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ORIGINAL ARTICLE

Molecular recognition of naphthalenediamine by polyamine modified β-cyclodextrin:yttrium metal complexes

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Abstract The 6-OH group of β-cyclodextrin was modified by diethylene triamine and triethylene tetramine, respectively, mono[6-diethylenetriamino]-6-deoxy-β-cyclo dextrin (DTCD) and mono[6-triethylenetetraamino]-6-deoxy-β-cyclodextrin (TTCD) were synthesized, which included 1,5-naphthalenediamine and 1,8-naphthalenediamine, respectively, in the presence of rare earth metal yttrium chloride. As a result, four ternary inclusion complexes (host–guest-metal) formed, which were characterized via ^{1}HNMR spectroscopy. The chemical shift variations of host and guest molecules were studied. The stoichiometric proportion of host and guest molecules is 2:1 for all the complexes. Signal degeneration still exists for the guest molecules after the inclusion process, which verifies the symmetrical conformation of guest molecules inside the cavities of two host molecules. All the four complexes exhibit "sandwich"-typed structure.

Keywords β-Cyclodextrin (β-CD) · Modification · Molecular recognition · Naphthalenediamine · Yttrium · NMR · Complexation

Introduction

Molecular recognition is defined as the bonding (non-covalent) or selective interactions between host molecules bearing special function and guest molecules. Since the recognition process could induce the variations of electrochemical, optical properties and conformation, also induce the changes of chemical properties and the changes referring to the store, transfer and treatment of chemical information, artificial molecular recognition has been more and more reactive ever since the mid-eighties in the last century, which led to the design, synthesis and investigation of molecular recognition model of amino acids, polypeptide, nucleic acid bases, nucleotide, carbohydrates, steroid [1, 2]. The host–guest chemical theory of molecular recognition, e.g., investigation of the inclusion process between enzyme and substrate molecules, and transfer of all kinds of information inside bodies, discovered that host molecules have high recognition ability to guest molecules. In this way, scientists have designed and synthesized various artificial receptors and artificial enzyme bearing special functions as cell membrane and enzyme, their application in all fields is extensive at present.

Cyclodextrins are cyclic organic compounds obtained by enzymatic transformation of starch. Among the class of "host" molecules, β-cyclodextrin (β-CD) is one of the most abundant natural oligomers and corresponds to the association of seven glucose units [3, 4], of which the cavity exhibits a hydrophobic character whereas the exterior is strongly hydrophilic. This peculiar structure allows various guest molecules to be included in the cavity via non covalent bonds to form inclusion complexes. Guest molecules include inorganic molecules, organic molecules, polypeptide, protein, metal ions, etc. The difference in the geometry and size of guest molecules, matching with the cavity of β-CD, hydrophobicity and host–guest interaction strength could result in different recognition ability of host molecules. A lot of molecular recognition investigation has been reported so far. At present, the molecular recognition

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by β-CD focuses on fullerene [5, 6], carbohydrates [7, 8], polymer [9–12] and ternary inclusion complexes [13–20].

Due to the less recognition sites and less reactivity in catalysis, the application of natural β-CD is restricted. Chemically modified β-CD could remedy the shortage. β-CD derivatives obtained in this way has better inclusion selectivity and higher chemical reactivity, has become one of the most important projects in chemistry and biochemistry frontiers.

In the present research of the ternary inclusion complexes of β-CD:metal ions:guest molecules, most research focused on copper coordinates [13–18], followed are cobalt, nickel and zinc [19, 20]. The research mainly investigated the multi-point molecular recognition and the interaction inside the ternary inclusion complexes. So far, the application of rare earth metals in the field of β-CD has rarely been reported, however, rare earth metal organic complex is an important luminescent material. The multi-point molecular recognition mechanism of the ternary inclusion complexes will be of a great help in the design and synthesis of luminescent materials, of which, yttrium is an important rare earth metal and has an extensive application in the fields of materials, catalysis, alloy, e.g., $Y_3Al_5O_{12}$ is a laser material, $Y_3Fe_5O_{12}$ can be used in the microwave technique, YVO_4:Eu and Y_2O_3:Eu are phosphors in color TV.

