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ORIGINAL ARTICLE

An inclusion complex of β-cyclodextrin with mnt anion (mnt = maleonitriledithiolate) studied by induced circular dichroism

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Abstract A new inclusion complex of β-cyclodextrin with sodium maleonitriledithiolate (Na_2mnt) was investigated by electronic spectra, induced circular dichroism (ICD), and quantum mechanics (QM) methods. The orientation of the guest anion inside the host cavity was studied by ICD spectra and analyzed by structural optimization using PM3 quantum chemical method. Finally, the inclusion constant was determined by both a linear and a non-linear fitting methods, which were based on the variation of ICD signals of the guest upon inclusion complexation with the host. The inclusion constant of Na_2mnt/β-cyclodextrin was estimated to be $(2.45 \pm 0.15) \times 10^3$ or $(3.10 \pm 0.11) \times 10^3$ M^{-1} in solution by these two fitting methods.

Keywords β-Cyclodextrin · Inclusion complex · Maleonitriledithiolate · Induced circular dichroism · Inclusion constant · PM3

Introduction

Cyclodextrins are naturally occurring macrocyclic oligomers of α-D-glucose composed of six, seven or eight units (α-, β-, γ-CD respectively), each having a slightly different cavity diameter. They appear as truncated cones with primary and secondary hydroxyl groups crowning the narrower and the wider rims of their molecular cavities, respectively. Since CDs have hydrophilic exteriors and hydrophobic cavities, they are good candidates for binding with various guest molecules, varying from organic molecules to organometallic compounds even rare gases, to form inclusion complexes [1]. Basically, the main driving force for the formation of inclusion complexes is attributed to the hydrophobic interactions between the cyclodextrin cavities and the hydrophobic guests or the hydrophobic ligands of the guests, especially in constructing cyclodextrin-based rotaxanes [2]. Therefore, the inclusion complexation between CDs and ionized guests is interesting. Herein we reported a new inclusion complex between β-CD and a bi-valenced anion guest, sodium maleonitriledithiolate (Na_2mnt), in solution. By using induced circular dichroism (ICD) spectrometry, the inclusion complex Na_2mnt/β-cyclodextrin was studied in detail, and the results suggested the strong interaction between the host and the guest. In this paper, we did not concentrate on the inclusion complex of Na_2mnt/β-cyclodextrin only because of its anion guest. Instead, we want to set up a model system, where more chromophors (for example when the p–π^* transition in Na_2mnt is involved) could be explored in terms of circular dichroism research. So far, very little was known for other chromophors except the π–π^* transitions in aromatic systems and the n–π^* transitions in azo groups. Therefore, the well-studied compound, Na_2mnt, is a good candidate for the induced circular dichroism studies in the inclusion complexes. Once its ICD spectrum is elucidated, the mnt motif can be used as a probe to investigate the interaction between the cyclodextrins hosts and the mnt-based coordination compounds guests.

Results and discussion

During the past several decades, much effort has been devoted to investigating the cyclodextrin inclusion complexes. Therefore many experimental methods such as UV,

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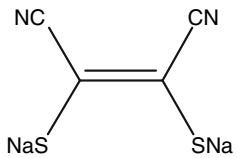
IR, NMR, cyclic voltammograms and thermogravimetric analysis have been established to study the host–guest inclusion complexation phenomena in cyclodextrin chemistry [3]. As our guest molecule, Na_2mnt (Scheme 1), is much soluble and contains no hydrogen atoms, the electronic spectrum was thus a simple and feasible method to investigate the formation of inclusion complex Na_2mnt/β-cyclodextrin in solution. As shown in Fig. 1, one strong and broad peak was observed for the guest (Na_2mnt) at around 366 nm (curve *a*). When titrated with the increasing concentrations of β-cyclodextrin solutions, the absorption maximum of the guest (Na_2mnt) gradually shifted to 375 nm where the host was about 19-fold excessive than the guest (curve *h*). This bathochromic effect indicated the formation of the inclusion complex in solution, which was ascribed to the more hydrophobic microenvironment change of Na_2mnt when included by β-cyclodextrin compared with that of the un-included Na_2mnt in aqueous solution [4]. In Fig. 1, two isosbestic points were observed locating at around 235 and 320 nm respectively. However, the precise isosbestic point was not recorded at around the absorption maximum (380 nm). Most likely, it's due to the different inclusion models that the guest was able to adopt within the host cavity. But the 1:1 stoichiometry was identified by the Job plotting method (Fig. 3).

