Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Khemtong, Chalermchai , Banerjee, Debasish , Liu, Yubiao , Khoury, Jouliana M. El , Rinaldi, Peter L. and Hu, Jun(2005) 'Formation of an Inclusion Complex of a New Transition Metal Ligand in β-Cyclodextrin', Supramolecular Chemistry, 17: 4, 335 — 341
To link to this Article: DOI: 10.1080/10610270500115563
URL: http://dx.doi.org/10.1080/10610270500115563

Supramolecular Chemistry, June 2005 Vol. 17 (4), pp. 335–341

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Formation of an Inclusion Complex of a New Transition Metal Ligand in β-Cyclodextrin

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Received (in Austin, TX, USA) 10 December 2004; Accepted 3 February 2005

The inclusion complex of a new transition metal ligand, 2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid (2,4,9-trithia-adamantane-7-carboxylic acid, TPCOOH) in β-cyclodextrin was studied by ^{1}H NMR, 2D NOESY NMR spectroscopy, host-induced CD spectroscopy, and tandem mass spectrometry. ^{1}H NMR, MS–MS and NOESY data show that the TPCOOH guest forms a 1:1 inclusion complex with the host β-cyclodextrin. The NOESY experiments also show that TPCOOH is oriented in the complex with the thioketal end preferentially located at the larger opening of β-cyclodextrin. The orientation of the guest in the host molecule is also confirmed by the induced CD of the ligand, which shows a positive Cotton effect. An association constant of 660 ± 20 M^{-1} was determined by ^{1}H NMR titration for the complex at room temperature in D_2O.

Keywords: Tripodal transition metal ligand; 2,4,9-Trithiaadamantane; β-Cyclodextrin; Inclusion complex; NOESY; Association constant

INTRODUCTION

Cyclodextrin is one of the best known chiral natural hosts for small organic molecules and it has been the subject of numerous detailed supramolecular chemistry studies [1]. The fruits of these inquiries include advanced materials for formulations, drug delivery, chiral separations, and catalysts for asymmetric synthesis. Many enzyme mimics based on modified cyclodextrins have been developed, but a catalyst based on the host cyclodextrin's chiral cavity and a guest transition metal complex active site is yet to be developed. We recently developed a new transition metal ligand based on 2,4,9-trithiaadamantane derivatives. The trithiaadamantane structure represents a C_{3v} chelating ligand, this complexes with several transition metals and metal clusters such as Au, Pt and Ru_3 [2]. From a structural point of view, the shape of this ligand fits well into the β-cyclodextrin cavity and the formation of the inclusion complex should break the C_{3v} symmetry of the ligand by the chiral host [3–4]. The resulting guest–host complex is potentially a new type of asymmetric transition metal ligand suitable for the development of new materials and for chiral catalysis and separation. To develop such an inclusion complex-based transition metal ligand, it is necessary to investigate the structure and properties of the 2,4,9-trithiaadamantane/β-cyclodextrin inclusion complex.

β-Cyclodextrin is perhaps the best known natural host for small organic molecules in the cyclodextrin family [1]. It is a cyclic oligosaccharide made up of seven α-(1 → 4)-linked D-(+)-glucopyranose units. It has a doughnut conical shape with a hydrophilic exterior and a moderately nonpolar internal cavity. The internal cavity is about 0.8 nm deep and 0.7 nm in diameter, providing a hydrophobic chiral environment for small organic guest molecules. Among the various known guest compounds of β-cyclodextrin, adamantane derivatives exhibit excellent binding stabilities because of the close match of the structure of the adamantane framework to the inner cavity of β-cyclodextrin such that the distance-dependent van der Waals-London dispersion forces can be maximized [5–7]. 2,4,9-Trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid differs from adamantane in that the three carbon atoms at the 2, 4 and 9 positions of the adamantane carbon framework are substituted by sulfur atoms (Fig. 1). The substitutions

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ISSN 1061-0278 print/ISSN 1029-0478 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/10610270500115563

