

二甲基取代五元瓜环与钾离子和钆离子的配位结构

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摘要: 利用 X-射线单晶衍射技术表征了 2 个二甲基取代五元瓜环(DMeQ[5])与金属离子形成的配合物的晶体结构, 2 个配合物分别为 $[\{K_2(H_2O)_3DMeQ[5]\}I_2 \cdot 5H_2O]$ (**1**) 和 $[\{Gd(H_2O)_3\}[K(H_2O)][(NO_3)_3@DMeQ[5]](NO_3)_3 \cdot 5H_2O]$ (**2**)。与 DMeQ[5] 和钆离子形成的配合物的结构不同的是, 配合物 **1** 和 **2** 中每个 DMeQ[5] 端口的所有羰基氧原子都和钾离子或钆离子配位, 形成全封闭结构。

关键词: 二甲基取代五元瓜环; 配位; 金属离子

中图分类号: O614.113; O614.33*9

文献标识码: A

文章编号: 1001-4861(2012)03-0626-06

Coordination of Dimethylcucurbit[5]uril with Potassium and Gadolinium Cations

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Abstract: Two dimethyl-substituted cucurbit[5]uril (DMeQ[5]) complexes with heterometallic potassium/gadolinium metal ions and with potassium ions only were structurally characterized by single-crystal X-ray diffractions. They are $[\{K_2(H_2O)_3DMeQ[5]\}I_2 \cdot 5H_2O]$ (**1**) and $[\{Gd(H_2O)_3\}[K(H_2O)][(NO_3)_3@DMeQ[5]](NO_3)_3 \cdot 5H_2O]$ (**2**). Compared to the complex of DMeQ[5] with gadolinium metal ions only, both opening portals of DMeQ[5] are fully capped by potassium cations or potassium and gadolinium cation ions in these two DMeQ[5]-based complexes. CCDC: 821247, **1**; 821248, **2**.

Key words: dimethyl-substituted cucurbit[5]uril; coordination; metal ions

0 Introduction

Since the cucurbituril (Q[6]) was structurally characterized by using single-crystal X-ray diffraction in 1981^[1], the features of Q[6] with two open portals with a unique cavity rimmed with carbonyl groups has extensively studied in Q[6]-based host-guest chemistry and coordination chemistry^[2-3]. The discovery of homologues of Q[6], including, (Q[5], Q[7], Q[8] and Q[10])^[4-6], and a series of fully or partially substituted derivatives and analogues^[7-13], results in the rapidly

development of cucurbit[n]uril chemistry^[2-3].

Based on the achievements of other research groups and our experimental results on Q[n]-based coordination chemistry, we have focused on the comparison of coordination of metal ions to the unsubstituted Q[n]s with the alkyl-substituted cucurbit[n]urils. Somewhat differences are found in our researches. For example, unsubstituted Q[5] interacts with KI, and forms discrete K-Q[5] complexes, while the alkyl-substituted cucurbit[5]urils (SQ[5]s) interacts with KI, and forms SQ[5]-based networks or frameworks^[14-15].

