7638 *Inorg. Chem.* **2010**, *49*, 7638–7640
DOI: 10.1021/ic1013494

Inorganic Chemistry
Communication

Complexation of Cyclohexanocucurbit[6]uril with Cadmium Ions: X-ray Crystallographic and Electrochemical Study

Xing Feng,[†] Zhong-Fei Li,[†] Sai-Feng Xue,[*,†] Zhu Tao,[†] Qian-Jiang Zhu,[†] Yun-Qian Zhang,[†] and Jing-Xin Liu[*,‡]

[†]*Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, People's Republic of China, and* [‡]*College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, People's Republic of China*

Received July 8, 2010

Complexation of cyclohexanocucurbit[6]uril (Q*[6]), a water-soluble cucurbit[*n*]uril derivative, with Cd^{2+} ions has been studied by means of cyclic voltammetry and differential pulse voltammetry. The electrochemical experimental data prove the formation of a highly stable 1:6 Q*[6]/Cd^{2+} complex. We also obtained the single-crystal X-ray structure of a cadmium ion complex with Q*[6], in which each portal of Q*[6] chelates three cadmium ions. The present study suggests the potential utility of Q*[6] as an effective cadmium ion chelator and extractant.

The sensing and removal of toxic heavy metals such as lead, cadmium, and mercury in the environment are a field of great interest at all times.[1−4] This is because the presence of toxic heavy metals in aquatic media and drinking water is potentially dangerous to the health of humans. They can cause multifarious diseases, depending on the exposure levels and the chemical form of the toxic heavy metal.[4] A well-known example of heavy-metal poisoning is the Itai-itai disease (itai = pain in Japanese), which was caused by cadmium pollution in the Jinzhu River Basin in Japan. However, the accumulation of toxic heavy metals in rivers and lakes is increasing significantly because of human activities such as mining and industrialization of countries around the globe, especially in developing countries such as India and China.

Many attempts have been made to design and synthesize practical, selective, and effective materials to remove these toxic heavy metals from aqueous media.[5−10] For example, García et al. synthesized eight novel aromatic and aliphatic−aromatic poly(amide urea)s, which exhibited moderate results in the extraction of different Pb^{2+} and Hg^{2+} salts from aqueous solution.[9] In 2008, Francis and co-workers reported a recyclable metallothionein-based system that could selectively sense and remove heavy-metal contaminants from water.[10] Although there are many toxic heavy metals that can detect and remove materials, the number of those with selectivity, water solubility, and a high metal-to-ligand molar ratio is very limited, especially for cadmium ions.

Recently, much of the research effort in this vein has been focused on the use of cucurbit[*n*]uril (hereafter abbreviated as Q[*n*], where $n = 5-8$ and 10), a class of organic macrocyclic cavitands with identical carbonyl-laced portals on each side.[11] The polar carbonyl groups of Q[*n*]s can, in principle, chelate toxic heavy metals, and Q[*n*]s appear to be promising candidates for the removal toxic metal-ion pollutants.[12] However, their poor water solubility and low metal-to-ligand molar ratio restrict their practical application. The recently

---

*To whom correspondence should be addressed. E-mail: gzutao@263.net (S.-F.X.), jxliu411@ahut.edu.cn (J.-X.L.). Fax: (+86) 8513620906.

(1) (a) Forstner, U.; Wittman, G. T. W. *Metal Pollution in the Aquatic Environments*; Springer-Verlag: New York, 1981. (b) Ireland, M. P. *Biological Monitoring of Heavy Metals*; Wiley: New York, 1991. (c) Vernet, J. P. *Impact of Heavy Metals on the Environment*; Elsevier: New York, 1992.

(2) Chen, Y. X.; Liu, H.; Zhu, G. W.; Chen, H. L.; Tian, G. M. *J. Environ. Sci.* **2004**, *16*, 34.

(3) (a) Francesconi, K. A. *Analyst* **2007**, *132*, 17. (b) Locatelli, C. *Electroanalysis* **2004**, *16*, 1478.

(4) Al-Saleh, I.; Coskun, S.; Mashhour, A.; Shinwari, N.; El-Doush, I.; Billedo, G.; Jaroudi, K.; Al-Shahrani, A.; Al-Kabra, M.; Mohamed, G. E. D. *Int. J. Hyg. Environ. Health* **2008**, *211*, 560.

(5) (a) Silbergeld, E. K. *Environ. Health Perspect.* **1991**, *91*, 63. (b) Silberstein, T.; Saphier, O.; Paz-Tal, O.; Trimarchi, J. R.; Gonzalez, L.; Keefe, D. L. *J. Trace Elem. Med. Biol.* **2006**, *20*, 205.