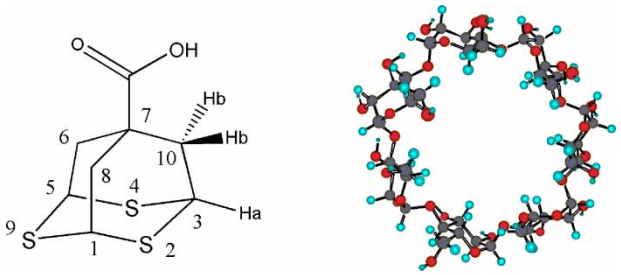


FIGURE 1 2,4,9-Trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid (left) and β-cyclodextrin (right).

produce two major structural perturbations in the adamantane framework: (1) the six-membered ring containing the sulfur atoms is enlarged because of the larger Van der Waals radii of sulfur compared with those of carbon; and (2) the compound becomes more polar because of the new C–S polar bonds. X-ray crystal structure and quantum mechanical calculations indicated that the structural perturbation should lead to a close size match between the 2,4,9-trithiaadamantane guest and the β-cyclodextrin host. The increased polarity of the thioacetal end should increase the water solubility of the compound and reduce the hydrophobicity of the guest. In addition, the thioacetal end is significantly larger than the carboxylic acid end. The graduation in the molecular shape of the guest is comparable to that of the inner cavity of β-cyclodextrin. Therefore, we hypothesized that 2,4,9-trithiaadamantane derivatives should be selectively oriented in the complex with the larger end at the larger opening of β-cyclodextrin to minimize the unfavorable intermolecular forces.

RESULTS AND DISCUSSION

The formation of an inclusion complex between TPCOOH and β-cyclodextrin was evident in the ^{1}H NMR experiments. TPCOOH dissolves slightly in water. When β-cyclodextrin was present in the solution, its solubility increases visibly. Thus, a 1:1 mixture of TPCOOH and β-cyclodextrin (3.5×10^{-3} M) formed a clear solution in D_2O in an NMR tube. At the low concentration limit, this change in the solubility of TPCOOH in water is attributed to the molecular interactions between water-insoluble TPCOOH and water-soluble β-cyclodextrin. The ^{1}H NMR spectrum of the resulting solution showed significant changes in the chemical shifts of TPCOOH and β-cyclodextrin (Fig. 2).

Similar phenomena in cyclodextrin inclusion complexes have been observed previously and studied extensively [8]. Accordingly, we attributed these spectral changes to the dynamic exchanges between uncomplexed species and the intimately included TPCOOH in β-cyclodextrin in the aqueous solutions. It is worth noting that we did not observe significant line broadening due to the complexation, indicating that the complexation equilibrium is at the fast exchange limit of the NMR time scale at room temperature. The simultaneous observation of changes in the chemical shift of the β-cyclodextrin at H-3 and H-5 also indicated the binding interaction

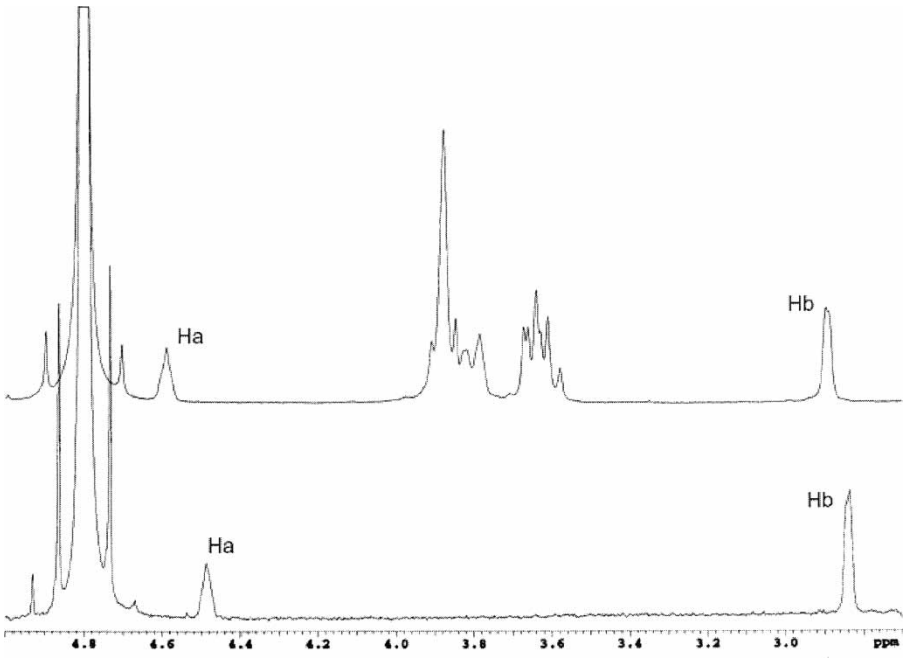
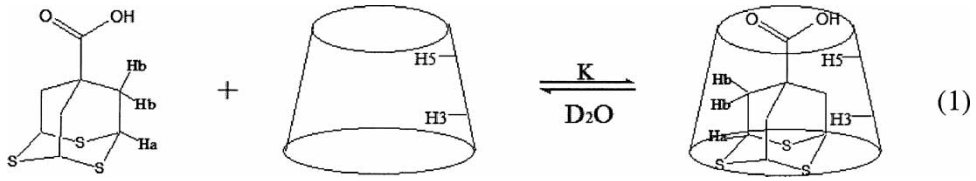


