Complexes of Copper(II) with Cyclodextrins

Yoshihisa Matsui, Toyoaki Kurita, and Yoshio Date
Department of Agricultural Chemistry, Faculty of Agriculture, Shimane University, Nishikawazu, Matsue

(Received June 22, 1972)

It is known that a number of organic and inorganic substances are enclosed and fixed within the void spaces of cyclodextrins, thus forming inclusion compounds.[1] However, the inclusion of metal cations in the dextrins has never been studied. We wish here to report that copper(II) reacts with cyclodextrins in alkaline solutions to form soluble complexes.

When two aqueous solutions, 0.2 N NaOH and 0.02 M $CuSO_4$, of an equal volume were mixed, the precipitate of $Cu(OH)_2$ formed immediately. The supernatant was virtually colorless and contained no appreciable amount of Cu(II) (below 10^{-5} M). However, upon the addition of β-cyclodextrin (I) to the mixture, a part of the precipitate was dissolved and the supernatant became blue. The concentration of the dissolved Cu(II) was titrimetrically determined by the use of EDTA and murexide, as a titrant and an indicator respectively, after the neutralization of the supernatant by an aqueous HCl. The Cu(II) concentration determined was then plotted against the concentration of I added (Fig. 1, Plot a). It is obvious that the plot is linear with the slope of *ca.* 1.9. Similar plots were obtained in solutions more basic than 0.1 N NaOH (Fig. 1, Plots b and c), although a small amount of Cu(II) had been dissolved before the addition of I. The results indicate that Cu(II) forms a complex with I in which two Cu(II) ions are bound to a molecule of I (2 : 1 complex).

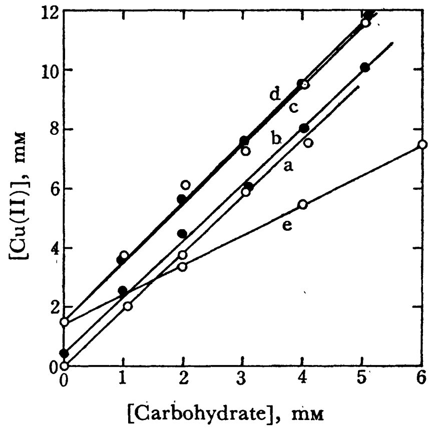

Fig. 1. Plots of the concentration of the dissolved Cu(II) *vs.* those of carbohydrates added.
a, I in 0.1 N NaOH; b, I in 0.5 N NaOH; c, I in 1 N NaOH; d, II in 1 N NaOH; e, III in 1 N NaOH

The Cu(II)-I complex was isolated from a solution. When 10 m*l* of ethanol was added to 12 m*l* of 2 N NaOH containing 0.01 M I and 0.02 M $CuSO_4$, blue crystal were precipitated; they were then filtered off, washed with aqueous ethanol, and dried *in vacuo*. The content of Cu(II) in the crystals was titrimetrically determined to be 0.59 mmol/g. The content of I was estimated to be 0.29 mmol/g by the measurement of the optical rotation of an aqueous solution of the crystals buffered at pH *ca.* 7, where the complex dissociates into I and Cu(II). In this estimation, the specific rotation of I was taken to be 162.5°.[1] The results also show the formation of the 2 : 1 Cu(II)-I complex.

The dissolution of $Cu(OH)_2$ in an alkaline solution also took place on the addition of α-cyclodextrin(II) or of methyl-α-D-glucopyranoside(III). In each case, the plot of the concentration of the dissolved Cu(II) *vs.* that of the carbohydrate added is linear (Fig. 1, Plots d and e). The slope of the plot for II was 2.0, while it was 1.0 for III. This shows that Cu(II) forms 2 : 1 and 1 : 1 complexes with II and III respectively.

The structures of the Cu(II)-I and -II complexes are presumed to be as is shown schematically in Fig. 2.

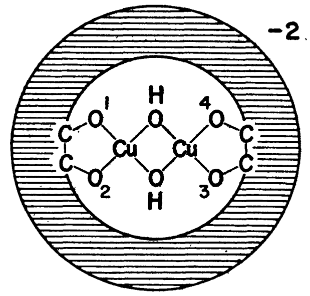

Fig. 2. Schematic structure of the Cu(II)-cyclodextrin complex.

The two pairs of C-2 and C-3 secondary hydroxyl groups of I and II may be ionized and cross-linked by the $Cu(OH)_2Cu$ ion bridge. Such a coordination of 1,2-diols to Cu(II) has often been reported to occur in alkaline solutions.[2] Since each bond length of Cu–O may be about 2 Å,[3] the distance between the oxygen atoms numbered 1 and 3 may be about 6.3 Å; this agrees well with the internal diameter (6 Å[4]) of the void of II. Thus, it seems that the $Cu(OH)_2Cu$ bridge is tightly fixed within the void of II. In the Cu(II)-I complex, the length of the $Cu(OH)_2Cu$ bridge may be somewhat shorter than the internal diameter (7.5 Å[4]) of the void of I. Hence, the direction of the bridge may not coincide with that of the internal diameter. In the Cu(II)-III complex, two molecules of III may be coordinated to both ends of the $Cu(OH)_2Cu$ bridge to form the 2 : 2 Cu(II)-III complex. The structures of the complexes will be discussed further in a subsequent communication.

The spectra of the Cu(II)-I and -II in 0.1 N NaOH at 25°C are characterized by maxima at 668 mμ ($\varepsilon=128\pm1$) and 666 mμ ($\varepsilon=118\pm1$) respectively.

---

[1] D. French, *Advan. Carbohyd. Chem.*, **12**, 189 (1957).

[2] R. E. Reeves and P. Bragg, *J. Amer. Chem. Soc.*, **84**, 2491 (1962).

[3] H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **4**, Ser. C, 43 (1953).

[4] F. Cramer, W. Saenger, and H.-Ch. Spatz, *J. Amer. Chem. Soc.*, **89**, 14 (1967).