收稿日期: 2011-07-10。收修改稿日期: 2011-10-24。

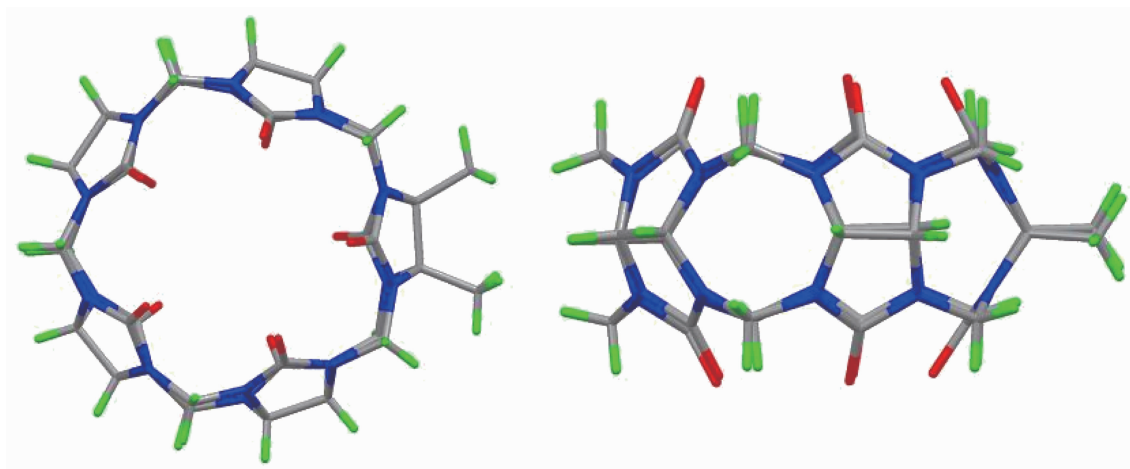
国家自然科学基金(No.20961002), 贵州省教育厅自然科学研究项目(No.2010001)资助项目。

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Although the $Q[n]$ -based coordination chemistry has been receiving considerable attention^[3], few heterometallic $Q[n]$ -based complexes, in which a kind of metal ion coordinates to one portal of a $Q[n]$, and the second kind of metal ion coordinates to the other portal of the $Q[n]$ ^[16-19]. Fedin et al. demonstrated a series of second metal-containing cluster interacting with $Q[6]$ through hydrogen bonding^[20-24], but the first several examples of such complexes were reported by Thuery, when uranyl nitrate was reacted with $Q[5]$ in the presence of alkali metal salts, heterometallic capsules, capped by one uranyl ion at one portal and K^+ or Cs^+ at the other portal, were obtained as dicationic species^[16]. When we focused on the comparison of coordination properties of the unsubstituted $Q[n]$ s with the alkyl-substituted cucurbit[n]urils, we found that the introduction of the third species, in particular, an inorganic salt into unsubstituted $Q[n]$ -metal systems could result in the formation of novel $Q[n]$ -based architectures. For example, one linear dimensional coordination polymers can be obtained in an aqueous solution containing $Q[5]$ and potassium ions^[25], when

$ZnCl_2$ salt is introduced into the $Q[5]$ - K^+ system, an infinite 1D supramolecular chain is constructed of heterometallic zinc and potassium ions/cucurbit[5]uril capsules through ion-dipole interaction and hydrogen bonding, and the supramolecular chain forms a novel hexagonal open framework^[18].

In the present study, we demonstrate two crystal structures obtained from two $SQ[5]$ -potassium systems, in which, $SQ[5]$ is a dimethyl-substituted cucurbit[5]uril (DMeQ[5], Fig.1), and a lanthanide salt, gadolinium nitrate is used as the third inorganic species in a $SQ[5]$ -potassium system. The two complexes are $\{[K_2(H_2O)_3 DMeQ[5]]I_2 \cdot 5H_2O$ (**1**) and $\{[Gd(H_2O)_3][K(H_2O)](NO_3) @DMeQ[5]\}(NO_3)_3 \cdot 5H_2O$ (**2**). Literature search shows that, there are no other reports about coordination structures of dimethyl-substituted cucurbit[5]uril and metal ions, except a few external reported by our research group^[14,26], the two crystals in this article is the first report. A previously reported complex $\{[Gd_2(H_2O)_9][DMeQ[5]@Cl]\}Cl_5 \cdot 13H_2O$ (**3**) is also described for the comparison of the coordination of DMeQ[5] with gadolinium and potassium cations^[26].



Color codes: carbon, gray; hydrogen, green; oxygen, red; nitrogen, dark blue

Fig.1 Structure of dimethyl-substituted cucurbit[5]uril

1 Experimental

1.1 General materials

Chemicals, such as potassium iodide, potassium nitrate, gadolinium nitrate, were of reagent grade and used without further purification. DMeQ[5] was prepared by procedures reported previously^[14]. Elemental analysis

was carried out on a EURO EA-3000 element analyzer.