FIGURE 2 ^{1}H NMR spectra of TPCOOH (above) and the TPCOOH/β-cyclodextrin inclusion complex (below) in D_2O at room temperature.

dominated by the inclusion of the TPCOOH guest inside the host β-cyclodextrin cavity.

The formation of the inclusion complex between TPCOOH and β-cyclodextrin was confirmed by electrospray tandem mass spectrometry. When a solution of TPCOOH and β-cyclodextrin in water was electrospray ionized, the corresponding 1:1 complex peak was observed ($m/z = 1368$ D) in the negative ion mass spectrum. The nature of this ion was confirmed by collisional activation of the mass-selected ion at $m/z = 1368$ D, which fragmented preferentially into the pseudo-molecular ion of β-cyclodextrin, $m/z = 1133$ in the MS/MS spectrum (Fig. 3).



(1) (1)

The detailed host–guest interactions of the TPCOOH/β-cyclodextrin inclusion complex were analyzed using 2D ^{1}H—^{1}H NOESY experiment (Fig. 4). NOESY has been widely used to obtain through-space interaction in 3D supramolecular complexes. The presence of cross-peak A between resonances H_a of TPCOOH and H-3 of β-cyclodextrin indicates that these protons are close to each other. Note that the resonance H_a does not exhibit a correlation with the remaining β-cyclodextrin protons. The resonance H_b of TPCOOH exhibits NOE cross-peaks with the resonances of H-5 (B) and H-3 (C). This can be attributed to the fact that the H_b protons are in close proximity to both H-3 and H-5 protons. These interactions are only possible if the carboxylic acid end group of TPCOOH is included in the smaller end of the β-cyclodextrin cavity and the thioacetal end is located in the bigger rim of the cavity as illustrated in Eq. (1).

The 2D NOESY study of the inclusion complex was confirmed by CD spectroscopy. TPCOOH is an achiral molecule that displays an absorption band at 267 nm. Cyclodextrin is a chiral molecule that does not absorb in the UV–vis region. As shown in Fig. 5, the TPCOOH and β-cyclodextrin mixture shows a distinctive positive Cotton effect near the UV–vis absorption peak of TPCOOH, because TPCOOH is C_{3v} symmetric and β-cyclodextrin is C_7 symmetric [9]. It was reported recently that certain cyclodextrin complexes form aggregates in water [10]. The NOESY spectrum does not display significant through-space couplings between the β-cyclodextrin