In aqueous media, DTCD and TTCD are able to complex metal ions via coordinate linkage. The complex could include naphthalenediamine to form ternary inclusion complexes, which were characterized by means of ^{1}H NMR spectra. The stoichiometric proportion between modified β-CD and guest molecules is 2:1, "sandwich"-typed structure form as a result.

Materials and methods

Reagents

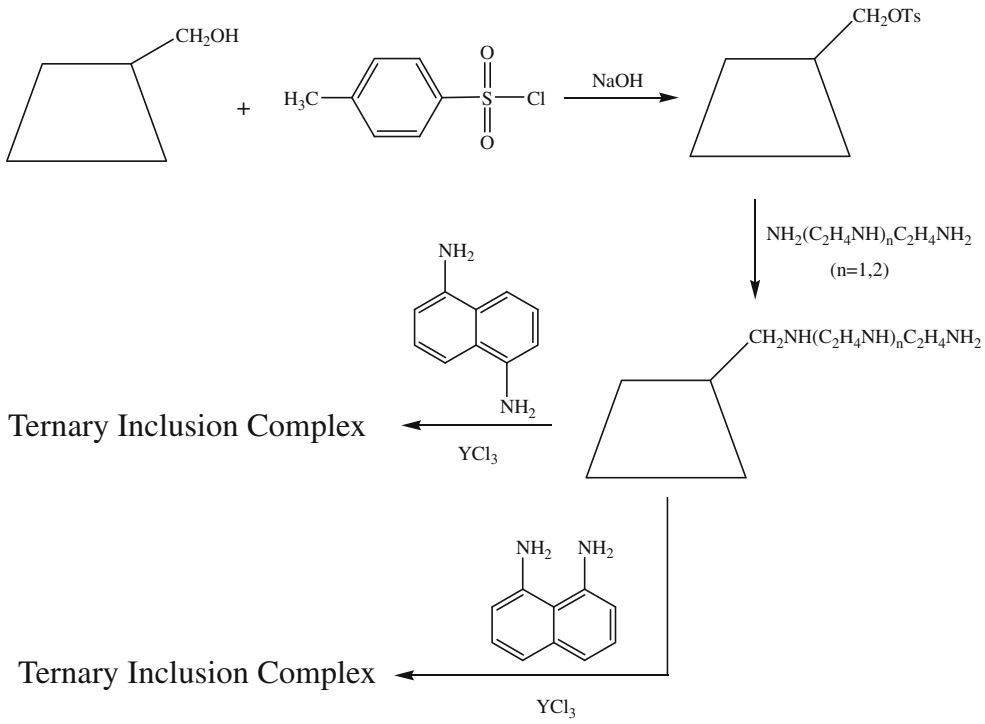
β-cyclodextrin, 1,5-naphthalenediamine, 1,8-naphthalenediamine, TsCl (Paratoluenesulfonyl chloride), diethylene triamine and triethylene tetramine were purchased from Aldrich and used without further purification. Y_2O_3 were obtained from Lab of Molecular Probe, College of Life Science, Dalian Nationalities University. YCl_3 were prepared by dissolving Y_2O_3 in concentrated hydrochloric acid.

NMR experiments

NMR spectra were obtained with a Varian Mercury AS400 instrument. All the experiments of the inclusion complexes were recorded using DMSO-d_6 as solvent. The solutions were transferred in 5 mm NMR tubes, giving a sample total volume of 600 µl. The probe temperature was regulated to 300 K. The resonance at 2.48 ppm (^{1}H NMR) due to residual solvents, present at impurities (DMSO), was used as internal reference.

Preparation of ternary inclusion complexes

Reaction scheme:



Preparation of 6-paratoluenesulfonate-β-CD

Add 100 mL of distilled water and 70 mL of THF into a 250 mL of three-necked flask, 10 g of β-CD and 0.4 g of KOH were added and kept stirring for 15 min., a solution of 1.68 g paretoluenesulfonyl chloride in 30 mL of THF were added into the flask dropwisely within 1.5 h and kept stirring for 3 h. Add 40 mL acetone to the reaction mixture and cool in a freezer, filter to collect the precipitate, recrystallize twice with distilled water.

