCl}_2$ **Fig. 6** The TG/DTG/DSC curves of  $\beta$ -CD complex with  $\text{CuCl}_2$

water visible on the TG line, mass loss is not observable on TG/DTG/DSC diagram (Figs. 7, 8).

Thus, except for manganese acetate (Fig. 7) the coordination results in considerable changes in the coordination sphere of the metal cations. The number of water molecules in complexes is significantly lower than in the case of noncoordinated  $\beta$ -CD.

The analysis of diagrams (Figs. 7, 8) indicates that the water in complexes is adsorbed on the surface of the complex, and is not coordinated to the central metal ions. In contrast to the broad peaks connected with drying of  $\beta$ -CD, the peaks corresponding to dehydration of salts plural are usually sharp and are localized in the higher temperature region.

Based on the observed TG/DTG/DSC diagrams it can be established, that two salts  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  have different properties than all considered salts. The Cu(II) nitrate, which undergoes sublimation in the 150–225 °C region [26], does not sublime from its  $\beta$ -CD complex. Also the mass loss is not observed even up to 194 °C. The Co(II)

nitrate, which decomposes into the oxide at 74 °C [26], does not decompose at this temperature when is complexed with  $\beta$ -CD.

The decomposition of copper (II) nitrate complexed with  $\beta$ -CD could be taken in account. However the observed decomposition may result from the existence of various effects occurring in this temperature region, and only extremely large enthalpy changes (not observed in our experiments) of corresponding endothermic processes would indicate such a possibility.

Oxidation of Cu(II) salts in acidic medium is well known as the Barfoed test for saccharides [8]. Such reaction however is not possible during the thermal decomposition of the  $\beta$ -CD/Cu(II) complex due to anhydrous conditions existing at that temperature.

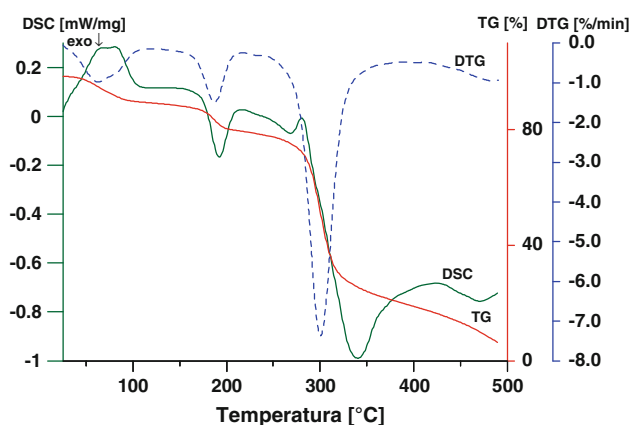
Nitrogen pentoxide resulting from the cobalt (II) nitrate can also act as an oxidant. Oxidation of saccharides by nitrogen oxides is well known [27], but such oxidation is not observed in the recorded thermograms of the  $\beta$ -CD/metal complexes.

On the DTG diagrams of all the  $\beta$ -CD complexes with chlorides and nitrates the main decomposition peaks appear at temperatures lower than the decomposition temperature of noncoordinated  $\beta$ -CD. It should be noted that the decomposition temperatures of complexes are always higher than the decomposition temperatures of metal salts. As a result, the formation of complexes may be accompanied by the acid-catalyzed hydrolysis of  $\beta$ -CD. On diagrams showing decomposition of complexes, peaks connected with the decomposition of metal salts are absent.

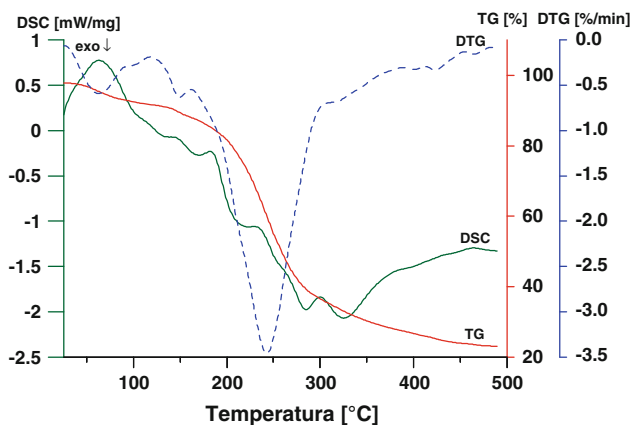
On diagrams for complexes with metal acetates, the main DTG peaks are found either at the same temperature, or at temperatures higher than the decomposition temperature of noncoordinated  $\beta$ -CD. This observation indicates that the salts do not undergo hydrolysis during formation of complexes. The decomposition for all (except for cobalt and nickel acetates) complexes is found at lower temperatures than the temperature at the start of the decomposition start of  $\beta$ -CD. This behavior may be due to the decomposition of  $\beta$ -CD in acidic medium resulting from hydrolysis of the metal salts.