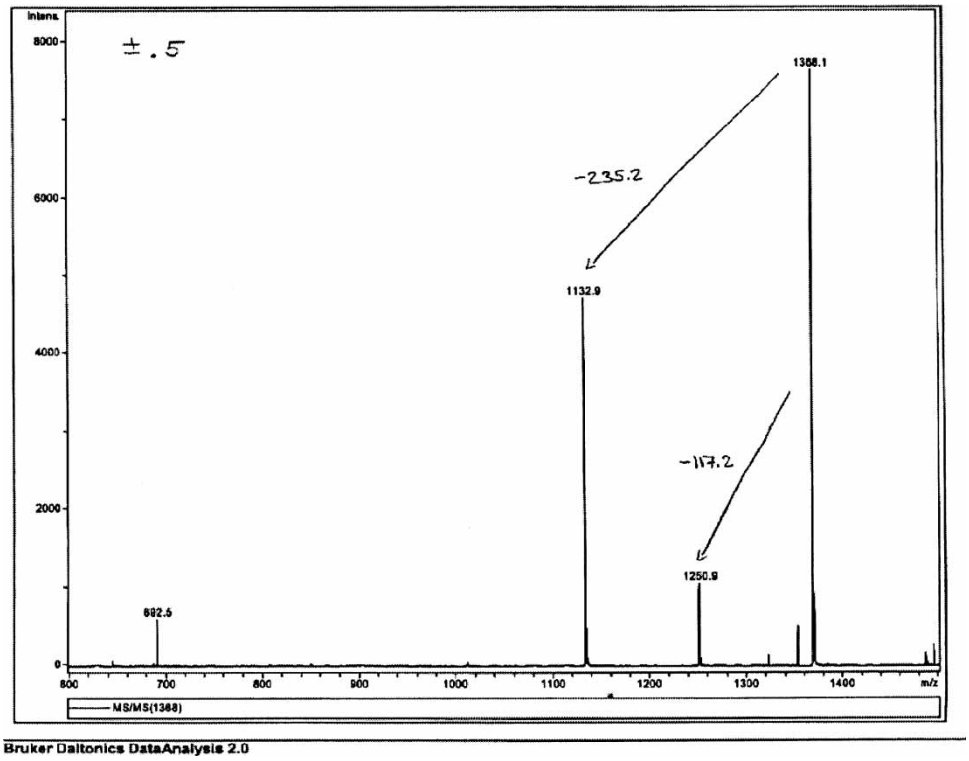


FIGURE 3 Electrospray MS/MS spectrum of the inclusion complex of TPCOOH and β-cyclodextrin.

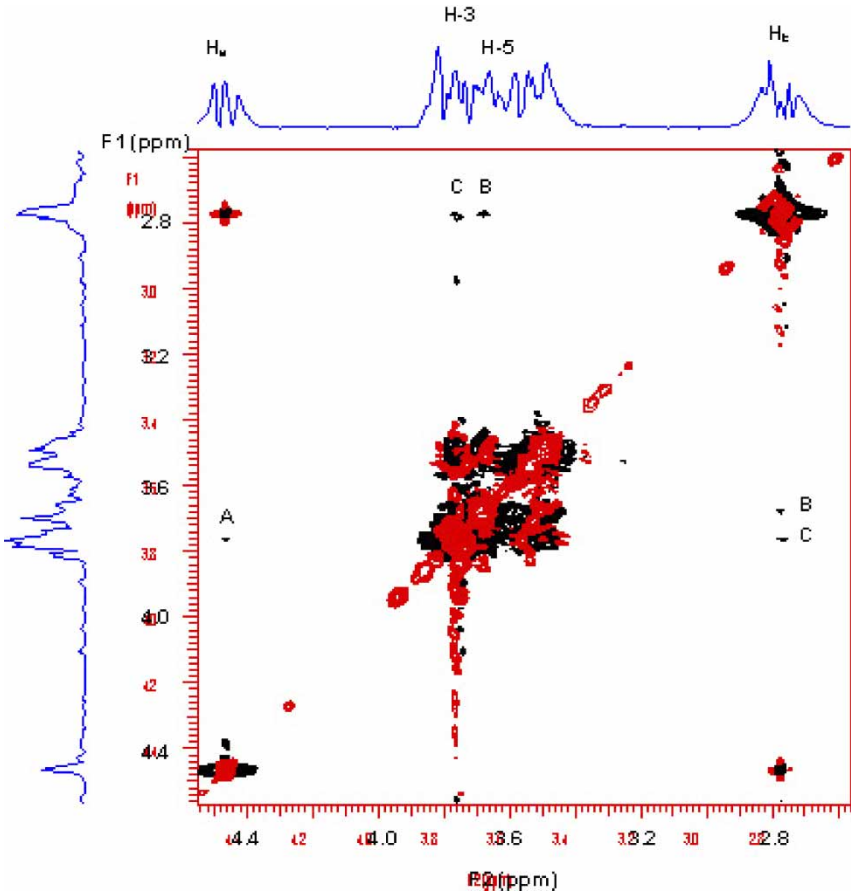


FIGURE 4 2D NOESY spectrum of the TPCOOH and β-cyclodextrin inclusion complex.

units, and does not support the possibility of formation of such aggregations in water in our system.