As the signal changes in UV spectra were minor (Fig. 1), the induced circular dichroism (ICD) was used as a much more sensitive method to explore the inclusion complexation and the co-conformation of Na_2mnt/β-cyclodextrin in solution. Now it's well known that an achiral guest will be induced, by the chiral cyclodextrins cavities, to produce circular dichroism signals [5]. And more important, the ICD signals were strongly in relate to the orientation of the guest in the host cavity. Therefore, ICD is a powerful tool to study the geometry or the structural information of the inclusion complexes in solution besides the X-ray crystallographic analysis in solid [6]. So, the ICD signals of our Na_2mnt/β-cyclodextrin system were recorded.

The electronic spectra of the guest, Na_2mnt, have been well studied. The absorption maximum in Figs. 1 and 2 was ascribed to the p–π^* transition [7]. As anticipated, the free (un-included) guest showed no ICD signal in solution (curve *a* in Fig. 2) due to its highly symmetric planar-structure. Upon inclusion complexation with the host, the guest was induced to produce a wide and strong peak around 385 nm in ICD spectra, which arose evidently from

Scheme 1 The guest molecule Na_2mnt



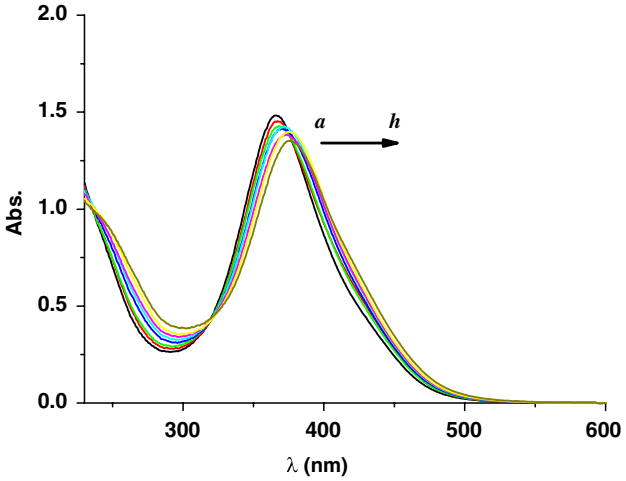


Fig. 1 UV spectra of Na_2mnt ([Na_2mnt] = 1.53×10^{-4} M) in water and in the presence of increasing concentrations of β-CD; [β-CD] = 0, 0.75×10^{-4}, 1.50×10^{-4}, 3.00×10^{-4}, 4.50×10^{-4}, 6.00×10^{-4}, 15.0×10^{-4}, 30.0×10^{-4} M ($a \rightarrow h$)

