

Review

Metal complexes based on native cyclodextrins: Synthesis and structural diversity



Daniel Prochowicz^{a,b,1}, Arkadiusz Kornowicz^{a,1}, Iwona Justyniak^b, Janusz Lewiński^{a,b,*}

^a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

^b Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Contents

1. Introduction	331
2. α -, β - and γ -CDs metal-based complexes	332
2.1. α -CD metal-based complexes	332
2.2. β -CD metal-based complexes	338
2.2.1. Heterometallic sandwich-type complexes	338
2.2.2. Homometallic sandwich-type complex	339
2.2.3. Mono- and dinuclear complexes	339
2.3. γ -CD metal-based complexes	340
2.3.1. Homometallic sandwich-type complexes	344
2.3.2. Heterometallic sandwich-type complexes	344
3. Conclusion	344
Acknowledgements	344
References	345

ARTICLE INFO

Article history:

Received 18 June 2015

Accepted 30 July 2015

Available online 13 August 2015

Keywords:

Cyclodextrins

Metal complexes

Synthesis

Structure

Supramolecular chemistry

ABSTRACT

Cyclodextrins (CDs) are well-known molecular hosts for forming stable host–guest inclusion complexes or supramolecular species due to their special hydrophobic internal cavity and hydrophilic external surface. The unique ability of CDs to form inclusion complexes is widely exploited in many areas, e.g. supramolecular chemistry, catalysis, drug carrier systems, food industry and cosmetics. While interactions of CDs with metal ions have been studied for decades, structurally well-defined systems are relatively rare and the application of CDs-based functional materials is in its initial phase. This review focuses on the synthesis, reactivity and structural diversity of well-defined metal complexes derived essentially from native CDs. Various structural motifs for metal complexes based on CDs were delineated ranging from monomeric species, dinuclear systems, homo- and heterometallic sandwich-type complexes to cylindrical, extended structures. The reported examples are discussed with an emphasis placed on how the character of used metal or auxiliary ions, and the formation of intra- and/or intermolecular hydrogen bonds can influence the mode of aggregation and supramolecular arrangement of the resulting metal complexes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

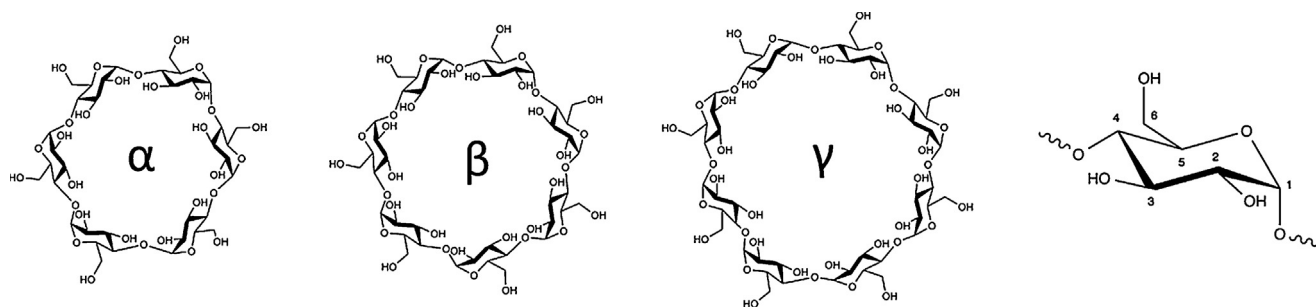
Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, or eight glucopyranose units in α , β and γ forms, respectively

(Scheme 1). The structure of these molecules is toroidal containing a relatively hydrophobic central cavity and hydrophilic outer surface. They are well-known molecular hosts for forming stable host–guest inclusion complexes or supramolecular species due to their special hydrophobic internal cavity and hydrophilic external surface [1–3]. Most of the reported studies on chemistry of CDs have focused on the utilization of this group of macrocycles as molecular recognition receptors [4], drug delivery carriers [5–7], scaffolds for biomimetics [8,9] or supramolecular hosts for organometallic complexes [10] and polyoxometalates [11]. A significant number of review

* Corresponding author at: Warsaw University of Technology, Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland. Tel.: +48 222347516.

E-mail address: lewin@ch.pw.edu.pl (J. Lewiński).

¹ These authors contributed equally to this work.



Scheme 1. A schematic representation of the native CDs and D-glucopyranosyl ring.

articles [1–3] and books [12,13] devoted to different aspects of these areas have been published. Recently, an intriguing extension of CD applications as supporting molecule to modify metal nanoparticles by the direct surface attachment [14,15] or semiconductor nanocrystals [16,17] by the host–guest surface modification has been demonstrated. Moreover, γ -CD has appeared as a very attractive building unit for the synthesis of nanoporous carbohydrate Metal–Organic Frameworks [18,19] with potential applications in gas storage [20] and as host templates for incorporating nanoclusters or nanoparticles [21,22].

