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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

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Ying Chen^a; Ping Xiang^a; Gang Li^a; Hui-Lan Chen^a; Kandasamy Chinnakali^b; Hoong-Kun Fun^b

^a Department of Chemistry, Coordination Chemistry Institute and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, People's Republic of China ^b X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Malaysia

Online publication date: 29 October 2010

To cite this Article Chen, Ying , Xiang, Ping , Li, Gang , Chen, Hui-Lan , Chinnakali, Kandasamy and Fun, Hoong-Kun(2002) 'Crystal Structure Investigations of Inclusion Complexes Between β -cyclodextrin and Alkyl(aqua)cobaloximes (Alkyl=Butyl, Hexyl and Cyclohexyl)', *Supramolecular Chemistry*, 14: 4, 339 – 346

To link to this Article: DOI: 10.1080/10610270290029317

URL: <http://dx.doi.org/10.1080/10610270290029317>

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Crystal Structure Investigations of Inclusion Complexes Between β -cyclodextrin and Alkyl(aqua)cobaloximes (Alkyl=Butyl, Hexyl and Cyclohexyl)

YING CHEN^a, PING XIANG^a, GANG LI^a, HUI-LAN CHEN^{a,*}, KANDASAMY CHINNAKALI^b and HOONG-KUN FUN^b

^aDepartment of Chemistry, Coordination Chemistry Institute and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China; ^bX-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

(Received 28 March 2001; Revised 7 June 2001; In final form 11 July 2001)

The crystal and molecular structures of alkylcobaloxime/ β -cyclodextrin (β -CD) inclusion complexes: butyl(aqua)cobaloxime/ β -CD (1), hexyl(aqua)cobaloxime/ β -CD (2) and cyclohexyl(aqua)cobaloxime/ β -CD (3) were determined by X-ray diffraction analyses. Crystal data for 1·14H₂O: $P2_12_12_1$, $a = 15.1335(3)$, $b = 18.9630(2)$, $c = 28.1545(5)$ Å, $Z = 4$; 2·12H₂O: $P2_12_12_1$, $a = 15.1135(4)$, $b = 19.1477(5)$, $c = 28.2715(7)$ Å, $Z = 4$; 3·10H₂O: $P2_12_12_1$, $a = 15.6898(2)$, $b = 16.9094(2)$, $c = 28.9762(2)$ Å, $Z = 4$. The structural and conformational comparisons for the three β -CD inclusion complexes with their guest molecules as well as other CD inclusion analogs are discussed.

Keywords: β -Cyclodextrin; Alkyl(aqua)cobaloximes; Coenzyme B₁₂; Crystal structures

INTRODUCTION

Cyclodextrins (CDs) are a class of cyclic oligosaccharides consisting of six (α), seven (β) or eight (γ) α -1,4 linked D-glucopyranose units, which have been proposed to act as artificial enzymes. They contain toroidal hydrophobic cavities capable of including a variety of inorganic and organic guest species, and show regiospecificity and stereospecificity with respect to the substrate and product during catalytic processing.^[1–3]

Alkylcobaloxime [RCo(DH)₂L, where DH=dimethylglyoxime, R=alkyl, L=neutral monodentate axial ligand], which contains a σ -type alkyl–metal bond and a flexible equatorial ligand, is a model

compound for the extensively studied coenzyme B₁₂ (5'-deoxyadenosylcobalamin, AdoCbl).^[4–6] It is now widely recognized that the key steps of these B₁₂-dependent 1,2-rearrangement reactions are initiated by homolysis of the Co–C bond to produce a 5'-deoxyadenosyl radical (Ad^o).^[7] It has been suggested that the enzymes are likely to induce conformational changes of the corrin ligand and cause steric interactions between the axial and equatorial ligands, thus leading to a weakening of the Co–C bond.^[8,9] The rate of Co–C bond cleavage in the holoenzyme complex is estimated to be at least 10¹² times faster than in the enzyme-free AdoB₁₂.^[10–13] Therefore, investigations of B₁₂ holoenzyme models have attracted more and more attention.^[14–17] Recently, alkyl(aqua)cobaloxime/CD inclusion complexes, an interesting B₁₂ artificial enzyme, were prepared and characterized by our research group.^[18–25] 1D and 2D NMR studies revealed that the organocobalt complexes associate with cyclodextrins via non-covalent interactions forming 1:1 adducts with stabilities that are dependent on both the length and the size of the R group.^[19] Generally, the crystals of cyclodextrin inclusion complexes suitable for X-ray analysis are difficult to be obtained. Since the first β -CD complex with potassium acetate^[26] was reported in 1965, only about a hundred crystalline complexes have been published.^[27,28] The crystal structures of cyclodextrin inclusion complexes for organometallic compounds are even fewer, some examples are [Rh(cod)(NH₃)₂/β-CD]^[29] and Ferrocene/α-CD^[30]. There is also no report for the light sensitive