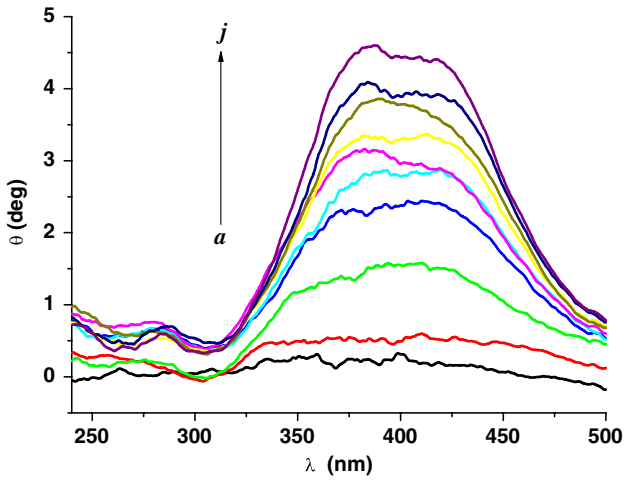


Fig. 2 ICD spectra of Na_2mnt ([Na_2mnt] = 1.53×10^{-4} M) in water and in the presence of increasing concentrations of β-CD; [β-CD] = 0, 0.5×10^{-4}, 1.50×10^{-4}, 3.00×10^{-4}, 4.50×10^{-4}, 6.00×10^{-4}, 7.5×10^{-4}, 11.3×10^{-4}, 15.0×10^{-4}, 30.0×10^{-4} M ($a \rightarrow j$)

the baseline (curve *a* in Fig. 2). Therefore, the formation of the inclusion complex Na_2mnt/β-cyclodextrin was confirmed by the ICD spectra. Compared with its UV spectra, the ICD spectra of the inclusion complex are more sensitive and applicable in identifying the host–guest complexation and determining the inclusion constant. Based on the minute shifts and the evident magnitudes of the characteristic peaks at around 385 nm in ICD spectra, it's reliable now to calculate the inclusion constant or the stability constant of the inclusion complex.

Before the calculation of the inclusion constant, we have to set up the inclusion model of Na_2mnt/β-cyclodextrin in solution. Therefore, the stoichiometry of our inclusion

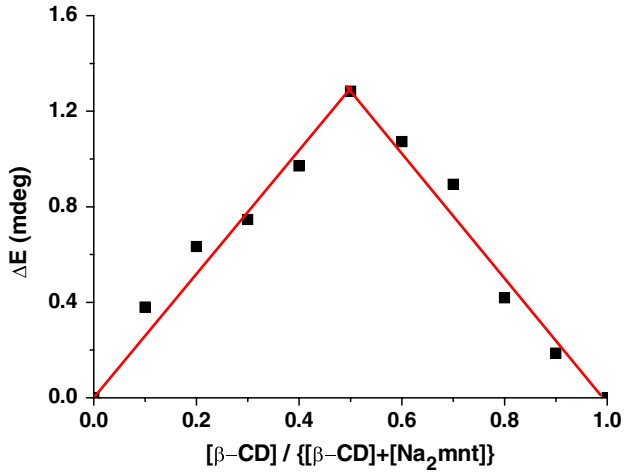


Fig. 3 Continuous variation measurements for the Na_2mnt/β-CD systems ([CD] + [Na_2mnt] = 1.85 × 10^{-4} M) in water at 20 °C (λ = 385 nm)

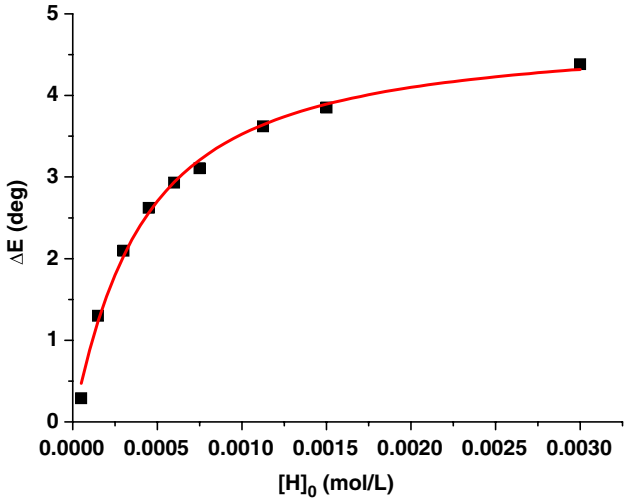


Fig. 5 Determination of the inclusion constant by using a non-linear fitting method, where the ΔE was plotted versus $[H]_0$ (λ = 392 nm)