Further steps show decomposition of complexes and complexation of used metals with formed oligosaccharides. The scope and rate of mass loss during decomposition processes are also strongly dependent on used metal salts.

Above 216 °C  $\beta$ -CD undergoes a two-step decomposition (Fig. 3). The first, exothermic process is fast, the slope of the TG line, i.e.  $\text{tg}\alpha$  is equal to 3.20 (the slope is defined as a mass loss percent (%) for 1 °C). The DSC results show that the enthalpy of this process is relatively low (–59.8 J/g). The second, exothermic process is considerably slower ( $\text{tg}\alpha = 0.82$ ), but its enthalpy is 1.5 orders plural lower than in the first step. In all cases the fastest step of



**Fig. 7** The TG/DTG/DSC curves of  $\beta$ -CD complex with  $\text{Mn}(\text{CH}_3\text{COO})_2$



**Fig. 8** The TG/DTG/DSC curves of  $\beta$ -CD complex with  $\text{FeCl}_3$

decomposition of  $\beta$ -CD complexes is always proceeded by one or two slower processes.

The DSC results indicate that in some cases, such as for  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{Ni}(\text{CH}_3\text{COO})_2$ , the main decomposition process is exothermic, with high enthalpy changes. The decomposition of  $\beta$ -CD complexes with  $\text{FeCl}_3$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{Mn}(\text{CH}_3\text{COO})_2$  is endothermic, with low enthalpy changes, and the decomposition of  $\beta$ -CD complexes with  $\text{CoCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$  and  $\text{MnCl}_2$  is much more endothermic.

The irregularities of the influence of salt cations, obviously dependent on the nature of the anion, may result from the differences in thermal stability of salts and from the different role of anions taking part in formation of inner and outer coordination spheres of complexes.

We have established that the influence of salts on the temperature of main peak of decomposition of complexes decreases in the order  $\text{Co} > \text{Cu} > \text{Fe} > \text{Mn} > \text{Ni}$ . Some irregularities observed here result mainly from the heterogeneity of complexes. This ordering shows the stabilities of metal complexes with dextrans which form in these processes.

It may be noted that even though acetates afford more resistant and more thermally stable complexes, their decomposition occurs with the highest rate. The copper and manganese salts strongly accelerate the decomposition of the saccharide ligand, while such ligand is considerably stabilized by chloride and nitrate anions.

The used calculations indicate that the stability of the hydrated cations present in the environment of chloride and nitrate ions has been established in the order:  $\text{Mn}(\text{H}_2\text{O})_4^{2+} > \text{Fe}(\text{H}_2\text{O})_6^{3+} > \text{Co}(\text{H}_2\text{O})_6^{2+} > \text{Ni}(\text{H}_2\text{O})_4^{2+} > \text{Cu}(\text{H}_2\text{O})_6^{2+}$ . In the case of acetate ions, however, this sequence is:  $\text{Fe}(\text{H}_2\text{O})_6^{3+} > \text{Ni}(\text{H}_2\text{O})_4^{3+} > \text{Mn}(\text{H}_2\text{O})_6^{2+} > \text{Cu}(\text{H}_2\text{O})_4^{2+} > \text{Co}(\text{H}_2\text{O})_6^{2+}$ . The above irregularity may be due mainly to the structure of inner coordination sphere of the aqua complex of central metal ion.

Except for the case of coordination in the presence of nitrate ion, where the calculations indicate the coordination of four  $\beta$ -CD glucose units and two water molecules, the results obtained for all  $\beta$ -CD/metal complexes studied show ca. 20 kJ/mol preference for the structure a coordination sphere consisting of six coordinated  $\beta$ -CD glucose units. In all cases the calculations indicate a water free structure of the coordination sphere of  $\text{Mn}(\text{CH}_3\text{COO})_2$  with  $\beta$ -CD glucose units. The water observed on the TG/DTG/DSC curves is adsorbed on the surface of the complex, and is not coordinated to the central metal ions. It is not observed peaks responsible for evaluation of coordinated water molecules.

It was found that the central  $\text{Co}(\text{II})$  ion in the complex with  $\beta$ -CD either does not bind water, or forms a complex consisting of four  $\beta$ -CD glucose units and two water

molecules. In the case of complexes of  $\beta$ -CD with  $\text{Co}(\text{NO}_3)_2$  (Fig. 5) was observed the additional peak in the temperature about 150 °C assigned evaluation of coordinated water molecules. However in the case of complexes of  $\beta$ -CD with  $\text{CoCl}_2$  (Fig. 4) this peak is not observed. Such situations has been observed also in the case of calculations for  $\text{Co}(\text{II})$  ions. The calculations inform that the complex  $\beta$ -CD with  $\text{Co}(\text{NO}_3)_2$  contains four glucose units and two water molecules, while the complex  $\beta$ -CD with  $\text{CoCl}_2$  contains six glucose units in the coordination sphere.