The equilibrium constant of the inclusion complex is an important parameter for the development of supramolecular materials. We carried out NMR titrations by measuring chemical shift changes as a function of the relative concentrations of the host and guest. We measured the changes in the chemical shifts for the H-3 and H-5 peaks of the host as well as H_a and H_b of the guest (Table I).

The formation of the inclusion complex induces upfield shifts of the resonances for both H-3 and H-5 of β-cyclodextrin. The resonances of TPCOOH shifted downfield. The stoichiometry of the complex was calculated by using the anomeric proton H-1 of the host as the internal reference [11]. Plotting the changes in chemical shifts of H-3 and H-5 against the guest/host ratio (r), we obtained two lines with steep slopes at low guest concentration but leveling off when $r \geq 1$, indicating the complex to be 1:1 stoichiometry for TPCOOH and β-cyclodextrin (Fig. 6). Quantitative analysis of the association constant of the guest and host was achieved by NMR titration in similar experiments. In these experiments, the total concentration of β-cyclodextrin (host) was varied while the total concentration of TPCOOH (guest) was held constant. NMR spectra of the solutions were recorded. To determine the binding constant (K), the increasing total concentration of β-cyclodextrin ($[\beta\text{-CD}]_0$) was plotted against the chemical shift change (δ_i) and K was determined according to Eq. (2).

$$[H]_0 = \frac{\frac{1}{K} - [G]_0\left(\frac{\delta_i}{\delta_c} - 1\right)}{\frac{\delta_c}{\delta_i} - 1} \tag{2}$$

The binding constant (K) was estimated from Eq. (2) by performing a nonlinear curve fitting using the data analysis software Origin (Microcal™ software, Inc.). $[H]_0$ and $[G]_0$ are the initial concentrations of the host and guest, respectively, δ_i is the difference between the observed chemical shift of the guest and the chemical shift of the free guest, and δ_c is the difference between the chemical shift of the completely complexed guest and the free guest. As indicated in Fig. 7, an association constant of $6.63 \times 10^2\,M^{-1}$ was obtained. Because the host solubility reaches saturation when its concentration approaches 0.01 M, the two data points at higher β-cyclodextrin concentration were removed from the fitting process.

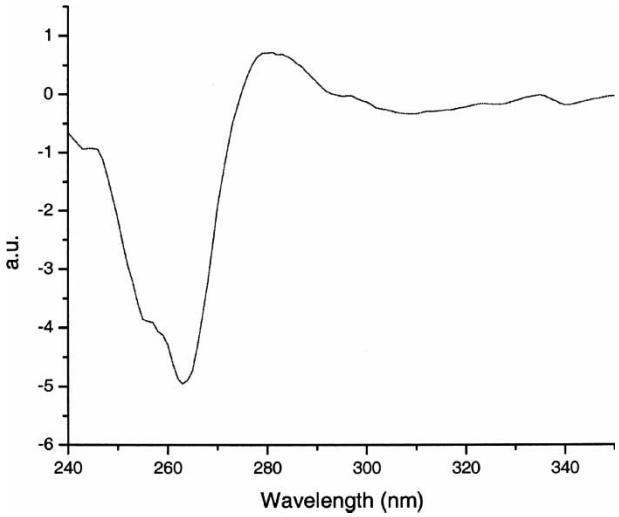


FIGURE 5 Induced positive Cotton effect observed for the TPCOOH and β-cyclodextrin inclusion complex in water.

CONCLUSIONS

In this study, we developed a new synthesis of 2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid ethyl ester and investigated its inclusion complex in β-cyclodextrin. In the synthetic development, a new method for the preparation of small thioacetal crown was developed. Useful quantities of the 2,4,9-trithiaadamantane derivatives are now available through this optimized synthetic route. In the inclusion complex synthesis, we demonstrated the formation of a structurally well-defined inclusion complex of 2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid with β-cyclodextrin in water by multiple spectroscopic methods, particularly NMR spectroscopy. The NMR and MS–MS studies showed that the guest and host molecules formed a 1:1 inclusion complex. The guest molecule was found to be predominantly oriented with the carboxylic acid end towards the small opening and the trithiaacetal end towards the large opening of the conically shaped β-cyclodextrin inner cavity by 2D NOESY NMR spectroscopy. Finally, an association constant of $660 \pm 20\,M^{-1}$ was determined by ^1H NMR titration for the complex at room temperature in neutral D_2O, indicating that TPCOOH is a useful guest for β-cyclodextrin. The well-defined structure and the good binding affinity of the inclusion complex provides exceptional hope for future developments of new supramolecular materials for separation and catalysis based on this new guest-host complex.

