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ARTICLE TYPE

Unexpected crystallization of the metastable tubular coordination polymer of cucurbit[6]uril with magnesium ions which spontaneously transforms into discrete coordination complex

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We report on the the kinetic crystallization of the unpredicted tubular coordination polymer where magnesium ions bridge adjacent cucurbit[6]uril molecules. This metastable phase transforms spontaneously into thermodynamically favored discrete coordination complex.

10 The complexation of metal cations at the carbonyl-rimmed portals of cucurbiturils due to ion-dipole interactions is the inherent property of these pumpkin-shaped macrocyclic cavitands. It should be mentioned that the first structural characterization and revealing cucurbit[6]uril (CB6) macrocyclic nature was performed on its calcium sulfate coordination complex.¹ An early work on the one-dimensional coordination polymer of CB6 with rubidium ions was performed by Kim and coworkers.² Since then, a large number of structural studies have been conducted on the various cucurbituril complexes with metal cations, metal clusters and their corresponding counter-anions elucidating their rich coordination chemistry and potential for diverse nanoscale applications. The main achievements in the areas of cucurbituril-based coordination and host-guest/coordination chemistry have been recently highlighted by Tao and coworkers in their comprehensive review on the coordination complexes of the whole cucurbituril family.³ However, the coordination chemistry of cucurbiturils with light metal ions, such as lithium, beryllium and magnesium, has remained largely an unexplored area. Wei et al reported the 1:2 discrete coordination complex of tetramethylCB6 with Li⁺ ion.⁴ In the same study the authors suggested that Li⁺ and Mg²⁺ ions are too small to effectively coordinate to two adjacent cucurbituril molecules forming a polymeric structure. It was stated that strong repulsion would occur between the two portals of the two adjacent cucurbituril molecules bridged by the metal ions with small ionic radii. Recently, we have discovered that in the solid state only one portal of CB6 is coordinated to magnesium aqua complex cation, while another portal remains noncoordinated and is involved in multiple C-H...O interactions with the backbone of the neighboring CB6.⁵ We wondered if it is possible to obtain a complex with both portals of CB6 being magnesium covered and, furthermore, if such small cation can form coordination polymers with CB6. The unique advantages of divalent magnesium such as non-toxicity and biocompatibility make it promising for potential biomedical applications, for example, as drug carrier.⁶ Interestingly, the magnesium ions used to enhance CB6 solubility in water, turned out to be active

participants in the cocrystallization of cucurbit[6]uril with a catecholamine drug isoprenaline, evidently affecting the kinetics of crystallization of the host-guest complex, as well as its supramolecular aggregation in the crystal lattice.⁷ Namely, in the presence of magnesium ions the rapid crystallization of the metastable CB6-isoprenaline complex was observed, that transformed slowly into more stable magnesium-captured form of host-drug complex via a solution-mediated transformation. Lately, magnesium due to its potential gravimetric advantage for gas storage applications, turned out to be cheap, nontoxic, and green alternative to conventional MOFs, mostly based on transition or rare-earth metal ions.⁸ These has prompted us to undertake a detailed study on the magnesium coordination chemistry with cucurbiturils. Herein, we would like to report three crystal structures of CB6 coordination complexes with magnesium ions based on direct coordination of Mg²⁺ to cucurbituril portals. For the first time the unpredicted tubular coordination polymer with magnesium ions coordinated to adjacent CB6 molecules was obtained. However, the resulting crystals proved to be a metastable phase suffering spontaneous dissolution followed by crystallization of a new discrete coordination complex. In order to obtain CB6 coordination complexes with both portals being magnesium covered, we tried to manipulate the metal salt to CB6 ratio in the crystallization medium. However, no suitable crystalline material during evaporation of such aqueous solutions was obtained. Fortunately, the slow liquid diffusion of ethanol into solution containing CB6 and 100-fold excess of MgCl₂ resulted in the formation of small plate-like crystals of complex [Mg₂(CB6)(H₂O)₈]₄Cl₁₆·16H₂O (**1**). The X-ray analysis of **1** revealed the tubular coordination polymer of alternating CB6 and Mg²⁺ ions that extends parallel to the *a* axis. The asymmetric unit of **1** consists of one fourth of a CB6 molecule, half of a magnesium ion disordered over two positions Mg1 and Mg2 (refined as 53 and 47% occupancies), one half and two quarters of chloride anion, and numerous water molecules. Although the presence of ethanol is necessary for the crystallization of the coordination polymer, the ethanol itself is not involved in the