1.2 Preparation of complex 1

To prepare crystals of **1**, DMeQ[5] (0.10 g, 0.11 mmol) and KI (0.10 g, 0.60 mmol) were dissolved in 10 mL water, then the solution was allowed to stand at room temperature. The single crystal of **1** formed after two weeks. Anal. Calcd. for $C_{32}H_{50}N_{20}O_{18}K_2I_2$ (%): C,

28.79; H, 3.78; N, 20.99. Found (%): C, 28.75; H, 3.64; N, 21.06.

1.3 Preparation of complex 2

The single crystals of DMeQ[5] adduct with $\text{Gd}(\text{NO}_3)_3$ and KNO_3 was obtained by dissolving DMeQ[5] (0.10 g, 0.11 mmol) in a solution of $\text{Gd}(\text{NO}_3)_3$ (0.34 g, 1.00 mmol) and KNO_3 (0.12 g, 1.19 mmol) in 10 mL water. The solution was mixed thoroughly and filtered to remove insoluble impurities, then allowed to stand at room temperature. Rock crystals formed after one week. Anal. Calcd. for $\text{C}_{32}\text{H}_{52}\text{N}_{24}\text{O}_{31}\text{GdK}$ (%): C, 26.23; H, 3.58; N, 22.94. Found(%): C, 26.75; H, 3.24; N, 23.06.

1.4 X-ray crystallography

The crystal data of DMeQ[5] coordinated with metal ions were collected on a Bruker Apex-2000 CCD

diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) in ω scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package^[27-28] respectively. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not added to the disordered water molecule O9W in **2**. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data, data collection conditions, and refinement parameters for two compound **1** and **2** are listed in Table 1.

CCDC: 821247, **1**; 821248, **2**.

Table 1 Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{32}\text{H}_{50}\text{N}_{20}\text{O}_{18}\text{I}_2\text{K}_2$	$\text{C}_{32}\text{H}_{52}\text{N}_{24}\text{O}_{31}\text{GdK}$
Formula weight	1 334.92	1 465.33
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.991 06(11)	2.100 47(17)
b / nm	1.199 69(7)	1.143 84(9)
c / nm	2.801 20(12)	2.100 47(17)
$\beta / (^\circ)$	134.185(2)	99.545(7)
V / nm^3	4.798 1(5)	4.976 7(7)
Z	4	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.848	1.956
T / K	173(2)	173(2)
μ / mm^{-1}	1.579	1.545
Unique reflns	9 439	9 778
Obsd reflns	8 088	7 411
Params	670	802
R_{int}	0.044 9	0.058 1
$R_1, wR_2 (I > 2\sigma(I))$	0.056 3, 0.140 7	0.040 6, 0.096 2
R_1, wR_2 (all data)	0.064 3, 0.144 5	0.058 3, 0.107 4

2 Results and discussion

2.1 Crystal structures of complexe 1 and 2

The Q[5] molecules in the two complexes (**1** and **2**) are fully capped by two metal ions on the portals. For complex **1**, the two portals of the Q[5] molecule are fully capped by two same potassium ions, while for complex **2**, the two portals of the Q[5] molecule are fully capped

by heterometallic potassium and gadolinium ions (Fig.2 and Fig.3).

Fig.2a shows that each K ion (K1 or K2) coordinates directly to five carbonyl oxygen atoms at each portals, leading to the formation of a Q[5]-based molecular cage. The distances between potassium ion (K1 or K2) and carbonyl oxygen are in the range of 0.271 3 and 0.294 2 nm. In addition, K1 ion coordinates