*Corresponding author. E-mail: hlchen@nju.edu.cn

organometallic compounds. In our former study, the crystal structures of some alkylcobaloxime/cyclodextrin inclusion complexes have been determined.^[22–25] The results are consistent with that of solution NMR investigations.^[18–21] That is, the alkyl group of the guest molecule inserts into the hydrophobic cavity of CD, while the equatorial moiety of the cobaloxime is located near the wider opening of the truncated cone-shaped CD. It is interesting to note that some bond distances, bond angles around the cobalt and bending angles of the equatorial DH ligand are changed in the *n*-C₃H₇-Co(DH)₂H₂O/ α -CD.^[22] Furthermore, distortions induced by inclusion of α -CD are somewhat different from those in β -CD derivative of isobutylcobaloxime.^[23] However, the influence of different alkyl groups on structural and conformational changes of the alkylcobaloximes is still unknown. In order to further understand the influence of the length and bulk of the alkyl groups to these structures, we prepared three new β -CD inclusion complexes, *n*-C₄H₉Co(DH)₂H₂O/ β -CD **1**, *n*-C₆H₁₃Co(DH)₂H₂O/ β -CD **2**, and *c*-C₆H₁₁Co(DH)₂H₂O/ β -CD **3**, in which the guest molecules have longer carbon chains or bulkier R groups. Here we report their crystal and molecular structures. The structural and conformational comparisons for the three β -CD complexes with their guests as well as other analogs are also discussed.

EXPERIMENTAL SECTION

All chemicals used were of analytical reagent grade. β -CD was supplied by Nanjing Food Ferment Institute. It was recrystallized twice from distilled water and then dried in vacuum at 80°C before use.

RCo(DH)₂H₂O was prepared by the method described by Toscano *et al.*^[31]

n-C₄H₉Co(DH)₂H₂O

EA Found: C, 38.02; H, 6.90; N, 14.04%. Calcd for C₁₂H₂₇N₄O₆Co: C, 37.70; H, 7.12; N, 14.65%. ¹H NMR (D₂O, 500 MHz): δ (ppm) for *n*-C₄H₉: 0.77 (5H, m, CH₂CH₃), 1.16 (2H, m, CH₂), 1.76 (2H, t, CH₂); for Co(DH)₂ 2.23 (12H, s, CH₃).

n-C₆H₁₃Co(DH)₂H₂O·C₂H₅OH

EA Found: C, 44.03; H, 7.65; N, 13.15%. Calcd for C₁₆H₃₅N₄O₆Co: C, 43.83; H, 7.99; N, 12.79%. ¹H NMR (D₂O, 500 MHz): δ (ppm) for *n*-C₆H₁₃: 0.81 (5H, m, CH₂CH₃), 1.18 (6H, m, CH₂CH₂CH₂), 1.77 (2H, m, CH₂); for Co(DH)₂ 2.24 (12H, s, CH₃).

c-C₆H₁₁Co(DH)₂H₂O

EA Found: C, 43.55; H, 6.82; N, 13.95%. Calcd for C₁₄H₂₇N₄O₅Co: C, 43.08; H, 6.97; N, 14.35%. ¹H NMR (D₂O, 500 MHz): δ (ppm) for *c*-C₆H₁₁: 0.84 (2H, m, CH₂), 1.08 (2H, m, CH₂), 1.27 (2H, m, CH₂), 1.40 (4H, m, 2CH₂), 2.29 (1H, m, CH); for Co(DH)₂ 2.24 (12H, s, CH₃).