Preparation of DTCD and TTCD

Add 2 g of 6-paratoluenesulfonate-β-CD and 30 mL of diethylene triamine or triethylene tetraamine into a 100 mL of three-necked flask, input nitrogen, stir the mixture at 70 °C for 7 h, distill extra polyamine by means of vacuum distillation, transfer the remains to 200 mL of acetone, collect the precipitate, recrystallize with H_2O/acetone twice, dry in vacuo.

Preparation of ternary inclusion complexes

0.1 g of DTCD or TTCD and 0.02 g of YCl_3 were dissolved in 30 mL of sodium bicarbonate buffered deionized water, 0.01 g of naphthalenediamine was dissolved in 1 ml of DMSO and added to the above aqueous solution by dropwise. The mixture was kept stirring at room temperature for 3–4 h. Centrifugate the mixture to collect the precipitate. Recrystallize twice from a mixture of DMSO/H_2O, dry in vacuo.

Results and discussion

NMR spectra results and discussion

Figure 1 lists the hydrogen labeling of host and guest molecules.

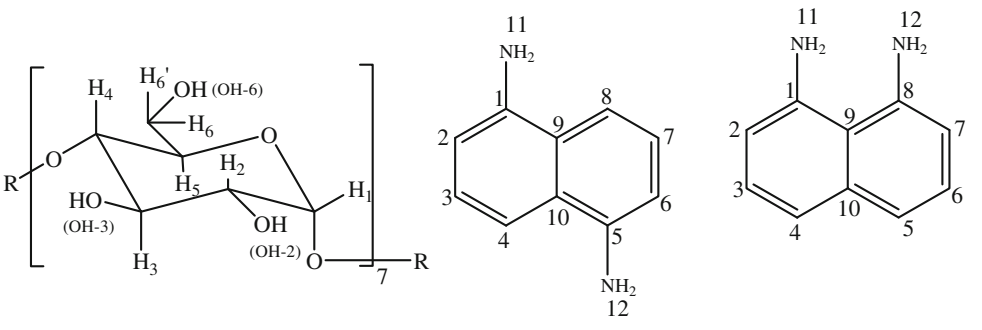
For each molecule, we observed the difference in the chemical shifts between host molecules, naphthalenediamines, and their inclusion complexes.

Tables 1, 2, 3, 4, 5, 6, 7 and 8 lists the ^{1}H NMR chemical shift difference of host and guest molecules in free and inclusion states.

Tables 1, 2 lists the chemical shift variations of host and guest molecules in the complex DTCD-YCl_3-1,5-naphthalenediamine.

^{1}H NMR chemical shifts provides unambiguous evidence on the formation of the complexes. The effect is qualitatively studied.

After the complexation, host and guest molecules doesn't show pronounced chemical shift variations, since the main interaction forces between host and guest molecules are weak Van der Waals forces, e.g., dipole–dipole force, dispersion force, etc. Although amino groups are good coordination groups, no coordination process occurs between yttrium and the amino group in 1,5-naphthalenediamine, which is verified by minute chemical shift variation of the corresponding amino groups (Table 1). Accordingly, we can elucidate that the amino groups locate far away from the narrow rim of β-CD cavity in the complex. Yttrium only coordinates with the amino groups from the side chain of DTCD and it is verified from the NMR signals of hydroxyl groups in DTCD. Before the complexation process occurs, the hydrogen signals in hydroxyl groups are broad (Table 2), however, they reappear as sharp peaks after the complexation process. It's the hydrogen bonding that affects the signal configuration. In free DTCD molecules, strong hydrogen bonds exist between the amino groups in the side chain and hydroxyl groups in the cavity rim, fast hydrogen exchange results in the lost hydroxyl signals. As the coordination process occurs, the amino groups in the side chain form strong coordination bond with yttrium ion, which sets hydroxyl groups free, consequently, their NMR signals reappear as sharp peaks. The chemical shift variation of hydroxyl groups is less than 0.04 ppm, verifies that no complexation occurs between yttrium and hydroxyl groups.