EXPERIMENTAL

Materials

β-Cyclodextrin was used as received. TPCOOH was prepared by base hydrolysis of ethyl 2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylate, which was produced according to a modified literature procedure [12]. Specifically, through a solution of 2,2-diallylpent-4-enoic acid ethyl ester (2.85 g, 13.70 mmol) in freshly distilled CH_2Cl_2 (100 mL) in a 250 mL three-necked flask was bubbled O_3 generated *in situ* with an OREC ozone generator (Ozone Research and Equipment Inc.) at −78°C. The reaction was allowed to continue while stirring, until the reaction mixture displayed a light blue color. The ozone line was then replaced by an argon line to flush the reaction mixture for 10 min. After addition of $(CH_3)_2S$ (3.5 mL, 41.10 mmol), the reaction mixture was allowed to warm up slowly from −78°C to the ambient temperature and was then transferred to a 250-mL round-bottom flask. After removing the solvent by using a rotary evaporator and subsequently a mechanical pump at ambient temperature, the resulting yellow viscous residue was redissolved in CH_2Cl_2 (100 mL). Lawesson's reagent (5.54 g, 13.7 mmol) and then boron trifluoride etherate (5.80 mL, 41.10 mmol) were added to the solution, which was then refluxed for 100 h under argon. The reaction mixture was allowed to cool to ambient temperature, washed with aqueous potassium carbonate (0.2 M, 3 × 15 mL), and dried over anhydrous magnesium sulfate. A brownish oily residue was produced after filtration and evaporation of the solvent, and column chromatography using 25% ethyl acetate in hexanes as an eluting solvent furnished white crystals (1.23 g, 38% yield). Mp 155–157°C (lit. 156°C) [12]; ^1H NMR ($CDCl_3$): δ 1.27 (3 H, CH_3, t, J = 7.20 Hz), 2.89 (6 H, CH_2, d, J = 3.00 Hz), 4.17 (2 H, OCH_2, q, J = 7.20 Hz), 4.32 (3 H, broad, CH, s) ppm;

TABLE I ^1H NMR chemical shifts and the corresponding changes in H-3 and H-5 of β-cyclodextrin for the inclusion complex of TPCOOH and β-cyclodextrin

$Ratio_{(TPCOOH/\beta\text{-CD})}$	0	0.30	0.50	0.70	1.00	1.50	2.00	3.50	4.50
$\delta_{H\text{-}3(ppm)}$	3.978	3.911	3.881	3.843	3.803	3.801	3.801	3.799	3.798
$\delta_{H\text{-}5\ (ppm)}$	3.891	3.837	3.811	3.790	3.770	3.768	3.769	3.767	3.766
$\delta_{Ha\ (ppm)}$	0	4.596	4.594	4.592	4.583	4.580	4.579	4.580	4.575
$\delta_{Hb\ (ppm)}$	0	2.898	2.903	2.897	2.894	2.895	2.894	2.894	2.889
$\Delta\delta_{H\text{-}3\ (ppm)}$	0	−0.067	−0.097	−0.135	−0.175	−0.177	−0.177	−0.179	−0.180
$\Delta\delta_{H\text{-}5\ (ppm)}$	0	−0.054	−0.080	−0.101	−0.121	−0.123	−0.122	−0.124	−0.125
$\Delta\delta_{Ha\ (ppm)}$	0	0.241	0.239	0.237	0.228	0.225	0.224	0.225	0.220
$\Delta\delta_{Hb\ (ppm)}$	0	−0.052	−0.047	−0.053	−0.056	−0.055	−0.056	−0.056	−0.061