RCo(DH)₂H₂O/ β -CD was prepared by dissolving RCo(DH)₂H₂O and β -CD in 1:1 molar ratio in water. After stirring the mixture for 30 min at 50°C, it was filtered and the filtrate was stored at 25°C in the dark. One week later, brown crystals were obtained.

n-C₄H₉Co(DH)₂H₂O/ β -CD **1**

Yield 52%, EA Found: C, 41.65; H, 6.66; N, 3.57%. Calcd for C₅₄H₉₇N₄O₄₁Co: C, 41.28; H, 6.61; N, 3.57%. ¹H NMR (D₂O, 500 MHz): δ (ppm) for *n*-C₄H₉: 0.78 (5H, m, CH₂CH₃), 1.17 (2H, m, CH₂), 1.85 (2H, t, CH₂); for Co(DH)₂: 2.29 (12H, d, CH₃); for β -CD: 3.57 (7H, t, H-4), 3.64 (7H, dd, H-2), 3.75 (7H, m, H-5), 3.86–3.90 (21H, m, H-3, H-6), 5.08 (7H, d, H-1).

n-C₆H₁₃Co(DH)₂H₂O/ β -CD **2**·2H₂O

Yield 57%, EA Found: C, 42.46; H, 6.60; N, 3.61%. Calcd for C₅₆H₁₀₃N₄O₄₂Co: C, 43.02; H, 6.64; N, 3.58%. ¹H NMR (D₂O, 500 MHz) δ (ppm) for *n*-C₆H₁₃: 0.78 (5H, m, CH₂CH₃), 1.20 (6H, m, CH₂CH₂CH₂), 1.84 (2H, m, CH₂); for Co(DH)₂: 2.38 (12H, d, CH₃); for β -CD: 3.60 (7H, t, H-4), 3.65 (7H, m, H-2), 3.71 (7H, m, H-5), 3.82–3.85 (21H, m, H-3, H-6), 5.08 (7H, d, H-1).

c-C₆H₁₁Co(DH)₂H₂O/ β -CD **3**

Yield 50%, EA Found: C, 40.56; H, 7.02; N, 3.52%. Calcd for C₅₆H₁₁₃N₄O₄₈Co: C, 40.29; H, 6.82; N, 3.36%. ¹H NMR (D₂O, 500 MHz) δ (ppm) for *c*-C₆H₁₁: 0.88 (2H, m, CH₂), 0.91 (2H, m, CH₂), 1.28 (2H, m, CH₂), 1.48 (2H, m, CH₂), 1.54 (2H, m, CH₂), 2.38 (1H, m, CH); for Co(DH)₂: 2.32 (12H, d, CH₃); for β -CD: 3.55 (7H, t, H-4), 3.66 (7H, dd, H-2), 3.76 (7H, m, H-5), 3.85–3.88 (21H, m, H-3, H-6), 5.05 (7H, d, H-1).

It can be seen that after formation of the β -CD inclusion complexes, the proton resonances of the R ligands are shifted by different extents. The chemical shifts of the methyl groups in the equatorial ligand move downfield and the singlet resonance is split into a doublet. From the integrated signal areas, the molar ratios of RCo(DH)₂H₂O to β -CD are 1:1. These suggest that 1:1 RCo(DH)₂H₂O/ β -CD inclusion complexes were formed in the aqueous solution.