β-CD 1,5-naphthalenediamine 1,8-naphthalenediamine

Fig. 1 Structure and hydrogen labeling of host and guest molecules

Table 1 Chemical shift and variations of 1,5-naphthalenediamine in the ternary complex DTCD-YCl_3-1,5-naphthalenediamine

1,5-naphthalenediamine	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-2, 6	6.62 (d)	6.58 (d)	−0.04
H-3,7	7.07 (t)	7.04 (t)	−0.03
H-4,8	7.23 (d)	7.19 (d)	−0.04
H-11,12	5.41 (s)	5.40 (s)	−0.01

Note $\Delta\delta = \delta$ (complex) − δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 2 Chemical shift and variations of DTCD in the ternary complex DTCD-YCl_3-1,5-naphthalenediamine

DTCD	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-1	4.83 (d)	4.83 (d)	0
H-3	3.64 (t)	3.61 (t)	−0.03
H-6,6′	3.67 (t)	3.66 (t)	−0.01
H-5	3.57 (d)	3.56 (d)	−0.01
H-4	3.34 (t)	3.34 (t)	0
H-2	3.29 (d)	3.28 (d)	−0.01
OH-2	5.72 (broad)	5.73 (d)	0.01
OH-3	5.72 (broad)	5.68 (d)	−0.04
OH-6	4.49 (broad)	4.46 (t)	−0.03

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 3 Chemical shift and variations of 1,8-naphthalenediamine in the ternary complex DTCD-YCl_3-1,8-naphthalenediamine

1,8-naphthalenediamine	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-2,7	6.53 (d)	6.56 (d)	0.03
H-3,6	7.15 (t)	7.04 (t)	−0.11
H-4,5	7.15 (d)	6.96 (d)	−0.19
H-11,12	4.40 (s)	5.45 (s)	1.05

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

1,5-Naphthalenediamine matches the cavity of β-CD very well based on the comparison of the sizes of host and guest molecules [21]. It's able to enter the cavity in two perpendicular orientations [21]. The chemical shift variations of host–guest molecules clearly proves the formation of the inclusion complex, however, the average variation magnitude is lower than that of the inclusion complex between natural β-CD and 1,5-naphthalenediamine [21], which proves that the interaction between 1,5-naphthalenediamine and β-CD in the ternary inclusion complex is lower.

Based on the integration of host–guest molecules in the NMR spectrum, we observed that the stoichiometric proportion between host and guest molecules is 2:1, different to the inclusion between natural β-CD and 1,5-naphthalenediamine (1:1) [21]. The difference lies in the self-inclusion phenomenon in DTCD. After OH-6 of β-CD was modified by diethylene triamine, along with the coordination process between amino groups and yttrium ion, self-inclusion process between the side chain of DTCD and its cavity occurs, which decreases the effective cavity of DTCD. In Table 2, the chemical shift variations of H-3

Table 4 Chemical shift and variations of DTCD in the ternary complex DTCD-YCl_3-1,8-naphthalenediamine

DTCD	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-1	4.83 (d)	4.83 (d)	0
H-3	3.64 (t)	3.61 (t)	−0.03
H-6,6′	3.67 (t)	3.66 (t)	−0.01
H-5	3.57 (d)	3.56 (d)	−0.01
H-4	3.34 (t)	3.35 (t)	0.01
H-2	3.29 (d)	3.28 (d)	−0.01
OH-2	5.72 (broad)	5.74 (d)	0.02
OH-3	5.72 (broad)	5.69 (d)	−0.03
OH-6	4.49 (broad)	4.47 (t)	−0.02

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 5 Chemical shift and variations of 1,5-naphthalenediamine in the ternary complex TTCD-YCl_3-1,5-naphthalenediamine

1,5-naphthalenediamine	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-2,6	6.62 (d)	6.60 (d)	−0.02
H-3,7	7.07 (t)	7.05 (t)	−0.02
H-4,8	7.23 (d)	7.21 (d)	−0.02
H-11,12	5.41 (s)	5.41 (s)	0

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 6 Chemical shift and variations of TTCD in the ternary complex TTCD-YCl_3-1,5-naphthalenediamine

TTCD	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-1	4.83 (d)	4.83 (d)	0
H-3	3.64 (t)	3.61 (t)	−0.03
H-6,6′	3.67 (t)	3.66 (t)	−0.01
H-5	3.57 (d)	3.56 (d)	−0.01
H-4	3.34 (t)	3.34 (t)	0
H-2	3.29 (d)	3.29 (d)	0
OH-2	5.68 (broad)	5.74 (d)	0.06
OH-3	5.68 (broad)	5.69 (d)	0.01
OH-6	4.45 (broad)	4.45 (t)	0