Astonishingly, with over 120 years of the development of CDs contributing to the vastness of the scientific literature [3], their coordination chemistry with metal ions remains an area essentially little explored and a number of structurally characterized native CD-based metal complexes is relatively scant (undoubtedly, the paucity of structural data results from the difficulties with the isolation of well-defined systems). Moreover, to our best knowledge, there is no review dealing with the latter aspect of CDs chemistry besides special cases such as a review describing composition and stability of native CD-based metal complexes in solution [23] or reviews concerning metal complexes with functionalized CDs [24,25]. Functionalization of CDs permits various modes of metal ion complexation to further enhance the potential applications of the CD chemistry. In this regard, the design of biomimetic complexes for the modeling of metalloenzyme active sites has been particularly developed (for a selected example of metal complexes with CDs acting as enzyme mimic see Scheme 2a and b) [26,27]. Moreover, cavity-shaped metal complexes with functionalized CDs have also found application in the field of homogeneous catalysis and molecular recognition (cf. Scheme 2b and c) [25,28,29].

Native CDs have a large number of primary and secondary hydroxyl groups that can provide plenty of coordination sites to chelate metal ions and form covalent bonds at basic pH, where the OH groups can be deprotonated and act as nucleophiles. However, successful determination of the stability and type of the CD-based metal complexes requires the cooperation of several structural factors. The goal of this review is to fill the gap in the comprehensive depiction of ongoing research in the area of native CD-based metal complexes. We have comprehensively surveyed the structural diversity of well-defined metal complexes derived from native CDs reported in the literature. Various structural motifs are observed ranging from monomeric and dinuclear systems, homo- and heterometallic sandwich-type complexes to cylindrical extended structures. The examples are discussed emphasizing how the character of the metal or auxiliary ions used, and the formation of intra- and/or intermolecular hydrogen bonds can influence the mode of aggregation and supramolecular arrangement of the resulting metal complexes.

2. α -, β - and γ -CDs metal-based complexes

In this section we focus on the preparation methods of metal–organic complexes based on native α -, β - and γ -CDs,

and describe the variety of both their molecular structures and supramolecular architectures. The coordination flexibility of CDs to metal ions and structural diversity of the corresponding complexes is shown in Fig. 1. In general, deprotonation and complexation of secondary hydroxyl groups of CDs to metal ions leads to the formation of sandwich-type complexes in which partly or fully deprotonated CD molecules are connected through a multinuclear metallomacrocyclic ring. Such metallomacrocyclic ring can contain one or two different kinds of metal ions. To date, there are only two examples of structurally characterized homometallic sandwich-type complexes (type I, Fig. 1). In turn, reactions of metal salts with CDs in the presence of auxiliary alkali-metal ions (Li^+ , Na^+ , K^+ or Rb^+) lead to the formation of a family of heterometallic sandwich-type complexes. In the heterometallic systems, metal ion distribution in the metallomacrocyclic ring can appear in different patterns depending on the inherent number of coordination sites in a CD molecule and the character of auxiliary ions used. In particular, the utilization of Li^+ as auxiliary ions leads to the formation of sandwich-type complexes containing a metallomacrocyclic ring with $\{\text{M}, \text{Li}, \text{Li}\}_n$ -type rings (type II, Fig. 1) or $\{\text{M}, \text{Li}\}_n$ metallomacrocyclic ring with alternate metal centers (type III, Fig. 1). On the contrary, utilizing Na^+ as auxiliary ions usually promote the formation of $\{\text{M}, \text{Na}\}_n$ metallomacrocyclic ring. In the case of K^+ and Rb^+ , due to their larger size, such ions are located outside the cavity of sandwich-type complexes and link the adjacent molecules in a cylindrical more extended structures (type IV, Fig. 1). The formation of hydrogen bonds between the solvent molecules and the deprotonated and free hydroxyl groups of CDs influences the noncovalent-driven self-assembly processes. The structural analysis reveals that sandwich-type complexes can form diverse types of supramolecular architectures ranging from nonporous close packed structures to more extended layered networks. Another class of CD-metal based complexes constitutes mono- and dinuclear systems forming a bucket-wheel-shaped assembly (type V, Fig. 1).

2.1. α -CD metal-based complexes

The literature search shows that a native α -CD appears as an efficient first-sphere coordination ligand for metal ions. A series of heterometallic sandwich-type complexes in which partly or fully deprotonated α -CD molecules are connected through multinuclear metallomacrocyclic ring has been reported. However, there is lack of examples of the homometallic α -CD-based complexes. In the heterometallic systems, metal ions in the metallomacrocyclic ring appear in different patterns depending on the auxiliary ions used. By utilizing Li^+ as the auxiliary ion, sandwich-type complexes containing a $\{\text{M}, \text{Li}\}_n$ - or $\{\text{M}, \text{Li}, \text{Li}\}_n$ -type metallomacrocyclic ring (type II and III, Fig. 1) have been observed. In the presence of Na^+ ions partly or fully deprotonated α -CDs molecules are capable of templating transition metal ions with the formation of $\{\text{M}, \text{Na}\}_n$ -type ring (type III, Fig. 1). In turn, coordination of K^+ or Rb^+ ions leads to the formation of dinuclear sandwich-type

Download English Version:

<https://daneshyari.com/en/article/1299629>

Download Persian Version:

<https://daneshyari.com/article/1299629>

[Daneshyari.com](https://daneshyari.com)