TABLE I Crystallographic data for 1·14H₂O, 2·12H₂O, and 3·10H₂O

	1·14H ₂ O	2·12H ₂ O	3·10H ₂ O
Empirical formula	C ₅₄ H ₁₂₃ CoN ₄ O ₅₄	C ₅₆ H ₁₂₃ CoN ₄ O ₅₂	C ₅₆ H ₁₁₇ CoN ₄ O ₅₀
Formula weight	1725.79	1719.32	1705.47
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
A (Å)	15.1335(3)	15.1135(4)	15.6898(2)
B (Å)	18.9630(2)	19.1477(5)	16.9094(2)
C (Å)	28.1545(5)	28.2715(7)	28.9762(2)
V (Å ³)	8079.7(2)	3738.2(1)	7687.53(14)
Z	4	4	4
D _c (g cm ⁻³)	1.419	1.396	1.474
μ (mm ⁻¹)	0.323	0.317	0.335
F(000)	3634	3624	3632
Crystal size	0.46 × 0.18 × 0.08	0.44 × 0.26 × 0.18	0.46 × 0.40 × 0.08
θ range (deg)	2.59 to 30.00	2.62 to 27.50	2.74 to 27.50
Limiting indices	-21 ≤ h ≤ 21, 0 ≤ k ≤ 26, 0 ≤ l ≤ 39	-23 ≤ h ≤ 22, -29 ≤ k ≤ 16, -37 ≤ l ≤ 42	-20 ≤ h ≤ 20, 0 ≤ k ≤ 21, 0 ≤ l ≤ 37
Reflections collected	60139	53752	50554
Independent reflections	22866 [R _{int} =0.104]	18737 [R _{int} =0.103]	17574 [R _{int} =0.074]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	22865:4:938	18712:6:984	17564:0:1135
Goodness-of-fit on F ²	1.07	1.062	1.08
Final R indices [I > 2σ(I)]	R1 = 0.106 wR = 0.225	R1 = 0.0807 wR = 0.1852	R1 = 0.058, wR = 0.087
R indices (all data)	R1 = 0.223, wR = 0.286	R1 = 0.1412 wR = 0.2246	R1 = 0.111, wR ₂ = 0.105
Absolute structure parameter	0.00(3)	-0.01(2)	-0.001(13)
Largest diff. peak and hole (eÅ ⁻³)	0.71 and -0.66	0.608 and -0.353	0.33 and -0.28

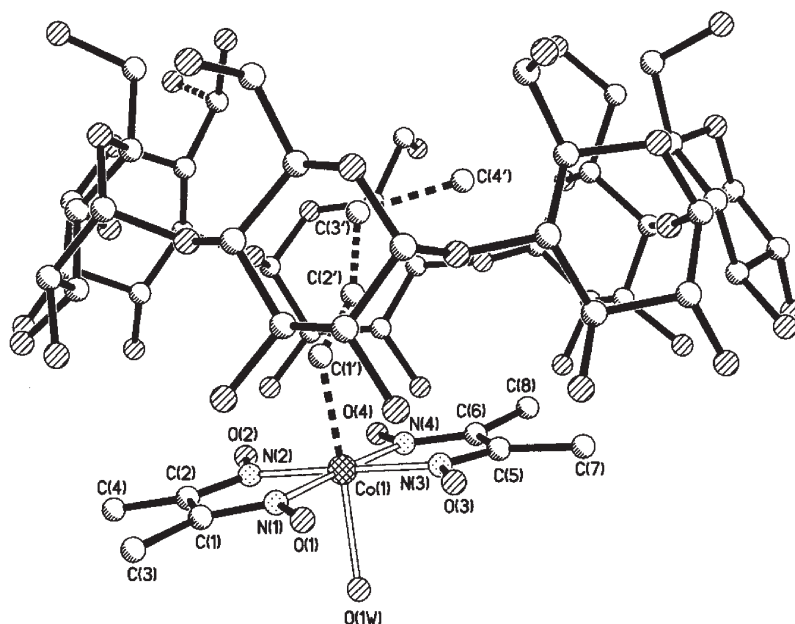


FIGURE 1 Structure and numbering scheme of $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ (1) in $1\cdot 14\text{H}_2\text{O}$.

Crystallography

Reflection data for all crystals were measured at 20°C with a Bruker 1K CCD SMART diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a detector distance of 4 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle ($0, 88, 180^\circ$) and each exposure of 30 s covered 0.3° in ω . The collected data were reduced by using the program SAINT^[32] and empirical absorption correction was done by using the SADABS^[33] program.

All the structures were solved by direct methods and refined by least squares method on $F_{\text{obs}}^4\text{--}6$ by using the SHELXTL^[34] software package. Except for

the water oxygen atoms, all non-hydrogen atoms were anisotropically refined. Also, except for hydrogen atoms at OH groups of **3** and the water hydrogen atoms, all the hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. The molecular graphics were created using SHELXTL. Crystallographic data for all structures are listed in Table I.

RESULTS AND DISCUSSION

The crystal structures of $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}$, $n\text{-C}_6\text{H}_{13}\text{Co}(\text{DH})_2\text{H}_2\text{O}$ and $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DH})_2\text{H}_2\text{O}$ have been determined and given as supplementary material.