stabilization of the crystal lattice. Probably, the role of ethanol as a cosolvent in the crystallization of **1** is in decreasing solubility of CB6 and directing the crystallization pathway into the kinetically controlled formation of the metastable coordination polymer.

There are two different coordination modes of metal ion in the polymeric tube: Mg1 directly coordinates two carbonyl oxygen atoms (O2 from each portal) of two neighboring CB6 and four water molecules (O1W, O2W, O3W and O4W), Fig. 1a. While Mg2 coordinates two oxygen atoms from one portal (O1 and O2A), and four water molecules (O1WA, O4WA, O5WA and O6WA), Fig. 1b. Two Mg2 cations from neighboring portals in the chain are connected by sharing water molecule O5WA. Additionally, pair of two Mg2 ions bridged by water molecule is disordered over two positions due to crystallographically imposed symmetry (mirror planes). The tubular coordination polymer is formed by perfect alignment of CB6 molecules by direct coordination of Mg1 ions to two neighboring portals (Fig. 6c) or by coordination of Mg2 pairs sharing one water molecule (due to disorder 53% Mg1 and 47% Mg2).

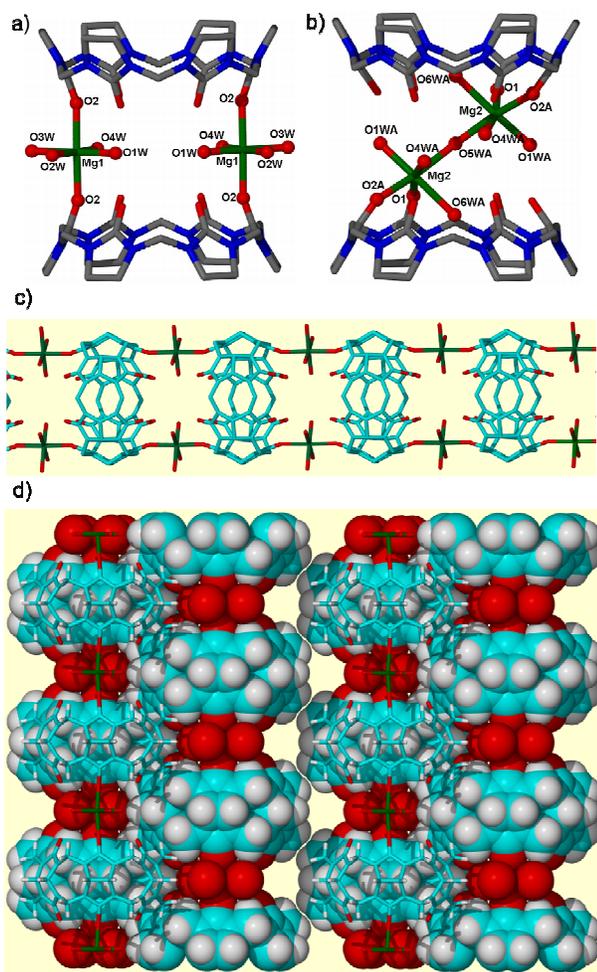


Figure 1. Coordination geometry around Mg1 (a) and Mg2 (b) ions in complex **1**. The Mg2 pair is disordered into two sites due to crystallographically imposed mirror symmetry (only one orientation is shown). (c) Tubular coordination polymer in complex **1** (only Mg1 ions are shown). (d) The packing arrangement of the coordination tubes along the *b* axis.

The crystals of complex **1** are not stable in the mother solution.

