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# Effect of noncovalent complexations on coordination interactions in a tricomponent system of β-cyclodextrin, copper chloride and hexamethylene tetramine

Jing Yang [a], Le Xin Song [a,b,*], Zheng Dang [a], Shu Zhen Pan [a], Fang Yun Du [a]

[a] *Department of Chemistry, University of Science and Technology of China, Hefei 230026, China*
[b] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

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## Abstract

This study reveals that the noncovalent complexation between β-CD and $Cu(HMTA)^{2+}$ makes a positive contribution to the coordination interaction between $Cu^{2+}$ and HMTA in a tricomponent system. Besides, mono- and binuclear complexes: $[\beta\text{-CD·Cu}]^+$ and $[\text{Cu·}\beta\text{-CD·Cu}]^+$ were observed under the condition of ESI-MS.

*Keywords:* Noncovalent complexation; Coordination interaction; β-Cyclodextrin; Copper chloride

Noncovalent complexations between β-cyclodextrin (CD) and guest molecules have been the subject of numerous investigations in supramolecular chemistry [1–9]. The crystal structure of the inclusion complex of β-CD with hexamethylene tetramine (HMTA) served as a guest was reported [10]. Also, many coordination compounds of HMTA served as a ligand indicated supramolecular architectures in one-, two- and three-dimensional forms [11]. In addition, there were a few reports on the interaction of either β-CD or HMTA with copper chloride ($CuCl_2$) [12–15]. In a recent work, we found that the molecule–ion interaction between β-CD and ethylenediaminetetraacetic acid disodium salt ($Na_2H_2EDTA$, a guest molecule with a flexible structure) caused a decrease in the intensity of the coordination interaction between $Na_2H_2EDTA$ (ligand) and $CuCl_2$ [16]. This leads us to consider that the structural change of $Na_2H_2EDTA$ from a flexible structure to a rigid structure before and after coordination may be one reason for the decrease. In order to examine this hypothesis, HMTA, a rigid ligand, is used to investigate the problem of concern. Undoubtedly, it is very interesting and valuable to better understand the relation between noncovalent complexations and coordination interactions in a multicomponent system.

Initially, $^1H$ nuclear magnetic resonance ($^1H$ NMR, 400 MHz, $D_2O$) measurements of mono-, bi- and tricomponent systems, as seen in Fig. 1, reveal significant results. We note that from the comparison between Fig. 1b and c, the coordination interaction between $CuCl_2$ and HMTA has led to an obvious downfield shift (Δδ, 0.025) of the H-a protons of HMTA. It is possibly due to the decrease of electron density of H atoms caused by the decrease of electron

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[*] Corresponding author at: Department of Chemistry, University of Science and Technology of China, Hefei 230026, China.
*E-mail address:* Solexin@ustc.edu.cn (L.X. Song).

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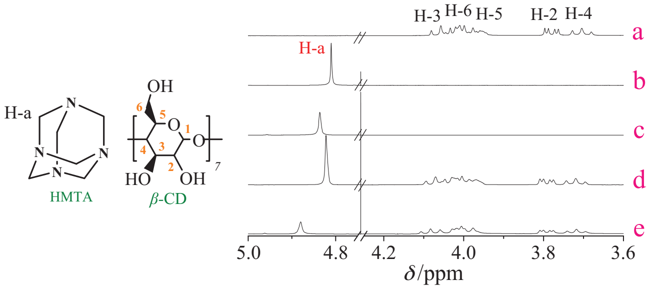

Fig. 1. Chemical shifts (δ/ppm) of the protons of β-CD (a), HMTA (b), $Cu(HMTA)^{2+}$ system (c), HMTA–β-CD system (d) and $CuCl_2$–HMTA–β-CD system (e) in $D_2O$. The concentrations of β-CD, HMTA and $CuCl_2$ in single, binary and ternary systems are all kept constant at $1.00 \times 10^{-3}$ mol $dm^{-3}$.

density of N atoms, as a result of Cu–N bonds. Although the H-a protons of HMTA in the presence of β-CD also show a similar shift (Δδ, 0.013) toward downfield (see Fig. 1d), the extent of the shift is clearly smaller than that observed in Fig. 1c. Likewise, the shifts of proton signals of β-CD were observed despite very small changes toward downfield. The above results suggest the noncovalent complexation between them.

Importantly, from Fig. 1e, we found that there is a much larger downshift (Δδ, 0.071) of H-a protons indicated by the light gray arrow in the ternary system relative to the two binary systems. This result gives us an impression that HMTA experienced simultaneously a coordination reaction between HMTA and $CuCl_2$ and a noncovalent complexation between β-CD and the chelate ion $Cu(HMTA)^{2+}$ in this case. Furthermore, the coordination interaction has been strengthened by the noncovalent complexation. At the same time, there is only a slight downshift of H-a protons of β-CD compared to Fig. 1d. This implies that it is not a simple combination of the above two interactions, but a synergistic effect on the proton environment of HMTA in the tricomponent system. The most probable reason is that the structure of $Cu(HMTA)^{2+}$ matches the hydrophobic cavity of β-CD better.

Next, Fig. 2 depicts the change in the UV–vis absorbance curves of $Cu(HMTA)^{2+}$ in the presence of β-CD. This absorbance corresponds to the ligand-to-metal charge transfer transition (LMCT) *via* electron donation from the lone-pairs of the nitrogen atoms of HMTA to the empty 4s orbital of $Cu^{2+}$ ions. Apparently, the gradually increasing concentration of β-CD in solution results in a gradual increase in the maximum absorbance of the chelate at 274.8 nm, which is an indication of the change in the surrounding hydrophobicity indices of the Cu–N bonds. This reflects that the intensity of the coordination interaction is closely related to the concentration of β-CD and it is a consequence of the mutual promotion between the coordination interaction of $Cu^{2+}$ with HMTA and the inclusion complexation of β-CD with the chelate. The conclusion stands in entire contrast to the result of the former study [16]. It strongly indicates that the two interactions are not a simple competitive relationship but affected by the property of the guest deeply.

And then, the charge status of the chelate was determined by measuring molar conductivities ($\Lambda_m$) in aqueous solutions. Fig. 3 shows a nonlinear decrease in $\Lambda_m$ values of aqueous solutions of the chelate formed by $Cu^{2+}$ and HMTA with increasing concentration of β-CD. The decrease in $\Lambda_m$ values follows approximately an exponential

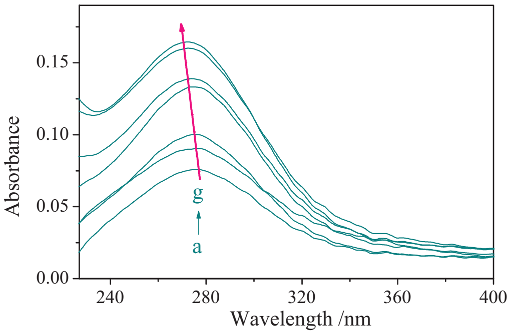

Fig. 2. UV–vis spectra of $Cu(HMTA)^{2+}$ formed by $1.00 \times 10^{-4}$ mol $dm^{-3}$ $CuCl_2$ and $1.00 \times 10^{-4}$ mol $dm^{-3}$ HMTA in the presence of β-CD from $0.10 \times 10^{-4}$ (a) to $8.00 \times 10^{-4}$ (g) mol $dm^{-3}$.