The molecular structures of $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ **1** in $1\cdot 14\text{H}_2\text{O}$, $n\text{-C}_6\text{H}_{13}\text{Co}(\text{DH})_2\text{H}_2\text{O}$ **2** in $2\cdot 12\text{H}_2\text{O}$ and $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ **3** in $3\cdot 10\text{H}_2\text{O}$ are described in Figs. 1–3, respectively. Selective bond lengths and bond angles are listed in Table II.

It has been found that from the cell packing diagram (see Figs. S1 and S2) that the lattice water molecules link the host/guest complexes into a three-dimensional network. Hydrogen bonds are formed in the individual complexes through coordination with water molecules or OH groups at the wider opening of the CDs, which stabilizes these host/guest inclusion complexes. It has been also found that the three title $\beta\text{-CD}$ inclusion complexes have similar crystallography structures, i.e. all of alkyl groups insert into the cyclodextrin's cavities from the wider opening and $\text{Co}(\text{DH})_2\text{H}_2\text{O}$ units are found outside of the cavities. However, differences

TABLE II Selected bond lengths (\AA) and angles ($^\circ$) for three $\beta\text{-CD}$ complexes

	1·14H ₂ O	2·12H ₂ O	3·10H ₂ O
Co–N(1)	1.880(6)	1.885(5)	1.879(3)
Co–N(2)	1.869(6)	1.883(5)	1.890(3)
Co–N(3)	1.881(6)	1.889(5)	1.877(3)
Co–N(4)	1.873(6)	1.874(5)	1.895(3)
Co–C(1')	2.010(8)	2.011(7)	2.048(3)
Co–O(1W)	2.106(5)	2.110(4)	2.140(3)
N(1)–Co–C(1')	89.8(3)	91.3(3)	94.53(14)
N(2)–Co–C(1')	89.8(4)	91.3(3)	92.6(2)
N(3)–Co–C(1')	90.9(4)	90.3(3)	90.9(2)
N(4)–Co–C(1')	92.5(3)	88.7(3)	89.4(2)
N(1)–Co–O(1W)	87.2(2)	90.9(2)	86.71(13)
N(2)–Co–O(1W)	88.3(2)	90.9(2)	88.5(2)
N(3)–Co–O(1W)	91.0(2)	87.5(2)	87.89(14)
N(4)–Co–O(1W)	90.5(2)	89.1(2)	89.5(2)
C(1')–Co–O(1W)	176.7(3)	177.0(3)	178.46(14)
C(2')–C(1')–Co	122.3(13)	122.0(9)	114.2(3)

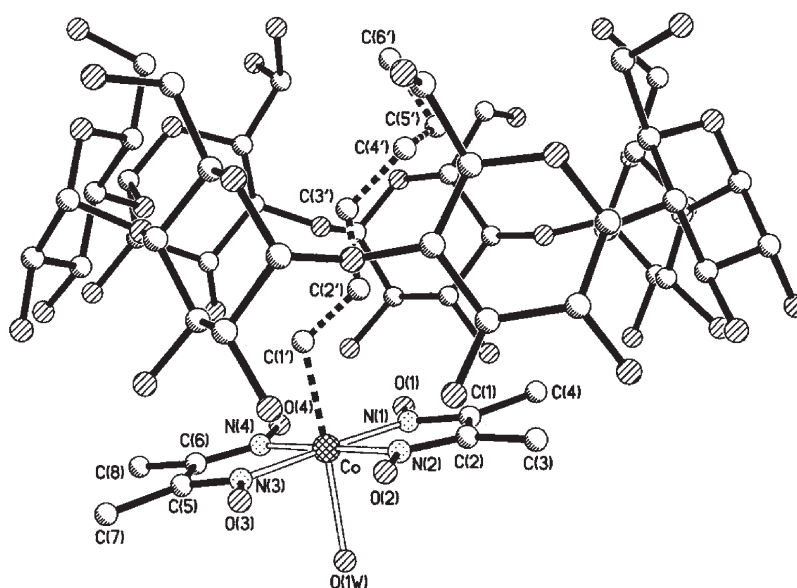


FIGURE 2 Structure and numbering scheme of $n\text{-C}_6\text{H}_{13}\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ (2) in $2\cdot 12\text{H}_2\text{O}$.

are observed among them through their various axial R groups of the organometallic guest compounds. Data for the structural parameters of 1–3 with their uncomplexed alkylcobaloxime are shown in Table III.