We noticed gradual vanishing of small plate-like crystals of **1** accompanied by appearance of larger block shaped crystals of **1** new phase over the period of several days. In other words, coordination polymer **1** is not stable enough to persist long in mother solution and is slowly transformed into more stable form of hydrogen-bonded supramolecular chain structure of complex [Mg₂(CB6)(H₂O)₈]₄Cl·14H₂O (**2**). Two complexes **1** and **2** have almost identical composition, but different coordination mode and connectivity between neighboring units. Obviously, the ionic radius of magnesium ion is too small to provide structure stability by direct coordination to two adjacent CB6 molecules, however, such coordination mode is still possible for such small cation!

The complex **2** was obtained from the water-ethanol solution of CB6 and magnesium chloride through dissolution of unstable complex **1**. In **2** both portals of cucurbituril are coordinated with magnesium cations in identical fashion, Fig. 2a. The asymmetric unit consists of half of the CB6 molecule with one coordinated magnesium, two chloride anions and water molecules. Each Mg²⁺ is coordinated with two carbonyl oxygen atoms (O3 and O4) and four water molecules (O1W, O2W, O3W and O4W). The coordinated water molecules are involved in extensive hydrogen bonding with carbonyl oxygen atoms and aqua ligands of the neighboring CB6, forming hydrogen-bonded supramolecular chain, Fig. 2c. The complex **2** is quite similar to tetramethylCB6 complex with Li⁺ ion where 1:2 stoichiometry and formation of hydrogen bonded supramolecular chains instead of coordination polymers was also observed.³

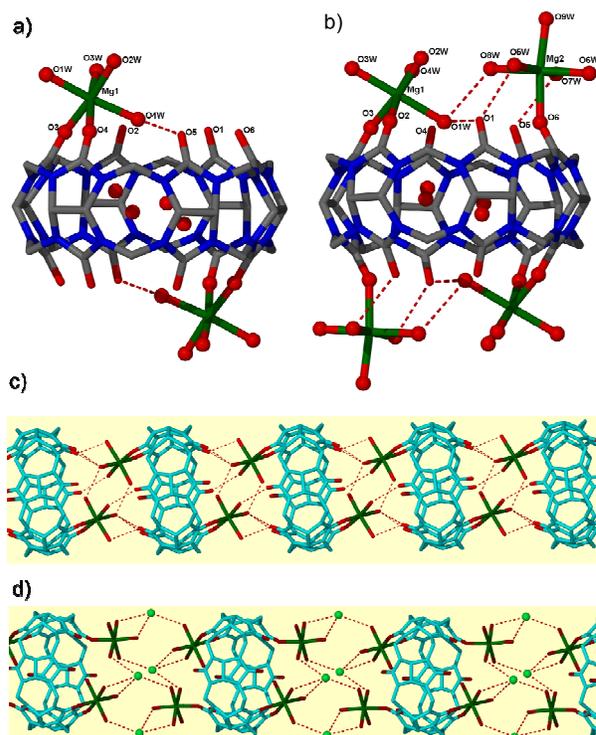


Figure 2. Discrete coordination complexes **2** (a) and **3** (b); (c) hydrogen bonded supramolecular chain in complex **2**; (d) anion-assisted hydrogen bonded supramolecular chain in complex **3**.

We have also found that it is possible to obtain 1:4 CB6 complex with magnesium when using very large excess of magnesium chloride (500 equivalents) in aqueous solution. In complex