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 7 Chemical shift and variations of 1,8-naphthalenediamine in the ternary complex TTCD-YCl_3-1,8-naphthalenediamine

1,8-naphthalenediamine	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-2,7	6.53 (d)	6.55 (d)	0.02
H-3,6	7.15 (t)	7.04 (t)	−0.11
H-4,5	7.15 (d)	6.96 (d)	−0.19
H-11,12	4.40 (s)	5.44 (s)	1.04

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

Table 8 Chemical shift and variations of TTCD in the ternary complex TTCD-YCl_3-1,8-naphthalenediamine

TTCD	δ (ppm) (free)	δ (ppm) (complex)	$\Delta\delta$ (ppm)
H-1	4.83 (d)	4.83 (d)	0
H-3	3.64 (t)	3.61 (t)	−0.03
H-6,6′	3.67 (t)	3.66 (t)	−0.01
H-5	3.57 (d)	3.56 (d)	−0.01
H-4	3.34 (t)	3.36 (t)	0.02
H-2	3.29 (d)	3.28 (d)	−0.01
OH-2	5.68 (broad)	5.72 (d)	0.04
OH-3	5.68 (broad)	5.70 (d)	0.02
OH-6	4.45 (broad)	4.46 (t)	0.01

Note $\Delta\delta = \delta$ (complex) – δ (free), *s* refers to singlet, *d* as doublet, *t* as triplet

(−0.03 ppm) is more pronounced than that of H-5 (−0.01 ppm), also showing the guest molecule approaches the wider rim of the cavity after forming the inclusion complex. 1,5-Naphthalenediamine could be included inside the cavity of natural β-CD completely, in which a 1:1 inclusion complex formed [21]. Due to the self-inclusion of side chain in the cavity of DTCD, two host molecules are necessary to hold the guest molecule completely, which results in a 2:1 stoichiometric proportion in our work.

The stoichiometric proportion of host–guest molecules in the ternary inclusion complex was obtained based on the integration of corresponding signals of host and molecules in NMR spectra. In the solution state, there is an association-dissociation dynamic equilibrium in the inclusion complex, which is dependent on the inclusion capability of host molecules to guest molecules and the competitiveness of solvent molecules to guest molecules. If both interactions are moderate, guest molecules will be in equilibrium of association-dissociation, there will be two mixed signals of guest molecules in NMR spectra, free state and inclusion state. However, if only one group of guest molecular signals appear, it proves the inclusion complex is stable, no dissociation occurs at room temperature. The integration of corresponding signals of host and guest molecules will provide the stoichiometric proportion of host–guest molecules in the inclusion complex clearly. In our research, we only observed one group of guest molecular signals in NMR spectra, the stoichiometric proportion of host–guest molecules was clearly obtained based on the integration of corresponding signals as a result.

After forming the ternary inclusion complex, the signals of 1,5-naphthalenediamine moves upfield, which is resulted from the shielding effect of the ring current existing inside the cavity of β-CD. H-3 and H-5 of β-CD locate inside the cavity, their chemical shifts also move upfield upon forming inclusion complexes due to the shielding effect of the ring current from guest molecules. Signal degeneration of the guest molecule still exists upon complexation with DTCD and yttrium ion, which proves that the conformation of the guest molecule is symmetrical inside the cavities of DTCD. In comparison with the chemical shift variations of different hydrogen atoms of 1,5-naphthalenediamine, we found that the variations were similar (−0.03 and −0.04 ppm), except that of amino groups (−0.01 ppm) (Table 1), showing that the three groups of hydrogen atoms in the naphthalene ring undergo similar shielding effect from the cavity. As a result, H-4,8 of 1,5-naphthalenediamine will stretch towards the cavity wall and H-2,6/H3,7 will stretch towards the deeper rim of the cavities of two host molecules. Accordingly, we elucidated the structure of the ternary inclusion complex: 1,5-naphthalenediamine is included by two DTCD molecules and a "sandwich" structure forms. C-2,3 and C-6,7 of 1,5-naphthalenediamine stretch towards the deeper rim of the cavities, two amino groups stretch toward the cavity wall of DTCD.