Comparisons are made between the three title inclusion complexes and their uncomplexed guest compounds. It has been found that the Co–C bond lengths in the present three $\beta\text{-CD}$ inclusion complexes are almost the same as the values in the uncomplexed guest molecules, while the Co–O bonds are much longer than those in the uncomplexed ones (~ 0.02 Å longer for $R=n\text{-C}_4\text{H}_9$, ~ 0.07 Å

for $R=n\text{-C}_6\text{H}_{13}$, and ~ 0.04 Å for $R=c\text{-C}_6\text{H}_{11}$, respectively). In addition, for the $n\text{-C}_4\text{H}_9\text{Co}(\text{DH})_2\text{H}_2\text{O}$ guest molecule, after insertion of the butyl group into the $\beta\text{-CD}$ cavity, there is a slight displacement (0.026 Å) of the cobalt atom from the mean plane of the four nitrogen atoms (see d values in Table III). Although no Co–C bond lengthening could be detected in the inclusion complex, the displacement of the Co atom from the 4N plane implies the relaxation of the Co–C bond to some extent.^[22] For $n\text{-C}_6\text{H}_{13}\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ and $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$, although the lengthening of Co–O bonds also could be observed after the formation of inclusion complexes,

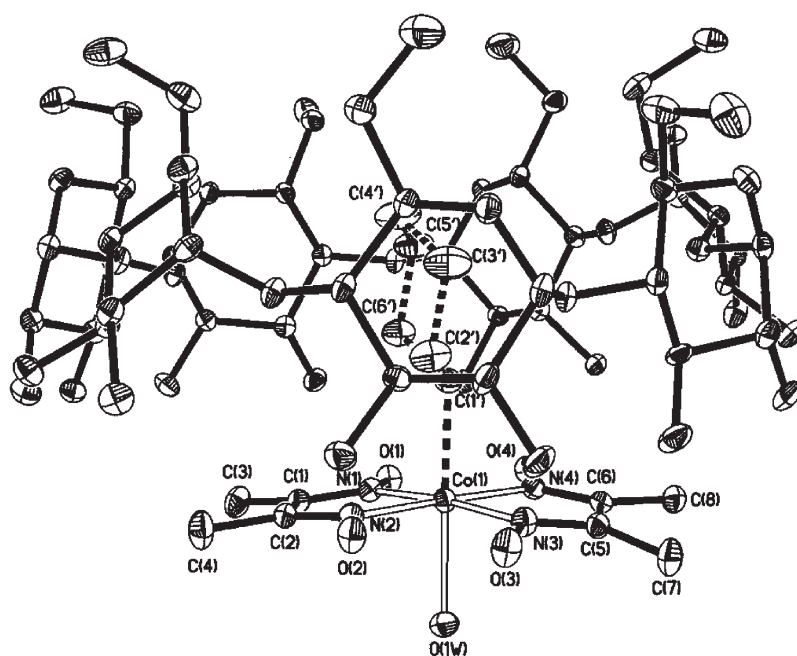


FIGURE 3 Structure and numbering scheme of $\text{Co}(\text{DH})_2\text{H}_2\text{O}/\beta\text{-CD}$ (3) in $3\cdot 10\text{H}_2\text{O}$.

TABLE III Comparison of structural parameters for the RCo(DH)₂H₂O and their CD inclusion complexes (R=acyclic and cyclic alkyls, We did not list the data for *i*-C₄H₉Co(DH)₂H₂O since there are three crystallographically independent molecules in the asymmetric unit)