[Mg₄(CB6)(H₂O)₁₈]·8Cl·7H₂O (**3**) both CB6 portals are coordinated with two magnesium ions, Fig. 2b. The asymmetric unit comprises half of the CB6 molecule with two coordinated magnesium ions, four chloride anions and water molecules. Two independent Mg²⁺ ions are coordinated to CB6 portals in different fashions. Namely, Mg1 is coordinated with two carbonyl oxygen atoms (O2 and O3) and four water molecules (O1W, O2W, O3W and O4W) in a similar way as in complex **2**. Another Mg2 ion is coordinated to one carbonyl oxygen atom O6 and five water molecules (O5W, O6W, O7W, O8W and O9W). The extended structure of **3** revealed the formation of hydrogen-bonded supramolecular chains, however, quite different to those in **2**. Evidently, the presence of two magnesium ions possessing a high charge-to-radius ratio per each portal provides strong repulsion between adjacent cucurbiturils and does not favor direct hydrogen bonding between aqua ligands from adjacent portals. Instead of this, the chloride anions serve as bridges and charge neutralizers between neighboring cucurbiturils holding them far apart from each other and stabilizing the structure, Fig 2d. The water-chloride distances are in the range 3.004-3.277 Å. So, in complex **3** the formation of anion-assisted hydrogen bonded supramolecular polymers is observed

In conclusion, we have described the kinetic crystallization of the unpredicted tubular coordination polymer followed by the thermodynamic crystallization of the discrete coordination complex on the dissolution of kinetic crystals. Both complexes are based on the direct coordination of magnesium ions to CB6 rims and are of the same molecular composition but differ in the coordination mode and connectivity between neighboring units. It is clear that metal-to-ligand ratio, i.e. the concentration of the magnesium salt in the crystallization set-ups, influences the stoichiometry of the CB6 coordination complexes that can vary from 1:1⁴ through 1:2 up to 1:4. Despite really extensive research in the area of cucurbituril coordination chemistry, our results highlight difficulty in the predictability of construction of cucurbituril coordination complexes, especially when kinetic factors come to play. Recently proposed design strategy based on the use of poly-chloride transition metal anions⁹ may prove useful in gaining more control in constructing CB6-Mg solid-state supramolecular assemblies in the future studies. On the other hand, knowledge about possibility of directing the crystallization of non-equilibrium cucurbituril complexes¹⁰ is likely to inspire new applications of these fascinating macrocyclic molecules.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, packing diagrams for complexes **1-3** and X-ray crystallographic files in CIF format. See DOI: 10.1039/b000000x/

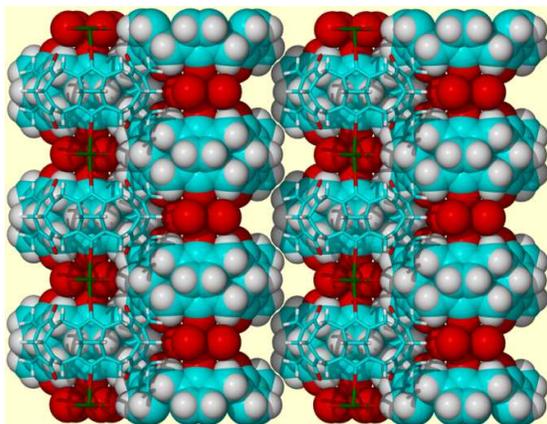
‡ **Crystal data for 1:** C₃₆H₈₄O₃₆Cl₄Mg₂N₂₄, *Mr* = 1619.6, colourless, 0.30 × 0.2 × 0.05, orthorhombic, space group *Pmnm*, *a* = 10.4811(4), *b* = 14.5008(5), *c* = 21.9334(8) Å, *V* = 3333.5(2) Å³, *Z* = 2, ρ_{calc} = 1.613 g·cm⁻³, $\mu(\text{Cu}_{\text{Ka}}$) = 2.786 mm⁻¹, θ_{max} = 71.7°, 8001 reflections measured, 3500

unique, 349 parameters, *R* = 0.088, *wR* = 0.247 (*R* = 0.104, *wR* = 0.264 for all data), *Goof* = 1.03. CCDC 970810.

Crystal data for 2: C₃₆H₈₀O₃₄Cl₄Mg₂N₂₄, *Mr* = 1583.6, colourless, 0.50 × 0.40 × 0.25, triclinic, space group *P-1*, *a* = 10.9150(2), *b* = 12.4577(2), *c* = 13.8264(2) Å, α = 106.243(1), β = 94.736(1), γ = 113.720(1)°, *V* = 1611.31(5) Å³, *Z* = 1, ρ_{calc} = 1.632 g·cm⁻³, $\mu(\text{Mo}_{\text{Ka}}$) = 0.315 mm⁻¹, θ_{max} = 28.7°, 13864 reflections measured, 8204 unique, 538 parameters, *R* = 0.043, *wR* = 0.112 (*R* = 0.047, *wR* = 0.115 for all data), *Goof* = 1.05. CCDC 970811.