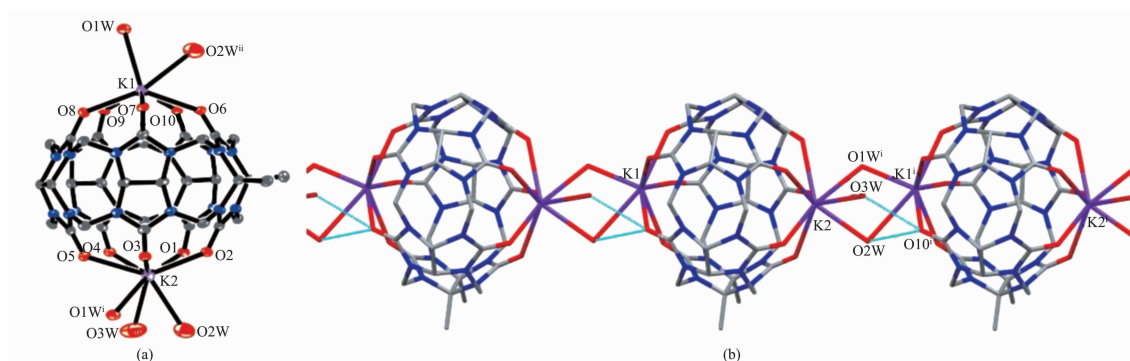


Fig.2 (a) ORTEP drawing of the K-Q[5] complex with 30% probability ellipsoids; (b) 1D supramolecular chain based on the K-Q[5] complexes

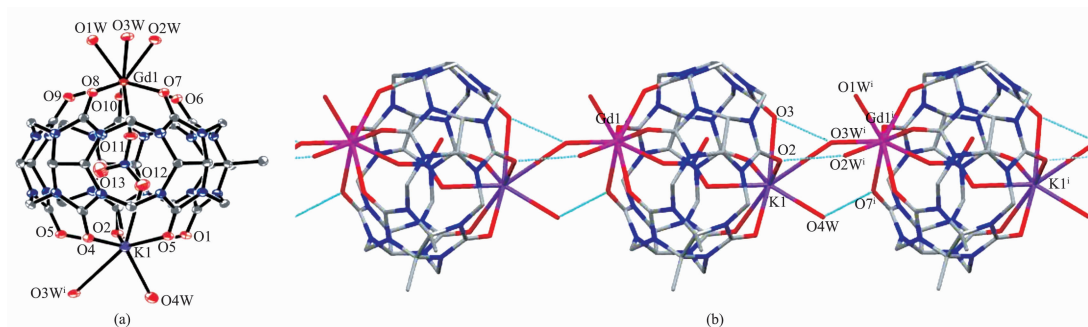


Fig.3 (a) ORTEP drawing of the heterometallic Gd³⁺/K⁺ ions/Q[5] capsule with 30% probability ellipsoids; (b) 1D supramolecular chain based on the heterometallic Gd³⁺/K⁺ ions/Q[5] capsules

to two water molecules (K1-O1W: 0.275 3 nm; K1-O2Wⁱⁱ: 0.315 1 nm) and K2 ion coordinates to three water molecules (K2-O1Wⁱ: 0.320 6 nm; K2-O2W: 0.280 5 nm; K2-O3W: 0.282 9 nm). Moreover, the coordination of K1 of a complex to the water molecules, which are shared with K2 of a neighboring complex, such as K2-O1Wⁱ-K1ⁱ and K2-O2W-K1ⁱ, results in the formation of a Q[5]-based one-dimensional chain. The hydrogen bonding interaction between these coordinated water molecules and the portal oxygen, such as O2W or O3W with O10ⁱ, further strengthens the Q[5]-based one-dimensional chain. The distances are 0.278 3 and 0.297 4 nm (Fig.2b).

The X-ray structure of 2 shows that the two opening portals of each DMeQ[5] are capped with a potassium cation (K1) and a gadolinium cation (Gd1) respectively, and a NO₃⁻ anion is encapsulated in the cavity of the DMeQ[5] molecule (Fig.3a). Both Gd

