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Short Communication

Crystal Structure of a Molecular Complex from Native β-Cyclodextrin and Copper(II) Chloride

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Reaction of β-cyclodextrin (β-CD) with $CuCl_2$ in neutral aqueous solutions gave a stable molecular complex without any side-arm support. The X-ray crystallographic analysis clarified that the copper ion was located at the bottom of the primary-hydroxy side as a $CuCl_2(H_2O)_2$ form. Hydrogen bonds were found between the Cl and H_2O ligands and β-CD hydroxy and ether groups. The copper ion is axially coordinated with a hydroxy group of a neighboring β-CD molecule, giving a one-dimensional β-CD/$CuCl_2$ array.

Keywords: β-Cyclodextrin; Copper(II) ion; Molecular complex; Coordination compound

Cyclodextrins (CDs; see Scheme 1 for β-CD) have been extensively studied for the development of catalysts and enzyme mimics [1–3]. There are several reports on CD-based catalysts for hydrolysis and hydrogenesis in the presence of transition metal ions [4–6]. These catalytic centers are usually coordinated with N-, O-, or P-donor side-arms in artificial CDs [7]. Complexes containing native CDs and simple inorganic molecules (iodine [8,9] for example) are very rare. Recently, complex formation between copper(II) and β-CD in basic solutions has been studied from the equilibrium constants point of view [10]. The deprotonated CDs can coordinate copper(II) and manganese(III) ions at high pHs [11,12] and the peculiar crystal structures of multinuclear copper(II) and lead(II) complexes have been characterized including β- and γ-CD polyanions as polydentate ligands [13,14]. To the best of our knowledge, however, there is no report on stable complexes consisting of neutral CDs and transition metal salts without any side-arm support. We report here the crystal structure of a β-CD/$CuCl_2$ complex, in which the intact β-CD plays a role in both the hydrogen-bond frame and O-donating ligand.

β-CD (238 mg, 0.21 mmol) and $CuCl_2 \cdot 2H_2O$ (434 mg, 2.54 mmol) were dissolved in hot water (20 ml). The light blue solution was concentrated on warming to a small volume (*ca.* 2 ml), and the resultant green solution was allowed to stand for a week. The precipitated light blue plates were separated on a filter, washed with a small amount of water and immediately used for further analysis. The yield was 96.9 mg (33%). The elemental analysis, magnetic susceptibility measurements, and X-ray crystallographic analysis indicated that the $CuCl_2$/β-CD ratio was typically 0.5–0.6 and could not be raised to unity in spite of the synthetic efforts. The elemental analysis (C, H, N) of the adduct on a Fisons EA-1108 by a usual combustion method suggests the following composition: Anal. Calcd for β-CD·$(CuCl_2)_{0.55} \cdot (H_2O)_{10}$: C, 36.31; H, 6.53%. Found: C, 35.79; H, 6.42%. Magnetic properties of the β-CD/$CuCl_2$ adduct were measured on a Quantum Design MPMS SQUID magnetometer. The temperature dependence of the magnetic susceptibility obeyed the Curie law ($\chi = C/T$). The observed Curie constant of $1.80 \times 10^{-4}\,cm^3\,K\,g^{-1}$ agrees well with the proposed formula containing 0.55 moles of copper(II) spins of $S = 1/2$ and $g = 2.2$.

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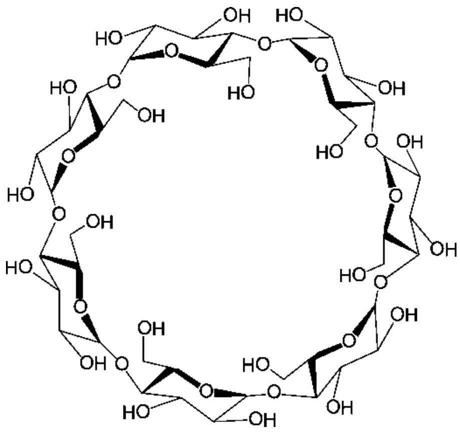

SCHEME 1 Molecular structure of β-CD.