Tables 3, 4 lists the chemical shift variations of host and guest molecules in the complex DTCD-YCl_3-1,8-naphthalenediamine.

As the complexation occurs, the chemical shifts of 1,8-naphthalenediamine show pronounced variations, which clearly proves the formation of the inclusion complexes. The hydrogen atoms in the naphthalene ring shows a variation between $-0.2 \sim 0.03$ ppm (Table 3), bigger than the magnitude of 1,5-naphthalenediamine (Table 1). The shift of amino groups reaches up to 1.05 ppm, similar to that of the inclusion complex between natural β-CD and 1,8-naphthalenediamine [21], also similar to that of 1,5-naphthalenediamine (Table 1). The pronounced chemical shift variation is due to the destroy of intramolecular hydrogen bonding of 1,8-naphthalenediamine after forming the ternary inclusion complex. In free 1,8-naphthalenediamine, a six-membered hydrogen bonding between two amino groups exists (Fig. 2), after it is included inside the cavity of β-CD, due to host–guest interactions, the intramolecular hydrogen bonding is destroyed, amino groups become free as a result. Similar hydrogen bonding doesn't exist in 1,5-naphthalenediamine, as a result, the amino group of 1,8-naphthalenediamine inside the inclusion

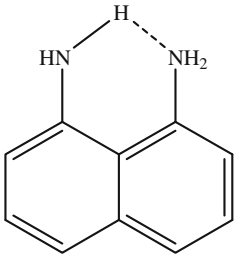


Fig. 2 Intramolecular hydrogen bonding of 1,8-naphthalenediamine

complex will reach similar chemical shift to that of 1,5-naphthalenediamine.

The stoichiometric proportion between DTCD and 1,8-naphthalenediamine is also 2:1 based on the integration result, similar to that of 1,5-naphthalenediamine, different to our reported result [21]. The chemical shift of H-3 (−0.03 ppm) (Table 4) is more pronounced that that of H-5 (−0.01 ppm), clearly proves that the guest molecule is closer to the wider rim of the cavity of DTCD in the ternary complex. Similar to 1,5-naphthalenediamine, 1,8-naphthalenediamine matches the cavity of β-CD very well, could enter the cavity in two perpendicular orientations completely. It's also the self-inclusion of side chain that decreases the effective cavity of β-CD, making two host molecules are required to hold the guest molecule completely. The signal degeneration of guest molecule still exists upon complexation, showing the symmetrical conformation of 1,8-naphthalenediamine inside the cavity of host molecules after forming the ternary inclusion complexes.

After forming the ternary inclusion complex, the chemical shift of H-3 and H-5 (Table 4) of host molecule move upfield, it's affected by the shielding effect of ring current of guest molecules since they are directing toward the cavity. The hydrogen atoms in the naphthalene ring are affected by two factors: shielding effect and the increasing electronic density after destroying the intramolecular hydrogen bonding upon complexation.

In the ternary complex, yttrium only coordinates with the amino groups from DTCD, similar to that of 1,5-naphthalenediamine. According to Table 4, the chemical shift variations of hydroxyl groups are in a range of 0.02 $\sim$ 0.03 ppm, which also reveals that no coordination occurs between yttrium and hydroxyl groups, similar to the analysis of complex DTCD-YCl_3-1,5-naphthalenediamine.

Based on the analysis of NMR spectra, we elucidated the structure of the ternary inclusion complex: 1,8-naphthalenediamine is included by two DTCD molecules and a "sandwich" structure forms. C-2,3 and C-6,7 of 1,8-naphthalenediamine stretch towards the deeper rim of the cavities, two amino groups stretch toward the cavity wall of DTCD.

Tables 5, 6 lists the chemical shift variations of host and guest molecules in the complex TTCD-YCl_3-1,5-naphthalenediamine.

Tables 7, 8 lists the chemical shift variations of host and guest molecules in the complex TTCD-YCl_3-1,8-naphthalenediamine.