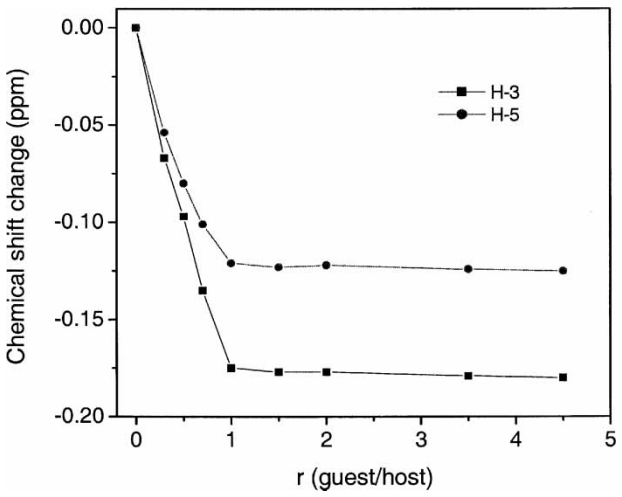


FIGURE 6 Changes in chemical shifts for H-3 and H-5 of β-cyclodextrin as a function of guest–host molar ratios in D_2O solutions.

^{13}C NMR ($CDCl_3$): δ 14.29, 38.46, 40.06, 41.31, 61.33, 175.06 ppm; IR (ATR): 1050, 1104, 1180, 1213, 1272, 1493, 1724, 2922 cm^{-1}. HRMS: calcd for $C_{10}H_{12}O_2S_3Na^+$: 285.00536, found 285.00435.

The above 2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane-7-carboxylic acid ethyl ester product (175 mg, 0.66 mmol) was dissolved in 2 mL of a 3:3:1 tetrahydrofuran: methanol:water mixture and added to $LiOH{\cdot}H_2O$ (140 mg, 6.6 mmol) in a 10-mL pear-shaped flask connected to a reflux condenser. The reaction mixture was stirred at room temperature for 1 h, refluxed for 15 min, and then allowed to cool to ambient temperature, diluted with water (2 mL), and acidified to pH $\sim$ 2 with HCl (6 M). The formation of a precipitate was completed overnight in a 5°C refrigerator. Filtration and high-vacuum drying overnight afforded a light yellow solid (140 mg, 90% yield).

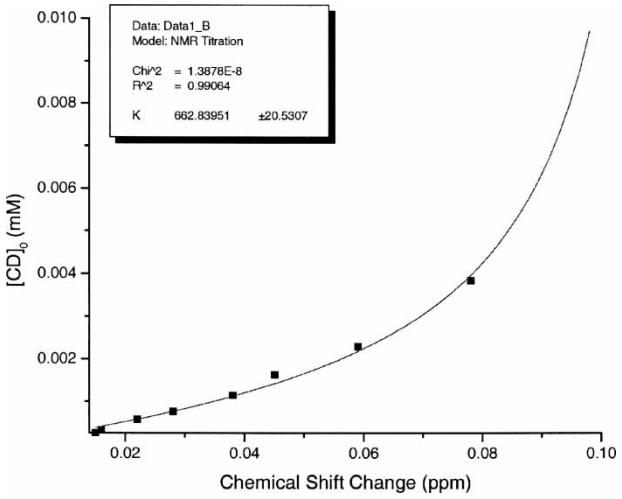


FIGURE 7 Determination of the guest–host association constant K from NMR titration.

Mp 235–237°C; ^1H NMR ($(CD_3)_2CO$): δ 2.82 (1 H, broad, OH, s), 2.88 (6 H, CH_2, d, $J = 3.30$ Hz), 4.49 (3 H, broad, CH, s) ppm; ^{13}C NMR ($CDCl_3$): δ 202.11, 42.09, 39.41, 38.90 ppm. IR (ATR): 826, 930, 1006, 1042, 1103, 1184, 1228, 1277, 1300, 1421, 1445, 1694, 2920, 2933, 2290–3300 cm^{-1}.

CD Study

The CD spectrum was obtained with a JASCO J-500A spectropolarimeter. The concentrations of TPCOOH and β-cyclodextrin were 10 and 11 mM, respectively, in 35% absolute ethanol and 65% doubly distilled water. The CD spectrum was recorded through a 10 mm quartz cuvet under ambient conditions. The original data were converted into a binary file and imported into the ORIGIN (Microcol™ software, Inc.) for generating the graph.