(6) Nampoothini, L. P.; Gupta, S. *Reprod. Toxicol.* **2006**, *21*, 179.

(7) Hegazy, E. S. A.; Kamal, H.; Khalifa, N. A.; Mahmoud, G. A. *J. Appl. Polym. Sci.* **2001**, *81*, 849.

(8) (a) Wildgoose, G. G.; Leventis, H. C.; Davies, I. J.; Crossley, A.; Lawrence, N. S.; Jiang, L.; Jones, T. G. J.; Compton, R. G. *J. Mater. Chem.* **2005**, *15*, 2375. (b) Wildgoose, G. G.; Leventis, H. C.; Simm, A. O.; Jones, J. H.; Compton, R. G. *Chem. Commun.* **2005**, 3694. (c) Xiao, L.; Wildgoose, G. G.; Grossley, A.; Knight, R.; Jones, J. H.; Compton, R. G. *Chem. Asian J.* **2006**, *1*, 614.

(9) San-José, N.; Gómez-Valdemoro, A.; García, F. C.; Calderón, V.; García, J. M. *React. Funct. Polym.* **2008**, *68*, 1337.

(10) Esser-Kahn, A. P.; Iavarone, A. T.; Francis, M. B. *J. Am. Chem. Soc.* **2008**, *130*, 15820.

(11) Reviews: (a) Kim, K. *Chem. Soc. Rev.* **2002**, *31*, 96. (b) Gerasko, O. A.; Samsonenko, D. G.; Fedin, V. P. *Russ. Chem. Rev.* **2002**, *71*, 741. (c) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621. (d) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844. (e) Ko, Y. H.; Kim, E.; Hwang, I.; Kim, K. *Chem. Commun.* **2007**, 1305 and references cited therein.

(12) (a) Zhang, X. X.; Krakowiak, K. E.; Xue, G. P.; Bradshaw, J. S.; Izatt, R. M. *Ind. Eng. Chem. Res.* **2000**, *39*, 3516. (b) Buschmann, H.-J.; Cleve, E.; Jansen, K.; Schollmeyer, E. *Anal. Chim. Acta* **2001**, *437*, 157. (c) Liu, J. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Cryst. Growth Des.* **2006**, *6*, 2611. (d) Liu, J. X.; Hu, Y. F.; Lin, R. L.; Sun, W. Q.; Liu, X. H.; Yao, W. R. *J. Coord. Chem.* **2010**, *63*, 1369. (e) Feng, X.; Lu, X. J.; Xue, S. F.; Zhang, Y. Q.; Tao, Z.; Zhu, Q. J. *Inorg. Chem. Commun.* **2009**, *12*, 849.

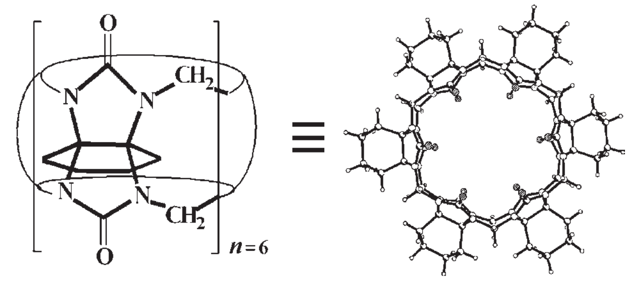

Figure 1. Q*[6] and its single-crystal X-ray structure.[13a]

synthesized cyclohexanocucurbit[6]uril (Q*[6]) (Figure 1), a water-soluble Q[6] derivative, attracted our attention.[13] In the current study, we investigated the binding affinity and molar ratio of Q*[6] to cadmium ions in aqueous solution by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. We also obtained the crystal structure of Q*[6] complexed with cadmium ions, which reveals that one Q*[6] molecule can chelate six cadmium ions to form a stable coordinated complex.

Electrochemistry experiments of CV were performed in a HAc−NaAc buffer (pH = 5.00) aqueous solution using Ag/AgCl as the reference electrode. Figure 2 shows the current−potential curves of 4 × 10^{-2} mM Cd^{2+} in the absence and presence of increasing concentrations of Q*[6]. As anticipated, Cd^{2+} shows one reversible wave corresponding to the redox couple $Cd^{2+/0}$ (black line). In the presence of increasing concentrations (from 2.0 × 10^{-3} to 6.4 × 10^{-3} mM) of Q*[6], the half-wave potential ($E_{1/2}$) of the reduction is shifted slightly to more negative values in the presence of Q*[6], whereas that of the oxidation is shifted slightly to more positive values. In addition to this, with the addition of Q*[6] (from 2.0 × 10^{-3} to 6.4 × 10^{-3} mM), a pronounced current level decrease is also observed. Obviously, the electrochemical behavior of Cd^{2+} is strongly affected by Q*[6]. The potentials shift and the currents decrease, indicating the formation of a Cd^{2+} coordinated complex with Q*[6], and the complex has a smaller diffusion coefficient than the free Cd^{2+}.