In the other two cases, i.e.  $\text{Fe}(\text{III})$  complexes with  $\beta$ -CD, in the presence of the acetate ion and chloride ion, the most stable is the system containing four  $\beta$ -CD glucose units and two water molecules, and two  $\beta$ -CD glucose units and four water molecules, respectively. For  $\text{Fe}(\text{NO}_3)_2$ , similarly as for  $\text{Mn}(\text{II})$ , the coordination sphere of  $\text{Fe}(\text{III})$  is water free. The TG/DTG/DSC curves of discussed complexes confirm this facts (Fig. 8).

For  $\text{Cu}(\text{II})$  as a central ion, only in the presence of nitrate ion, the complexes containing two  $\beta$ -CD glucose units and the two water molecules are preferred. However, in the two other cases (i.e. chloride and acetate ions), the calculations precisely show the environment of the  $\text{Cu}(\text{II})$  ion involve four glucose units. This was also observed for the  $\text{Ni}(\text{II})$  ion with all considered anions. The calculations reveal that except for  $\text{Mn}(\text{II})$ , all central ions studied may be ligated by water molecules.

The results shown in Table 2 indicate that for all studied anions the most stable complexes are those of  $\text{Co}(\text{II})$  and  $\text{Mn}(\text{II})$ .

Based on the obtained data (Table 2) it may be concluded that the stability of complexes increases in an irregular manner as the number of glucose units around the central ion increases. The least stable are complexes in which water molecules are localized on all coordination sites of the ion, and the most stable are those, in which all coordination sites are occupied by hydroxyl groups of  $\beta$ -CD glucose units.

Considerable discrepancies are found in complexes of  $\text{Co}(\text{II})$  and  $\text{Fe}(\text{III})$  ions, for which odd numbers of ligands are found in the coordination sphere, i.e. three  $\beta$ -CD glucose units and three water molecules, as well as in complexes of  $\text{Mn}(\text{II})$  ion by which show of four  $\beta$ -CD glucose units and two water molecules in coordination sphere.

Similar observation were made for complexes with central ion of a coordination number 4, which show a near linear change of stability. In the case of complexes of ions of coordination number 6 the complexes of the lowest stability are those having in coordination sphere only, while complexes of the highest stability are those where all coordination sites are occupied by  $\beta$ -CD glucose hydroxyl groups.

The high stability of all complexes, especially those containing the  $\text{Fe}(\text{III})$  ion may be explained in terms of



**Table 2** Calculated enthalpy values for formation of coordination sphere by  $\beta$ -CD glucose units around the central metal ion

The formation enthalpy, $-\Delta H$ [kJ/mol]												
Structure of coordination sphere (glucose units + water)												
Ion	0 + 4	0 + 6	1 + 3	1 + 5	2 + 2	2 + 4	3 + 1	3 + 3	4 + 0	4 + 2	5 + 1	6 + 0
<b>Cl<sup>-</sup></b>												
Co		-786		-812		-895		-654		-978	-953	-998
Cu	-695		-564		-826		-783		-854			
Fe		-954		-645		-956		-715		-987	-910	-752
Mn		-964		-704		-684		-497		-990	-494	-1005
Ni	-731		-781		-625		-589		-873			
<b>NO<sub>3</sub><sup>-</sup></b>												
Co		-517		-512		-607		-507		-785	-545	-765
Cu	-412		-759		-796		-598		-701			
Fe		-695		-688		-852		-362		-764	-852	-906
Mn		-556		-604		-464		-549		-799	-694	-952
Ni	-459		-681		-525		-689		-947			
<b>CH<sub>3</sub>COO<sup>-</sup></b>												
Co		-541		-792		-541		-575		-818	-459	-845
Cu	-542		-579		-617		-515		-791			
Fe		-695		-458		-552		-622		-684	-561	-596
Mn		-556		-484		-384		-699		-729	-342	-847
Ni	-654		-312		-421		-554		-561			

steric hindrance. In this case the geometry of the molecule (bond lengths, angle values, hybridization of bound electrons, the electron density distribution) changes. These changes occur in such a way that the maximal possible energetic stabilization may be achieved. Therefore values of this energy may be used for qualitative assessment of the relative chemical activity of formed complexes [28].

## Conclusions

The present work describes formation of complexes of  $\beta$ -CD with metal ions; they were obtained with the use of ethanol. The TG–DSC measurements results have shown interactions of  $\beta$ -CD with metal ions. The general trend in stability values determined by the theoretical calculations is in agreement with the experimental results.

We have established that the temperature of decomposition and the amount of thermally stable residue strongly depend on the kind of used metal ions. Effective intumescent fire retardant systems based on cyclodextrins can be developed, since a large choice of CD substituents is available for modification of their thermal behavior. Coordination of  $\beta$ -CD to the central metal ions could be a positive phenomenon if  $\beta$ -CD is considered as, for instance, aids for soil cementation, depressants in the flotation of complex metal ores, as well as binders and plasticizers in metal oxide based ceramics. Such

coordination can also be advantageous if  $\beta$ -CD is used as collectors of heavy metals, for example from a wastewater, and as components of drilling muds.

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