	Co-C (Å)	Co-O (Å)	α (°)	<i>d</i> (Å)	<i>D</i> ₁ (Å)	<i>D</i> ₂ (Å)
<i>n</i> -C ₃ H ₇ Co(DH) ₂ H ₂ O/ α -CD*	2.013(4)	2.083(2)	10	0.038	-0.28	2.05
<i>n</i> -C ₃ H ₇ Co(DH) ₂ H ₂ O*	2.008(8)	2.063(4)	1	0.008		
<i>i</i> -C ₄ H ₉ Co(DH) ₂ H ₂ O/ α -CD†	2.016(4)	2.159(3)	9	0.024	-0.58	1.66
<i>i</i> -C ₄ H ₉ Co(DH) ₂ H ₂ O/ β -CD‡	2.017(4)	2.104(2)	4	0.016	0.04	1.83
<i>n</i> -C ₄ H ₉ Co(DH) ₂ H ₂ O/ α -CD‡	2.011(4)	2.148(3)	6	0.004	-0.66	2.47
<i>n</i> -C ₄ H ₉ Co(DH) ₂ H ₂ O/ β -CD	2.010(8)	2.106(5)	5	0.026	0.12	3.12
<i>n</i> -C ₄ H ₉ Co(DH) ₂ H ₂ O [¶]	2.011(2)	2.081(1)	3	0.001		
<i>n</i> -C ₆ H ₁₃ Co(DH) ₂ H ₂ O/ β -CD	2.011(7)	2.110(4)	4	0.014	0.02	5.15
<i>n</i> -C ₆ H ₁₃ Co(DH) ₂ H ₂ O [¶]	2.005(3)	2.038(2)	2	0.007		
<i>c</i> -C ₆ H ₁₁ Co(DH) ₂ H ₂ O/ β -CD	2.048(3)	2.140(3)	12	0.060	0.05	2.86
<i>c</i> -C ₆ H ₁₁ Co(DH) ₂ H ₂ O (a) [¶]	2.045(7)	2.103(5)	14	0.063		
<i>c</i> -C ₆ H ₁₁ Co(DH) ₂ H ₂ O (b) [¶]	2.040(8)	2.100(5)	12	0.059		

* Ref. [22]. † Ref. [23]. ‡ Ref. [25]. ¶ See supplementary information.

d values, i.e. the displacement of the cobalt atom from the mean plane of the four nitrogen atoms, are almost not changed. Therefore there is no evidence of pulling Co atom from four nitrogen plane in 2 and 3.

Comparing the structures of 1–3 with our previously reported α -CD inclusion complexes.^[22–25] it has been found that (a) there is no obvious changes in the bending angles α of the two DH units (see Table III) in the present inclusion complexes compared to those of guest alone, while in our previously reported *n*-C₃H₇Co(DH)₂H₂O/ α -CD [22] and *i*-C₄H₉Co(DH)₂H₂O/ α -CD,^[23] the changes of α values are significant. Furthermore, in the present three β -CD inclusion complexes, the distance between the terminal carbon of the R group and the plane composed of secondary OH groups of CD, *D*₂, are all positive and their values increased with the alkyl chain lengthening. The longer alkyl group penetrates into the cavity of CD more deeply and causes stronger van der Waals forces and hydrophobic interactions, which have been generally accepted to be responsible for binding of guest molecules to the CD cavity.^[35,36] Thus, rather stable inclusion complexes could be formed with no significant bending angle changes. This is consistent with the result of our thermodynamic study in solution,^[19] that is, the longer the alkyl chain is, the larger the formation constant between β -CD and alkyl(aqua)cobaloxime. (b) It can be seen from Table III that the distance between the α -carbon atom of the R group, which is connected to the cobalt atom

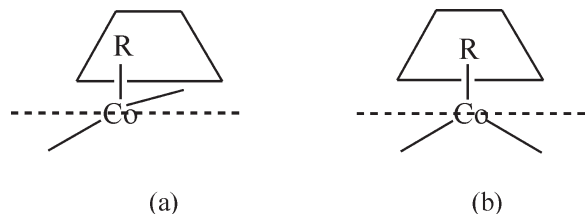


FIGURE 4 Orientation of RCo(DH)₂H₂O to β -CD: (a) R=*n*-C₄H₉ and *n*-C₆H₁₃; (b) R=*c*-C₆H₁₁.

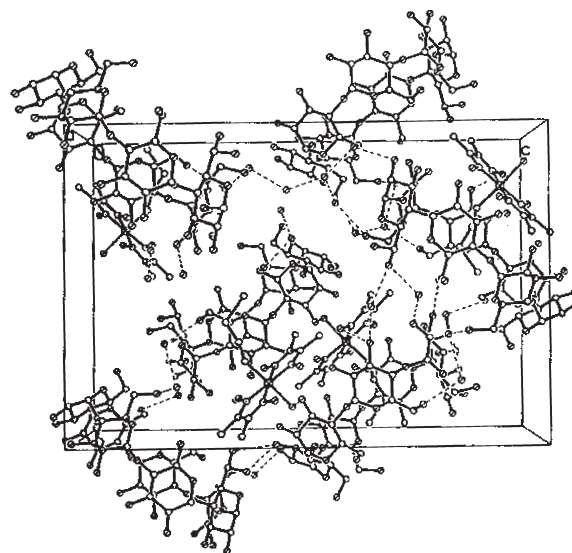


FIGURE S1 Stereodrawing of the packing of *n*-C₄H₉Co(DH)₂H₂O/ β -CD (1) in 1.14H₂O.