According to the mole ratio method, the experimental data of the peak current (I_{pc}) versus $N_{Q*[6]}/N_{Cd^{2+}}$ can be easily fitted to an unusual 1:6 ligand-to-metal coordination model. To the best of our knowledge, this is the highest coordination ratio ever reported for Q[*n*]s and their derivatives. When the Q*[6] concentration is more than 6.4 × 10^{-3} mM, the CV curves become less reversible and have no more shift upon the addition of Q*[6], which suggests that Cd^{2+} and Q*[6] reach a state of coordination equilibrium with their complex. The stability constant for the 1:6 Q[6]/Cd^{2+} coordination complex was measured by the current method and found to be as high as 1.58 × 10^{32} M^{-6} at 25 °C in water, of which log K = 32.20. This value (log K = 32.20) is remarkably larger than that of 3.04 in the Q[6]/Cd^{2+} complex,[12b] indicating that Q*[6] has a strong binding affinity to Cd^{2+}.

For a better understanding of the interaction between Q*[6] and Cd^{2+}, we carried out a DPV experiment at the same conditions. As shown in Figure 3, upon the addition of Q*[6], the current peak of the reduction decreases gradually, revealing complexation of Q*[6] with Cd^{2+}. Employing an equimolar continuous variation method, we obtained the curve of ΔI_{pc} versus $N_{Cd^{2+}}/(N_{Q*[6]} + N_{Cd^{2+}})$, which shows that the DPV data fit very well to the same 1:6 ligand-to-metal coordination model. The stability constant for the 1:6 Q*[6]/Cd^{2+} complex determined by the current method is 3.06 × 10^{33} M^{-6}, which is very similar to 1.58 × 10^{32} M^{-6}, which we previously mentioned. Obviously, the formation of the 1:6 Q*[6]/Cd^{2+} complex and its stability have been further confirmed by DPV.

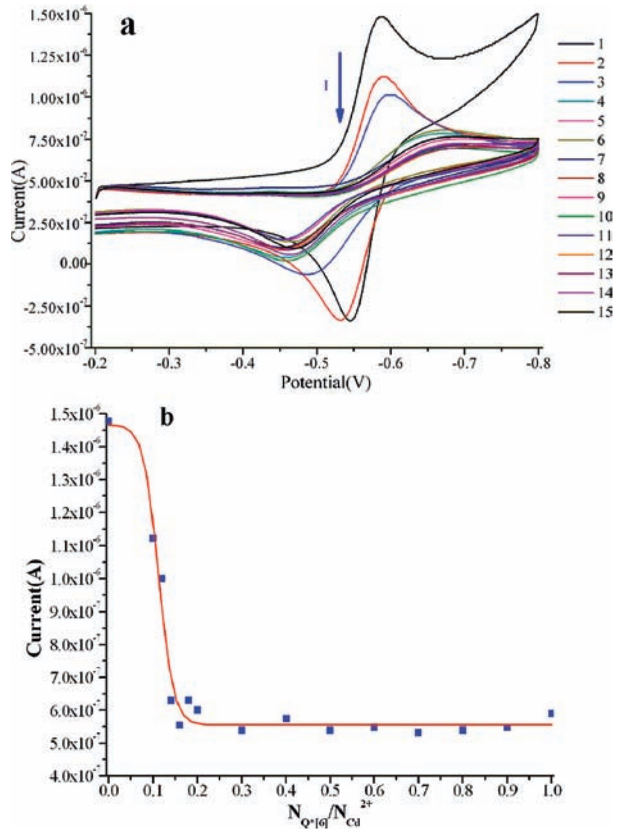

Figure 2. (a) Current−potential curves of 4 × 10^{-2} mM Cd^{2+} in the absence (1) and presence (2−15) of Q*[6]. Concentrations of Q*[6]: (2) 4 × 10^{-3} mM; (3) 4.8 × 10^{-3} mM; (4) 5.6 × 10^{-3} mM; (5) 6.4 × 10^{-3} mM; (6) 7.2 × 10^{-3} mM; (7) 8 × 10^{-3} mM; (8) 1.2 × 10^{-2} mM; (9) 1.6 × 10^{-2} mM; (10) 2.0 × 10^{-2} mM; (11) 2.4 × 10^{-2} mM; (12) 2.8 × 10^{-2} mM; (13) 3.2 × 10^{-2} mM; (14) 3.6 × 10^{-2} mM; (15) 4.0 × 10^{-2} mM. (b) Corresponding curve of I_{pc} vs $N_{Q*[6]}/N_{Cd^{2+}}$.