TTCD has four amino groups and could form stronger coordination bonds with yttrium ion than DTCD. With longer arm, TTCD will exhibit stronger steric hindrance for large molecules, which can still hold a benzene ring according to the NMR spectra of the inclusion complexes. In comparison with DTCD series, the chemical shift varying tendency is very similar, which means the changing of side chain within a range doesn't affect the inclusion phenomena of same guest molecules. In TTCD series, the stoichiometric proportion between TTCD and 1,5-naphthalenediamine or 1,8-naphthalenediamine is also 2:1, the analysis of NMR signals and conformation is similar to that of DTCD series.

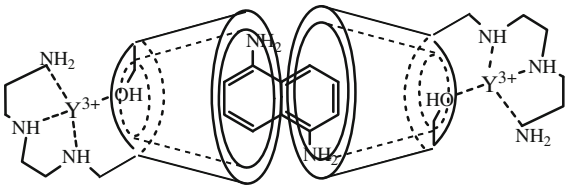
Molecular recognition and conformation analysis

According to NMR analysis, in the four ternary inclusion complexes, yttrium only coordinates with the amino groups from the side chain of β-CD. During the coordination process, the interaction of orbitals between yttrium and ligands doesn't play a significant role, since it is mainly electrostatic interaction. The bonding directions are not clear, similar to ionic compounds. The amount of ligands is dependent on steric hindrance and mutual distances, as well as available ligands. Due to the formation of multiple coordination bonds and self-inclusion, the effective cavity of β-CD is decreased, and hence, the molecular recognition of DTCD or TTCD to the same guest molecules (1,5-naphthaleendiamine or 1,8-naphthalenediamine) will be different in comparison to natural β-CD [21].

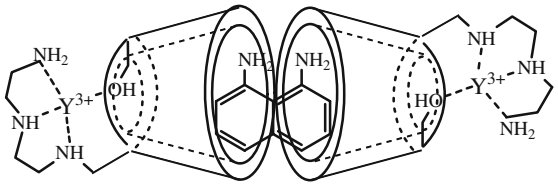
Based on the above analysis, we elucidated the structure of four ternary inclusion complexes, listed in Fig. 3.

Conclusion

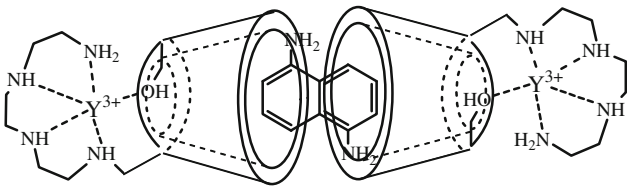
β-CD was modified by diethylene triamine and triethylene tetramine in its 6-OH position to form DTCD and TTCD, respectively, which can easily include hydrophobic guest molecules inside its cavity. In our work, we discussed the inclusion phenomena between modified β-cyclodextrin and 1,5-naphthalenediamine/1,8-naphthalenediamine. Due to the existence of amino groups which are good ligands in the side chain of β-CD, the inclusion complexes will coordinate with rare earth metal ion Y^{3+} to form ternary complexes, four complexes were prepared. In the ternary complexes, the chemical shifts of host and guest molecules



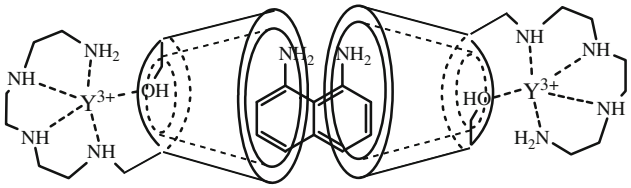
Ternary inclusion complex of DTCD:YCl_3:1,5-naphthalenediamine



Ternary inclusion complex of DTCD:YCl_3:1,8-naphthalenediamine



Ternary inclusion complex of TTCD:YCl_3:1,5-naphthalenediamine



Ternary inclusion complex of TTCD:YCl_3:1,8-naphthalenediamine

Fig. 3 Structure of ternary supramolecular complex

show diverse variations, which clearly prove the formation of complexes. The stoichiometric proportions between host and guest molecules in the four ternary inclusion complexes are 2:1, different to our reported result [21]. Signal degeneration of guest molecules inside the cavities of DTCD or TTCD still exists, revealing the symmetrical conformation of guest molecules. Based on the NMR analysis, we elucidated that the four ternary inclusion complexes all exhibit "sandwich"-typed structure.

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