cation and K cation in this Q[5] capsule are coordinated not only to five portal carbonyl oxygen atoms but also to oxygen atoms of the included NO₃⁻ anion, of which one oxygen atom O11 of NO₃⁻ coordinates with Gd1 cation, while another oxygen atoms O12 of the nitrate coordinate with K1 cation. The distances of Gd1-O11 and K1-O12 are 0.234 7 and 0.274 2 nm. The distances between Gd1 and portal oxygen atoms are in the range of 0.241 7 and 0.261 9 nm while the distances between K1 and portal oxygen atoms are in the range of 0.268 5 and 0.290 3 nm. It is similar to the complex 1, Gd1 and K1 ions coordinate to two and three water molecules, respectively (Gd1-O1W: 0.245 2 nm; Gd1-O2W: 0.245 2 nm; Gd1-O3W: 0.240 8 nm; K1-O3Wⁱ: 0.322 6 nm; K1-O4W: 0.282 4 nm;). The hydrogen bonding interaction of the coordinated water molecules and portal oxygens between the neighboring capsules, such as O2-O2Wⁱ, O3-O3Wⁱ and O4W-O7ⁱ, leads to the

formation of the capsules-based one dimensional chain (Fig.3b).

2.2 Coordination of DMeQ[5] with potassium and gadolinium cations

In the previous study, we demonstrated a complex of DMeQ[5] with gadolinium cation^[26]. However, the coordination of gadolinium ions to portals of a DMeQ[5] was different from the cases in the present study (referring to Fig.4a and Fig.5a). Compared to the two fully capped portals in the complexes (**1** and **2**), a portal of a DMeQ[5] molecule is fully capped with a Gd1 cation, while the other portal of the DMeQ[5] is only partial capped with a Gd2 cation in the Gd-DMeQ[5] complex. The ionic radius of K^+ and Gd^{3+} is 0.133 nm and 0.094 nm, respectively, the ionic radius of K^+ is approximately 0.04 nm larger than Gd^{3+} . When a Gd^{3+} full capped on a portal of a DMeQ[5], the distances between the Gd cation to the portal O atoms are in the range of 0.235 9 and 0.252 6 nm, and the distances of two neighboring carbonyl oxygens are in the range of

0.280 7 and 0.294 0 nm, while the distances of two neighboring carbonyl oxygens on the other portal are in the range of 0.289 0 and 0.332 2 nm, indicating that the partial capped portal is enlarged so that it is too large to be fully capped by the second Gd cation (Fig.4a). It is reasonable that the second gadolinium cation Gd2 is only partially capped on the portal of the DMeQ[5] molecule. However, the potassium cation, which has a larger ionic radius and suitable for both portals of a DMeQ[5], could perfectly coordinate to both portals of the DMeQ[5] and form a stable K-DMeQ[5] complex. Fig.4b shows that the distances of two neighboring carbonyl oxygens coordinated with K1 are in the range of 0.305 3 and 0.317 7 nm, while the distances of two neighboring carbonyl oxygens coordinated with K2 are in the range of 0.305 7 and 0.320 6 nm, indicating that the sizes of both portals of DMeQ[5] are almost the same in the complex **1**. It should be noted that in complex **2**, when a portal of DMeQ[5] is capped by a gadolinium cation Gd1, the distances of two neighboring carbonyl

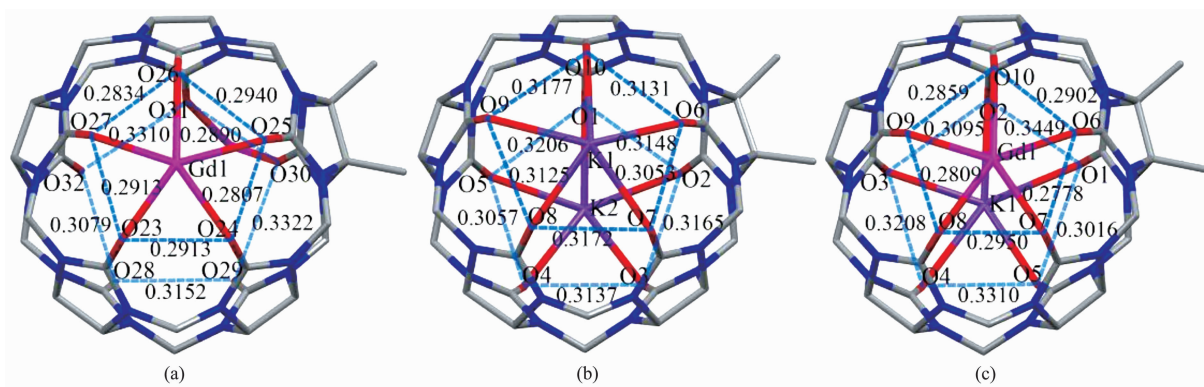


Fig.4 Portal size (nm) of DMeQ[5] (a) in the complex **3**, (b) in complex **1**, (c) in complex **2**