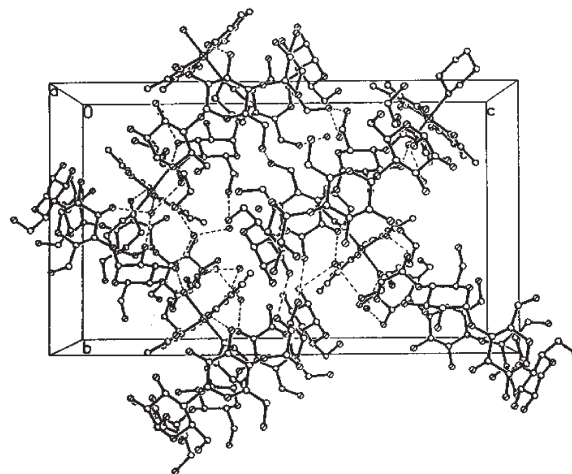


FIGURE S2 Stereodrawing of the packing of *c*-C₆H₁₁Co(DH)₂H₂O/ β -CD (3) in 3.10H₂O.

directly, and the plane composed of the secondary OH groups of CD, the D_1 value, are positive for all β -CD inclusion complexes. This means, the α -carbon atom of the R group inserts into the cavity of β -CD. However in all α -CD inclusion complexes, the negative D_1 values indicate that all α -carbon atoms are outside the CD's cavity. This might be due to the different cavity diameters of the α -CD (4.7–5.2 Å) and β -CD (6.0–6.4 Å). It has been proposed that CD inclusion complexes are only formed if there is a tight spacial fit between guest and host components.^[37] The deeper the alkyl group inserts, the stronger the binding force is obtained. However, the steric interactions between the Co(DH)₂ plane and the hydroxyl groups at the wider opening of cyclodextrin hinders the insertion of the alkyls. As in the case of α -CD, the steric interactions between its smaller rim and Co(DH)₂ unit causes the R group from the guest to be unable to insert into the cavity of α -CD as deeply as of the β -CD. In fact, as mentioned above, more structural and conformational changes of the guest were observed in α -CD complexes.

According to the X-ray analysis, asymmetric bending of the two DH planes with respect to β -CD can be observed in n -C₄H₉Co(DH)₂H₂O/ β -CD and n -C₆H₁₃Co(DH)₂H₂O/ β -CD. That is, one DH plane bends away from β -CD, while the other bends toward the rim of β -CD (see Fig. 4a). This orientation is same as the one in our previously reported i -C₄H₉Co(DH)₂H₂O/ β -CD [24]. While for the c -C₆H₁₁Co(DH)₂H₂O derivative, its β -CD complex presents a symmetric bending mode for the two DH planes (see Fig. 4b), a different manner from **1**, **2** and other alkylcobaloxime/ β -CD inclusion complexes. It is presumed that such an orientation could make the bulkier cyclohexyl group fit into the β -CD's cavity more snugly and almost no structural distortion for the guest molecule would have occurred (see α and d values in Table III).

CONCLUSION

This work provided new structural information about inclusion complexes of β -CD and organocobalt B₁₂ models. Crystal structure analysis of **1–3** and comparison of them with uncomplexed alkylcobaloximes and/or other alkylcobaloxime/cyclodextrin inclusion complexes have shown that there are different structural and conformational changes of the guest compounds after inclusion. This depends on the length and bulk of the alkyl group in the alkylcobaloxime as well as the cavity diameter of the cyclodextrin. It is concluded that the more suitable the fit of the R group into the cyclodextrin cavity, the less the structural and conformational changes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 29823001 and 20071017), the Research Found for the Doctoral Program of Higher Education, China (No. 2000028401), and the Malaysian Government research grant R&D (No. 190-9609-2801). K.C. thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Fellowship and Anna University, India, for his sabbatical leave.

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