complex was determined by the method of continuous variation (Job plotting analysis), which was based on the 385 nm ICD signal intensity. The maximum at 0.5 strongly indicated the 1:1 ratio of the guest to the host in solution (Fig. 3). Therefore, the data from Fig. 2 were collected and applied to either a linear or a non-linear fitting method (see Materials and Methods). As shown in Figs. 4 and 5, all the experimental data exhibited good fitting in both methods. And the inclusion constant or stability constant (K_s) of the inclusion complex Na_2mnt/β-cyclodextrin were calculated to be (2.45 ± 0.15) × 10^3 and (3.10 ± 0.11) × 10^3 M^{-1}, respectively. Compared with those reported in literatures, this inclusion constant indicated a strong interaction between the host and the guest molecules. It's weaker than that discovered in the 1-adamantanecarboxylate/β-cyclodextrin system (1.82 × 10^4 M^{-1}) [8], a little higher than that reported in ferrocenecarboxylate/β-cyclodextrin system (2.14 × 10^3 M^{-1}) [9], and much stronger than that found in most benzene-derivatives/β-cyclodextrin systems (3.72 × 10^2 M^{-1} for benzoic acid/β-cyclodextrin) [10]. Considering the highly negative charge of the mnt anion, the encapsulation of Na_2mnt into β-cyclodextrin cavity seems interesting, although some monovalent anion guest was previously observed to be able to bind the host better than their neutral forms did [11]. A recent study showed that 4-nitrophenolate bound to the α-cyclodextrin host ten times better than 4-nitrophenol did when the inclusion constant was took into consideration (K_s were 2,500 and 250 M^{-1}, respectively). Based on their quantum mechanics calculations, Liu and Guo claimed that this unusual binding effect was owing to the strong charge transfer interaction between 4-nitrophenolate and α-cyclodextrin [12]. Therefore, most likely the strong inclusion complexation in our Na_2mnt/β-cyclodextrin system could be elucidated in terms of the charge transfer interaction between the host and guest molecules, since mnt anion is preferentially an electron donor and subjects to electronic polarization [7].

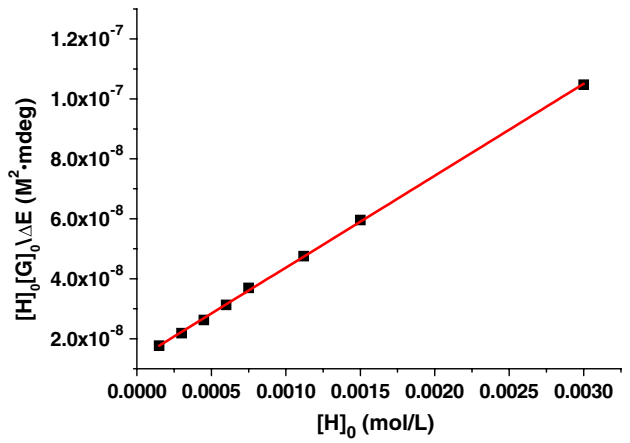


Fig. 4 Determination of the inclusion constant by using a linear fitting method, where the $[H]_0[G]_0/\Delta E$ was plotted versus $[H]_0$ (λ = 392 nm)

As the crystal structure of Na_2mnt/β-cyclodextrin is not available at present, the quantum chemical method, PM3 from the Gaussian03 [13] package, was utilized to study the co-conformation of this inclusion complex. It's known that PM3 tends to give more reliable structure than other methods, such as AM1, when applied in the cyclodextrin chemistry field [14]. As shown in Fig. 6a, the Na_2mnt/β-cyclodextrin system did display a potential energy minimum in the curve (the red point around z = 4 Å) while the guest kept moving from z = 0 to z = 8.5 Å across the host cavity with its two sulfur atoms trafficking parallel to the z-axis. The center of the carbon–carbon double bond of the guest was determined to be in the right middle of the host