X-Ray diffraction data were collected on a Rigaku RAPID IP diffractometer using graphite-monochromated Mo Kα radiation at 100 K. The structure was directly solved and expanded using Fourier techniques in the *CrystalStructure* program package.[†] Population analysis was applied for the $CuCl_2$ moiety, giving the occupancy of 0.545(4). The β-CD/$CuCl_2$ adduct crystallized in a monoclinic $P2_1$ space group,[‡] and the absolute configuration was manually assigned based on the known D-glucopyranose structure in the β-CD. Ten water solvate molecules were found in an asymmetric unit. The hydrogen atoms on the water molecules and hydroxy groups could not be located in the analysis.

Figure 1 shows the molecular structure of β-CD·$CuCl_2(H_2O)_2$. The copper ion is coordinated by two chloride ions at the *trans*-equatorial positions with Cu1–Cl1 and Cu1–Cl2 distances of 2.220(5) and 2.274(6) Å, respectively. Two water molecules are coordinated at the other *trans*-equatorial positions with the Cu1–O36 and Cu1–O37 distances of 1.96(1) and 2.007(6) Å, respectively. The copper ion has a saddle-type configuration. The Cl1–Cu1–Cl2 and O36–Cu1–O37 angles were 154.6(2) and 170.3(5)°, respectively, and each pair of the ligands is located in the opposite hemisphere of the copper(II) averaged equatorial plane.

The hydrophobic cavity of the β-CD could not accommodate $CuCl_2(H_2O)_2$ inside, but the $CuCl_2$ $(H_2O)_2$ group was situated at almost the center of the bottom of the primary-hydroxy side. Hydrogen bonds were found between the Cl and H_2O ligands and the β-CD hydroxy and ether groups. Since most OH hydrogen atoms could not be determined experimentally, we evaluated possible hydrogen bonds by the van der Waals contacts and close interatomic distances within 3.6 Å among the non-hydrogen atoms. As Fig. 1(b) shows, there are five endohedral water molecules (Ow38–Ow42) and three exohedral ones (Ow43–Ow45). Hydrogen bonds are suggested between the β-CD primary-hydroxy groups and the ligand water oxygen or chlorine atoms (O25–O36, O20–O36, O35–Cl2, etc.). A hydrogen-bonding network penetrates into a cavity (O37–Ow40, Ow41–Ow42–Ow39, etc.).

As the side view (Fig. 1(c)) shows, the outer axial site of the copper ion was occupied with a hydroxy group of a neighboring β-CD molecule, forming a linear polymeric chain $[\beta\text{-CD}\cdot CuCl_2(H_2O)_2]_n$ along the crystallographic *b*-axis. The Cu1–O3* distance is 2.398(6) Å and the O3*–Cu1–Cl1 and O3*–Cu1–Cl2 angles are 94.2(1) and 109.9(2)°, respectively.

Interestingly, the β-CD host alone crystallizes from an aqueous solution as the eleven-hydrated form in practically the same crystal packing motif belonging to a monoclinic $P2_1$ space group[¶] [15,16]. When we refined the occupancies of O36 and O37 independently from those of $CuCl_2$ group in the adduct, we obtained occupancies of nearly 1.0 and not 0.55. This finding implies that O36 and O37 are present irrespective of the $CuCl_2$ defect. The β-CD primary-hydroxy rim as well as the clusterized water framework seem to be preorganized for the $CuCl_2$ capping. The $CuCl_2$ group was intercalated to the rather rigid host lattice, only giving rise to slight *b*-axis elongation (3.1%) and cell volume expansion (2.7%). Actually we determined the β-CD·$(H_2O)_{11}$ molecular structure with the aid of the β-CD geometry in the β-CD/$CuCl_2$ adduct as an initial structure.