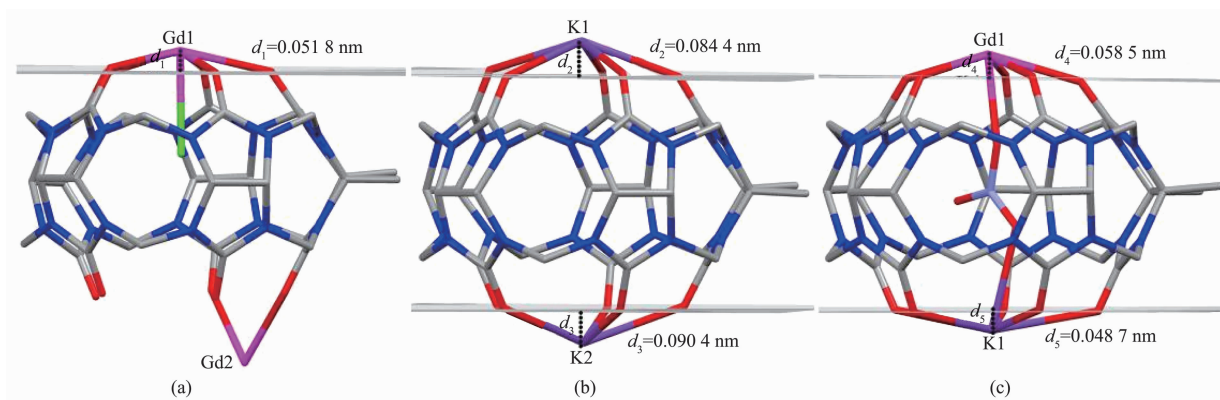


Fig.5 Distance from the metal ion to the plane of carbonyl atoms (a) in complex **3**, (b) in complex **1**, (c) in complex **2**

oxygens are in the range of 0.277 9 and 0.294 8 nm, while the distances of two neighboring carbonyl oxygens on the other portal capped with K1 are in the range of 0.301 7 and 0.345 3 nm, the enlarged portal size is also suitable for the coordination of potassium cation, which has a larger ionic radius, to the portal of DMeQ[5] (Fig.4c).

Fig.5 shows the distances of coordinated metal ions to the planes of five carbonyl oxygens. In the Gd-DMeQ[5] complex **3**, the cation Gd1 to the plane is 0.051 8 nm, similar to that in the complex **2** (0.058 5 nm). In complex **1**, the distances of potassium cation K1 and K2 to the portal planes are 0.084 4 and 0.090 4 nm respectively, there is no obvious difference. However, the distance of potassium cation K1 in complex **2** to the portal plane is only 0.048 7 nm, approximately 0.03 nm shorter than that in complex **2**. It suggests that the coordination of Gd1 to the other portal enlarges the size of the portal which coordinates with K1 cation, in order to effectively coordinate to the portal carbonyl oxygens, the K1 cation has to be close to the plane of five carbonyl oxygens. Thus, a shorter distance of K1 to the portal plane is observed in complex **2**.

3 Conclusions

In the present study, the coordination of two complexes (K-DMeQ[5] and Gd/K-DMeQ[5]) is discussed. The metal ions with larger ionic radius could lead to the full portal coordination, while the metal ions with smaller ionic radius could lead to the partial portal coordination in the Q[5]-based coordination chemistry. In conclusion, the metal ionic radius could significantly affect the coordination of a metal ion to the Q[n], and the study of this effect is in progress in our laboratory.

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