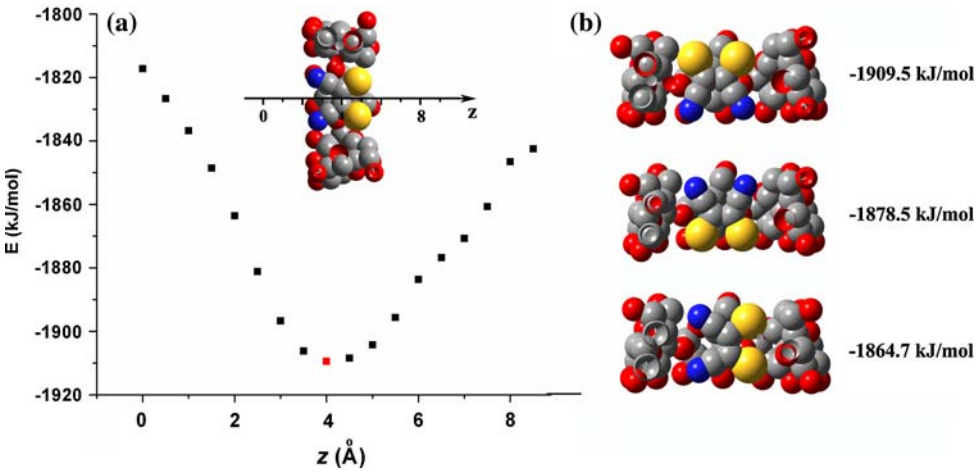


Fig. 6 The calculated potential energy curve upon the variation of the alignment of the guest to the host (**a**), and the results for three selected co-conformations of the inclusion complex Na_2mnt/β-cyclodextrin (**b**). (Half of the host cavities were deleted for clarity, and the coordination system was set up in Materials and Methods.)

cavity, thus resulting in good geometry complementarity in the inclusion complex of Na_2mnt/β-cyclodextrin. However, this was merely one of the most optimized co-conformations, in which the deep penetration of the guest into the host cavity was achieved and accounted for the strong inclusion complexation (Fig. 6a). So, the guest molecule was then subjected to rotating around the central point of its C–C double bond within the molecular plane to scan other energy-favored orientations in the host cavity. Three co-formations were then selected and illustrated in Fig. 6b, among which the top one (the same alignment as that demonstrated in Fig. 6a) showed the lowest potential energy. The energy gaps between this most stabilized co-conformation and the other two possible ones are 31.0 and 44.8 kJ/mol, respectively. So, this alignment of the inclusion complex was calculated to be the most energy-satisfied. It's well known that the wider rim of β-cyclodextrin is more hydrophobic than the narrower one because of the sequentially intramolecular hydrogen bonding between hydroxyl groups O2–H/O3–H around the secondary rim of the host cavity [1, 3]. Consequently, the above-mentioned co-conformation (Fig. 6a) where the hydrophobic moiety (two nitrile groups) of mnt was facing the secondary rim while the hydrophilic moiety (two sulfur anions) facing the primary rim of β-cyclodextrin, was much more favored compared with the other two co-conformations.

Furthermore, Harata's rule [6] has been successfully used to predict the co-conformations of some inclusion complexes of cyclodextrins. It claims that a guest chromophore locating inside the host cavity will give rise to a positive Cotton effect (+ICD signal) if the transition dipole moment of the guest is aligned parallel to the symmetric axis of the host (the z-axis in our case). So far, very little was studied for other chromophors except the π–π^* transitions in aromatic systems and the n–π^* transitions in azo groups [15]. Therefore, we took advantage of the latter model (n–π^* transitions in azo groups) to explore the relationship between the ICD signal of Na_2mnt/β-cyclodextrin system and its co-conformation. As shown in Fig. 2, the ICD signal of Na_2mnt/β-cyclodextrin was assigned to the p–π^* transition of the guest. As far as the similarity between the nitrogen–nitrogen double bond in azo group and the carbon–carbon double bond in mnt was concerned, the p–π^* transition in our guest molecule was supposed to be parallel to the z-axis (as shown in Fig. 6a). Therefore, a positive Cotton effect was expected (Fig. 2). If it is true, the results from ICD experiments could be in good accordance to those predicted by the quantum chemical methods, which are bridged by Harata's rule. Further studies concerning about the applications of other established rules in elucidating the ICD signals of our Na_2mnt/β-cyclodextrin system are in process in our lab.