Crystal data for 3: C₃₆H₈₆O₃₇Cl₈Mg₄N₂₄, *Mr* = 1828.1, colourless, 0.60 × 0.50 × 0.2, triclinic, space group *P-1*, *a* = 12.4536(2), *b* = 12.4913(2), *c* = 13.0575(2) Å, α = 110.575(1), β = 102.185(1), γ = 98.711(1)°, *V* = 1801.45(5) Å³, *Z* = 1, ρ_{calc} = 1.676 g·cm⁻³, $\mu(\text{Mo}_{\text{Ka}}$) = 0.456 mm⁻¹, θ_{max} = 28.7°, 29941 reflections measured, 9239 unique, 605 parameters, *R* = 0.044, *wR* = 0.096 (*R* = 0.052, *wR* = 0.103 for all data), *Goof* = 1.05. CCDC 970812.

- 1 W. A. Freeman, W. L. Mock, N.-Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367.
- 2 J. Heo, S.-Y. Kim, D. Whang, K. Kim, *Angew. Chem. Int. Ed.*, 1998, **38**, 641.
- 3 X.-L. Ni, X. Xiao, H. Cong, L.-L. Liang, K. Cheng, X.-J. Cheng, N.-N. Ji, Q.-J. Zhu, S.-F. Xue, Z. Tao, *Chem. Soc. Rev.*, 2013, DOI: 10.1039/C3CS60261C.
- 4 W.-J. Chen, D.-H. Yu, X. Xiao, Y.-Q. Zhang, Q.-J. Zhu, S.-F. Xue, Z. Tao, G. Wei, *Inorg. Chem.*, 2011, **50**, 6956.
- 5 O. Danylyuk, V. P. Fedin, *Cryst. Growth Des.*, 2012, **12**, 550.
- 6 H.-N. Wang, X. Meng, X.-L. Wang, G.-S. Yang, Z.-M. Su, *Dalton Trans.*, 2012, **41**, 2231.
- 7 O. Danylyuk, V. P. Fedin, V. Sashuk, *CrystEngComm*, 2013, **15**, 7414.
- 8 (a) A. E. Platero-Prats, V. A. de la Peña-O'Shea, D. M. Proserpio, N. Snejko, E. Gutiérrez-Puebla, Á. Monge, *J. Am. Chem. Soc.*, 2012, **134**, 4762; (b) D. Banerjee, J. Finkelstein, A. Smirnov, P. M. Forster, L. A. Borkowski, S. J. Teat, J. B. Parise, *Cryst. Growth Des.*, 2011, **11**, 2572; (c) Y. Filinchuk, B. Richter, T. R. Jensen, V. Dmitriev, D. Chernyshov, H. Hagemann, *Angew. Chem. Int. Ed.*, 2011, **50**, 11162.
- 9 (a) L. L. Liang, X. L. Ni, Y. Zhao, K. Chen, X. Xiao, Y. Q. Zhang, C. Redshaw, Q. J. Zhu, S. F. Xue, Z. Tao, *Inorg. Chem.*, 2013, **52**, 1909; (b) L. L. Liang, K. Chen, N. N. Ji, X. J. Cheng, Y. Zhao, X. Xiao, Y. Q. Zhang, Q. J. Zhu, S. F. Xue, Z. Tao, *CrystEngComm*, 2013, **15**, 2416.
- 10 (a) L. Liu, N. Nouvel, O. A. Scherman, *Chem. Commun.*, 2009, 3243; (b) O. Danylyuk, V. P. Fedin, V. Sashuk, *Chem. Commun.*, 2013, **49**, 1859.



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