2D ^1H—^1H NOESY Experiments

The 2D ^1H—^1H NOESY [13] experiment was performed on the complex at 30°C using a Varian INOVA 400 MHz spectrometer. A $\pi/2$ pulse width of 7 μs was used along with a mixing time of 100 ms; 16 transients were collected for each of the 2×256 t_1 increments. Linear prediction was used in the F1 dimension to improve the quality of the data. The data were zero filled to a 2048×1024 data matrix before Fourier transformation. Data processing was performed using Varian VNMR software on a SUN workstation.

^1H NMR Studies

NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer at 298 K. In the NMR titration measurements, the samples were prepared by varying the ratio of TPCOOH to β-cyclodextrin in D_2O [$(1 - 10) \times 10^{-3}$ M]. The NMR samples were allowed to mix thoroughly and equilibrate overnight in NMR tubes before the spectra were acquired.

Titration and Calculation of the Stability Constant *K*

The NMR titration of the association constant of the inclusion complex was carried out in D_2O at 20°C. The NMR samples were prepared from a stock solution of TPCOOH in acetone (1.15 mM). The TPCOOH solution (0.700 mL) was placed in a set of NMR tubes using a micropipet and the solvent acetone was subsequently evaporated under vacuum. The solutions of β-cyclodextrin were prepared in hot D_2O and cooled to room temperature before being transferred to the NMR tube by micropipet. The NMR samples were sonicated and allowed to mix thoroughly. The final volumes of the NMR samples were 0.700 mL. ^1H NMR

TABLE II Chemical shifts of TPCOOH and the corresponding changes in H_a and H_b of TPCOOH as a function of concentration of β-cyclodextrin in D_2O

[β-CD] (mM)	0	0.26	0.33	0.58	0.77	1.15	1.64	2.30	3.84	11.5	23.0
δ_{Ha} (ppm)	4.487	4.502	4.503	4.509	4.515	4.525	4.532	4.546	4.565	4.602	4.602
δ_{Hb} (ppm)	2.841	2.845	2.843	2.851	2.854	2.862	2.866	2.870	2.876	2.907	2.907
$\Delta\delta_{Ha}$ (ppm)	0	0.015	0.016	0.022	0.028	0.038	0.045	0.059	0.078	0.115	0.115
$\Delta\delta_{Hb}$ (ppm)	0	0.004	0.002	0.010	0.013	0.021	0.025	0.029	0.035	0.066	0.066

spectra of the samples were recorded and the chemical shifts of H_a and H_b of β-cyclodextrin are summarized in Table II.

The concentrations of β-cyclodextrin ($[\beta\text{-CD}]_0$) in the samples were plotted against the chemical shift changes (δ_i) of H_a and H_b of TPCOOH (Fig. 7). The binding constant K was determined through non-linear curve fitting according to Eq. (2), derived from Conners' method as outlined below.

$$G + H \rightleftharpoons GH$$

$$K = \frac{[GH]}{[G][H]}$$

	$[G]$		$[H]$		$[GH]$
Initial	$[G]_0$		$[H]_0$		0
Equilibrium	$[G]_0$	−	$[H]_0$	−	$[GH]$
m	$[GH]$		$[GH]$		

(3)

$$K = \frac{[GH]}{([G]_0 - [GH])([H]_0 - [GH])} \quad (4)$$

$$\frac{1}{K} = \frac{[G]_0[H]_0}{[GH]} - [G]_0 - [H]_0 - [GH]$$

Because [14]

$$\delta_{obs} = \frac{\delta_G[G] + \delta_{GH}[GH]}{[G]_0} \quad (5)$$

$$[GH] = \frac{[G]_0\delta_i}{\delta_c}; \quad \delta_i = \delta_{obs} - \delta_G \text{ and } \delta_c = \delta_{GH} - \delta_G \quad (6)$$

From Eqs. (4) and (6):

$$[H]_0 = \frac{\frac{1}{K} - [G]_0\left(\frac{\delta_i}{\delta_c} - 1\right)}{\frac{\delta_c}{\delta_i} - 1}$$

SUPPORTING INFORMATION

Spectra and crystallographic data of the compounds discussed here are available from the authors on request.

Acknowledgements

We thank the National Science Foundation (DMR0210508) and National Institute of Health (DK61316-01) for financial support and also the National Science Foundation (CHE-9977144 and CHE-8808587) for funds used to purchase the NMR instruments used in this work. J.H. thanks the University of Akron Research Foundation for a startup grant and a faculty research fellowship.

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