Materials and methods

Physical measurements and materials

The UV spectra were recorded on a Shimadzu UV-3100 spectrometer. The ICD measurements were performed on a JASCO J-810 circular dichroism spectrometer. 2-Butene-dinitrile-2,3-dimercapto disodium salt (Na_2mnt) was synthesized according to the method described in the literature [16].

Quantum chemical methods

The quantum mechanical calculations were performed with the program Gaussian03 [13]. Atom coordinates from the crystallographic data of β-cyclodextrin [17] was used as input structure. When using PM3 method from the Gaussian03 package to achieve the geometry optimization

of the inclusion complex, the z-axis was the real $C7$ symmetry-axis of the host. Then the guest, Na_2mnt, was placed along the z-axis of the coordination system with its molecular plane parallel to the z-axis while the carbon–carbon double bond perpendicular to the z-axis. It's allowed to enter and then pass through the β-cyclodextrin cavity by steps. At each step, the geometry of the inclusion complex was fully optimized by the PM3 method to find out the best alignment of the guest within the host cavity, where the energy minimum was achieved.

Determinations of inclusion constant

There is an inclusion equilibrium in the solution when the guest molecule (G) binds to the host molecule (H) to form a one-to-one inclusion complex, as shown in Eq. 1,

$$H + G \overset{K_s}{\rightleftharpoons} HG \tag{1}$$

where the stability constant or inclusion constant (K_s) can be expressed in Eq. 2.

$$K_s = \frac{[HG]}{[H]\cdot[G]} = \frac{[HG]}{([H]_0 - [HG])\cdot([G]_0 - [HG])} \tag{2}$$

$[H]_0$ and $[G]_0$ are initial concentrations of the host (cyclodextrin) and the guest, respectively. When in inclusion equilibrium, they change to [H] and [G] correspondingly and the concentration of the inclusion complex is recorded as [HG]. If $[H]_0$ is much higher than $[G]_0$, Eq. 2 can then be simplified as Eq. 3

$$K_s = \frac{[HG]}{[H]\cdot[G]} = \frac{[HG]}{[H]_0\cdot([G]_0 - [HG])} \tag{3}$$

The concentration of the inclusion complex, [HG], can be easily determined from Eq. 4,

$$[HG] = \Delta E/\Delta\varepsilon \tag{4}$$

where ΔE is the ICD signal change of the guest (as the ICD spectra was applied in our case) upon the variation of the host concentration. Theoretically, $\Delta\varepsilon$ is the ICD signal difference between the un-included and the fully included guests, which can be approximately regarded as the observed maximum of ΔE when $[H]_0 >> [G]_0$. The combination of Eq. 3 and 4 results in the Benesi–Hildebrand equation [18] (Eq. 5).

$$\frac{[H]_0[G]_0}{\Delta E} = \frac{1}{K_s\cdot\Delta\varepsilon} + \frac{[H]_0}{\Delta\varepsilon} \tag{5}$$

The plotting of $[H]_0[G]_0/\Delta E$ versus $[H]_0$, which was considered as a linear fitting method, is able to give the inclusion constant or stability constant (K_s). Based on Eq. 6 that derived from Eq. 3, we can conclude Eq. 7, which was defined as a non-linear fitting method.

$$[HG] = \frac{1}{2}\cdot\{([H]_0 + [G]_0 + 1/K_s) \pm \sqrt{([H]_0 + [G]_0 + 1/K_s)^2 - 4[H]_0[G]_0}\} \tag{6}$$

$$\Delta E = \frac{1}{2}\cdot\{\Delta\varepsilon([H]_0 + [G]_0 + 1/K_s) \pm \sqrt{\Delta\varepsilon^2([H]_0 + [G]_0 + 1/K_s)^2 - 4\Delta\varepsilon^2[H]_0[G]_0}\} \tag{7}$$

The plotting of ΔE versus $[H]_0$ is expected to give a K_s more accurately, since no approximation is applied here.

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