The copper(II) axial site facing inside the β-CD is vacant, which reminds us of the possibility of catalytic reactions within the β-CD chiral cavity by using the Lewis acidity of the copper(II) ion. Though the β-CD/$CuCl_2$ binding seems labile, we observed the color change during concentration of β-CD/$CuCl_2$ mother liquors which suggests an appreciable formation of a β-CD/$CuCl_2$ complex in concentrated solutions. This study may also provide a new supramolecular building block for CD-based polymeric rotaxanes [17] involving linear bridging ligands. We have investigated the reaction of $CuCl_2$ and β-CD in the presence of

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[†] *CrystalStructure*: Single Crystal Structure Analysis Software version 3.5.1, Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA, 2003.

[‡] Selected crystallographic data are: $C_{42}H_{90}O_{45}Cu_{0.55}Cl_{1.1}$, FW 1389.1, $a = 20.82(1)$, $b = 10.366(6)$, $c = 14.968(9)$ Å, $\beta = 110.12(4)°$, $V = 3033(2)$ Å^3, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.369\,\text{mm}^{-1}$, $R_{\text{int}} = 0.065$, $R(F)(I > 2\sigma(I)) = 0.078$, and $R_w(F^2)$ (all data) = 0.105 for 7749 unique reflections. All of the OH hydrogen atoms were not included in the refinement and aliphatic hydrogen atoms were located at calculated positions. CCDC reference number 231760.

[¶] The cell parameters of β-CD·$(H_2O)_{11}$ were determined under the same conditions as those of the β-CD/$CuCl_2$ adduct: $a = 20.910(6)$, $b = 10.057(3)$, $c = 14.888(5)$ Å, $\beta = 109.32(1)°$, $V = 2954(1)$ Å^3 and $R_{\text{int}} = 0.056$ at 100 K.