We also examined the complex structure of Q*[6] with cadmium ions by X-ray crystallography. The slow evaporation of an aqueous solution containing $CdCl_2$ and Q*[6], the molar ratio of which is 1:10, results in the formation of suitable yellow crystals of complex **1**, $[(C_{60}H_{72}N_{24}O_{12})Cd_6Cl_{14}]^{2-}(H_3O)_2^{2+}\cdot 6H_2O$. The single-crystal X-ray structure of complex **1**[14] (Figure 4) reveals that the molecule has a center of symmetry, and two $[Cd_3Cl_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)]^-$ clusters are coordinated to each portal of Q*[6].

Figure 5 shows the inner coordination of the cluster. As can be seen, the Cd_3 equilateral triangle is bridged by three Cl atoms along each edge and is capped by a μ_3-Cl ligand, with terminal Cl ligands completing the coordination sphere about

---

[13] (a) Zhao, J.; Kim, H.-J.; Oh, J.; Kim, S.-Y.; Lee, J. W.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4233. (b) Kim, B. S.; Ko, Y. H.; Kim, Y.; Lee, H. J.; Selvapalam, N.; Lee, H. C.; Kim, K. *Chem. Commun.* **2008**, 2756. (c) Kim, Y.; Kim, H.; Ko, Y. H.; Selvapalam, N.; Rekharsky, M. V.; Inoue, Y.; Kim, K. *Chem.—Eur. J.* **2009**, *15*, 6143.

[14] Crystallographic data for complex **1**: $C_{60}H_{90}Cd_6Cl_{14}N_{24}O_{20}$, M_r = 2638.26, cubic, space group $Pa\bar{3}$, a = 20.950(2) Å, V = 9195.4(18) $Å^3$, Z = 4, D_c = 1.906 g cm^{-3}, $F(000)$ = 5216, GOF = 1.099, R1 = 0.0463 [$I > 2\sigma(I)$], wR2 = 0.1413 (all data).

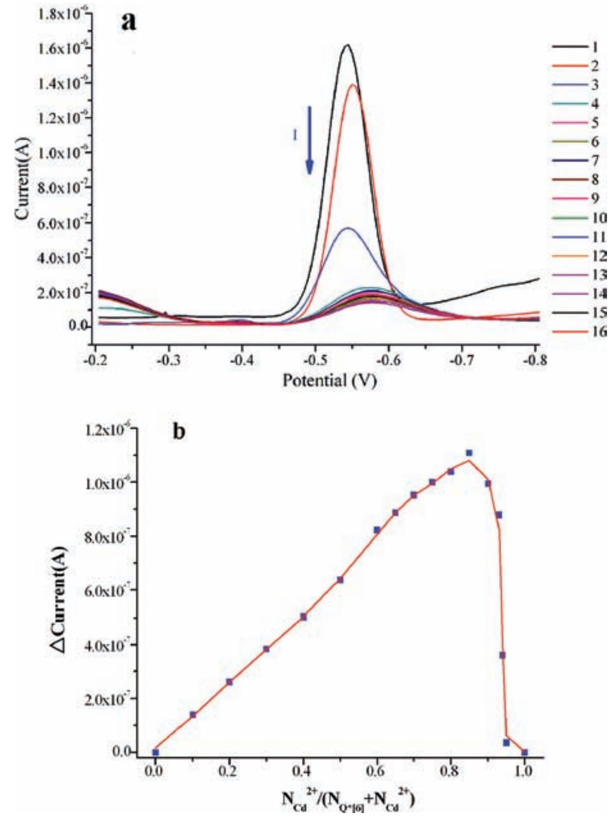

Figure 3. (a) Differential pulse voltammograms of 4 × 10^{-2} mM Cd^{2+} in the absence (1) and presence (2−16) of Q*[6]. Concentrations of Q*[6]: (2) 2 × 10^{-3} mM; (3) 4 × 10^{-3} mM; (4) 4.8 × 10^{-3} mM; (5) 5.6 × 10^{-3} mM; (6) 6.4 × 10^{-3} mM; (7) 7.2 × 10^{-3} mM; (8) 8 × 10^{-3} mM; (9) 1.2 × 10^{-2} mM; (10) 1.6 × 10^{-2} mM; (11) 2.0 × 10^{-2} mM; (12) 2.4 × 10^{-2} mM; (13) 2.8 × 10^{-2} mM; (14) 3.2 × 10^{-2} mM; (15) 3.6 × 10^{-2} mM; (16) 4.0 × 10^{-2} mM. (b) Corresponding curve of ΔI_{pc} versus $N_{Cd^{2+}}/(N_{Q^*[6]} + N_{Cd^{2+}})$.