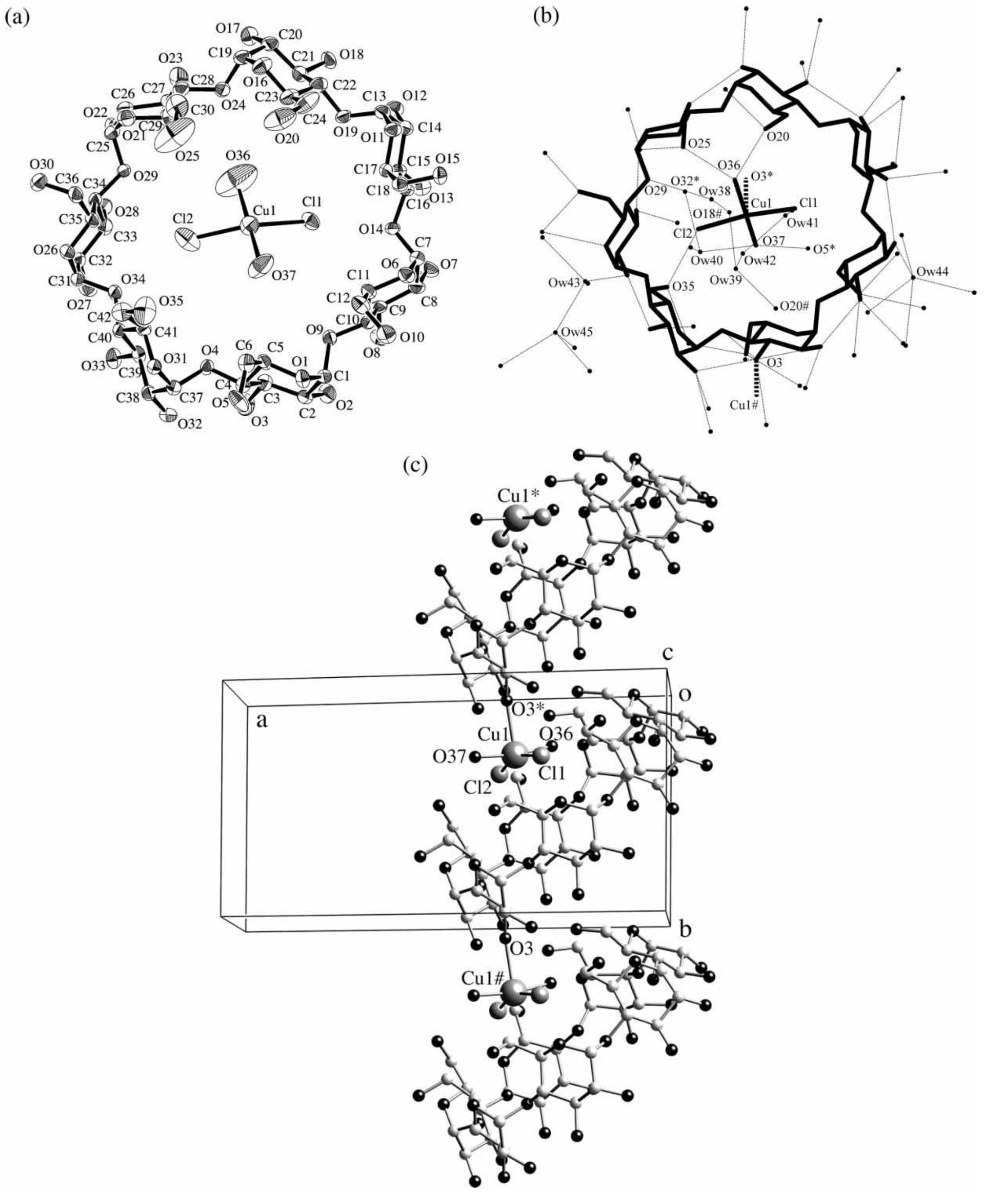

FIGURE 1 (a) ORTEP drawing of β-cyclodextrin·(CuCl$_2$)$_{0.55}$·(H$_2$O)$_{10}$ complex with the thermal ellipsoids at the 50% probability level. Uncoordinated water molecules and hydrogen atoms are omitted for clarity. (b) A stick model of β-cyclodextrin·CuCl$_2$ and water molecules (Ow36–Ow45). Selected atoms are labeled. Relatively short intermolecular O- - -O and O- - -Cl distances are indicated as thin lines. The axial coordination bonds, Cu1–O3* and O3–Cu1#, are also shown with broken lines. The symmetry operation codes for * and # are $x, y+1, z$, and $x, y-1, z$, respectively. (c) Three repeating units are shown in an infinite chain of β-cyclodextrin·CuCl$_2$(H$_2$O)$_2$ along the *b*-axis. Cu, large gray circles; Cl, middle gray circles; O, small black circles; C, small gray circles.

1,4-diazabicyclo[2.2.2]octane (DABCO) in water, but so far we have isolated only a 1/1 β-CD·DABCO inclusion complex[§] [18]. The guest DABCO seems to disturb the complexation of β-CD and CuCl$_2$ by reorganization of the hydrogen-bond frame around the β-CD primary-hydroxy bottom.

In summary, we have clarified that the reaction of β-CD with CuCl$_2$ gave the molecular complex β-CD·(CuCl$_2$)$_{0.55}$·(H$_2$O)$_{10}$, whose structure is highly isomorphous with that of β-CD·(H$_2$O)$_{11}$ [15,16]. The CuCl$_2$ moiety is hydrogen-bonded at the rim of the primary-hydroxy side; i.e., the present adduct is

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[§] Sekii, M., Ishida, T., Nogami, T., Unpublished results. X-Ray crystallographic analysis of DABCO·β-CD·(H$_2$O)$_{13}$ gave the following parameters: C$_{48}$H$_{108}$N$_2$O$_{48}$, FW 1481.3, monoclinic, $P2_1$, $a = 15.2981(4)$, $b = 16.4407(3)$, $c = 15.3985(3)$ Å, $\beta = 62.5439(7)°$, $V = 3436.7(1)$ Å^3, $Z = 2$, $\mu(\mathrm{Mo\,K\alpha}) = 0.129\,\mathrm{mm}^{-1}$, $R_{\mathrm{int}} = 0.031$, $R(F)(I > 2\sigma(I)) = 0.043$, and $R_{\mathrm{w}}(F^2)$ (all data) $= 0.068$ at $T = 100\,\mathrm{K}$ for 8155 unique reflections.

not a guest-“inclusion” compound but a novel kind of capped CD compound.

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