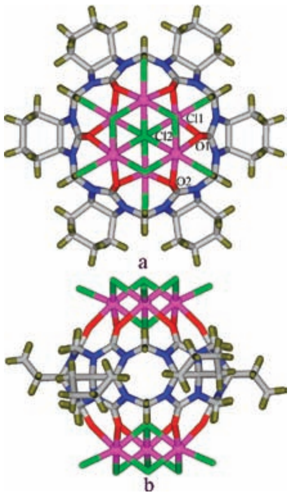

Figure 4. X-ray structure of complex **1**: (a) top view; (b) side view. Displacement ellipsoids are drawn at the 50% probability level. Solvate water molecules are omitted for clarity.

each Cd atom. The Cd−Cd distances (3.809 Å) indicate no metal−metal bonding between the three Cd atoms. Interestingly, two $[Cd_3Cl_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)]^-$ clusters effectively cover each portal of Q*[6], forming one closed molecular capsule. In the crystal structure of complex **1**, the $[Cd_3Cl_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)]^-$ clusters capping the Q*[6] molecular capsule are separated, the isolated molecular capsule is surrounded by water molecules, and they interact to form a hydrogen-bonded structure.

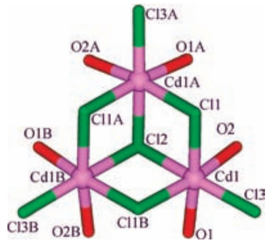

Figure 5. X-ray structure of a close inspection of the coordination of Cd^{2+} with a carbonyl O atom in complex **1**. Displacement ellipsoids are drawn at the 50% probability level.

It is well-known that the portal and cavity sizes of Q*[6] are essentially the same as those of Q[6], and Q*[6] is expected to show the same binding behavior as that of Q[6]. However, they exhibited binding affinities and coordination molar ratios different from those of cadmium ions.[12b,e] The stability constant (3.06 × 10^{33} M^{-6} or 1.58 × 10^{32} M^{-6}) for the 1:6 Q*[6]/Cd^{2+} complex is much larger than that (9.95 × 10^9 M^{-2}) for the 1:2 Q[6]/Cd^{2+} complex, as we previously reported.[12e] We postulate that the outstanding binding affinity of Q*[6] to cadmium ions may be attributed to its six cyclohexane rings. As an electron-donating group, the cyclohexane moiety can enhance the polar properties of the carbonyl O atoms at the portals of Q*[6], which results in the ion−dipole interaction enhancement between Q*[6] and cadmium ions. This postulation not only contributes to the understanding of the large binding affinity of Q*[6] to cadmium ions but also may provide insight into the design of new Q[*n*] derivatives for chelating other toxic heavy metals. It must be mentioned that the comparison experiments (complexation of two and three cyclohexane-substituted Q[6] with Cd^{2+} ions) and correlative density functional theory calculations are currently ongoing in our laboratory.

In summary, we have investigated the complexation behavior of Q*[6], a water-soluble Q[*n*] derivative, with Cd^{2+} ions by means of CV and DPV by an electrochemical method and X-ray crystallography. Electrochemical data indicate the formation of a highly stable 1:6 Q*[6]/Cd^{2+} complex, which shows that Q*[6] has a strong binding affinity to Cd^{2+} ions. Furthermore, we determined the single-crystal X-ray structure of the 1:6 Q*[6]/Cd^{2+} complex, which revealed that each portal of Q*[6] is covered effectively by one $[Cd_3Cl_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)]^-$ cluster. The remarkable stability and high coordinated ratio of Q*[6] with Cd^{2+} ions may be attribute to the electron-donating property of its six cyclohexane rings. The present study indicates the important potential utility of Q*[6] as an effective cadmium ion chelator and extractant of drinking water and environmental remediation.

Acknowledgment. We thank the National Natural Science Foundation of China (Grants 20961002 and 20971002), the "Chun-Hui" Fund of the Chinese Ministry of Education, the Science and Technology Fund of Guizhou Province, and the International Collaborative Project Fund of Guizhou Province for financial support.

Supporting Information Available: Synthetic details, experimental method, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.