Electronic Supplementary Information

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

Oksana Danylyuk*[a] and Vladimir P. Fedin[b]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland. e-mail: odanylyuk@ichf.edu.pl*

[b] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Acad. Lavrentiev. Ave., 600090 Novosibirsk, Russian Federation.*

Crystallization of complexes 1-3.

$[Mg_2(CB6)(H_2O)_8]\cdot 4Cl\cdot 16H_2O$ (**1**) and **$[Mg_2(CB6)(H_2O)_8]\cdot 4Cl\cdot 14H_2O$** (**2**). $CB6\cdot 10H_2O$ (20 mg, 17 μmol) and 100-fold excess of $MgCl_2\cdot 6H_2O$ (346 mg, 1.7 mmol) were dissolved in distilled water (1 ml) upon gentle heating. The ethanol (0.5 ml) was carefully layered upon solution of CB6 and $MgCl_2$ to create an interface. The slow liquid diffusion of ethanol into an aqueous solution containing CB6 and $MgCl_2$ resulted in the formation of small plate-like crystals of complex **1** after 2 days. When kept in mother liquid the crystals of complex **1** underwent gradual dissolution accompanied by crystallization of larger block-shaped crystals of complex **2** over the period of several days.

[Mg_4(CB6)(H_2O)$_{18}$]·8Cl·7H_2O (**3**). CB6·10H_2O (20 mg, 17 μmol) and 500-fold excess of $MgCl_2$·6H_2O 1730 mg, 8.5 mmol) were dissolved in distilled water (2 ml) upon heating and under stirring. The block-shaped crystals of complex **3** appeared after several days.

Crystallography. The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. Uniformity of the samples was checked by cell determination of several crystals for each sample. The X-ray data for complex **1** were collected at 100(2)K on a SuperNova Agilent diffractometer using Cu*Kα* radiation (λ = 1.54184 Ǻ). The data were processed with *CrysAlisPro.*[i] The X-ray data for complexes **2** and **3** were collected at 100(2)K on a Nonius KappaCCD diffractometer using Mo*Kα* radiation (λ = 0.71073 Ǻ). The data were processed with *HKL2000.*[ii] The solution, refinement and analysis of the structures were done using the software integrated in the *WinGX* system.[iii] Structures were solved by direct methods using *SHELXS-97*and refined using *SHELXL-97.*[iv] All non-hydrogen non-disordered atoms were refined with anisotropic displacement parameters. Some lattice water molecules and chloride anions were given partial occupancy factors in order to retain acceptable displacement parameters and/or to account for too close contacts. The magnesium ion and its aqua ligands in complex **1** were refined as disordered over two positions (Mg1 and Mg2) with sum of occupancy parameters restrained to 0.5 due to crystallographic symmetry imposition: Mg1 ion lies on the mirror plane, while occupancy parameter for Mg2 ion accounts for its closeness to its image by another mirror plane. One of the CB6 carbonyl oxygen atoms in **1** was modeled as disordered over two positions O2 and O2A, coordinated to Mg1 or Mg2, respectively. Where possible the hydrogen atoms of water molecules were found on Fourier-difference maps. Some solvent water molecules in compounds **1** and **2** have been modeled without hydrogen atoms. The figures were prepared using *X-Seed*[v]*/ POV-Ray.*[vi]

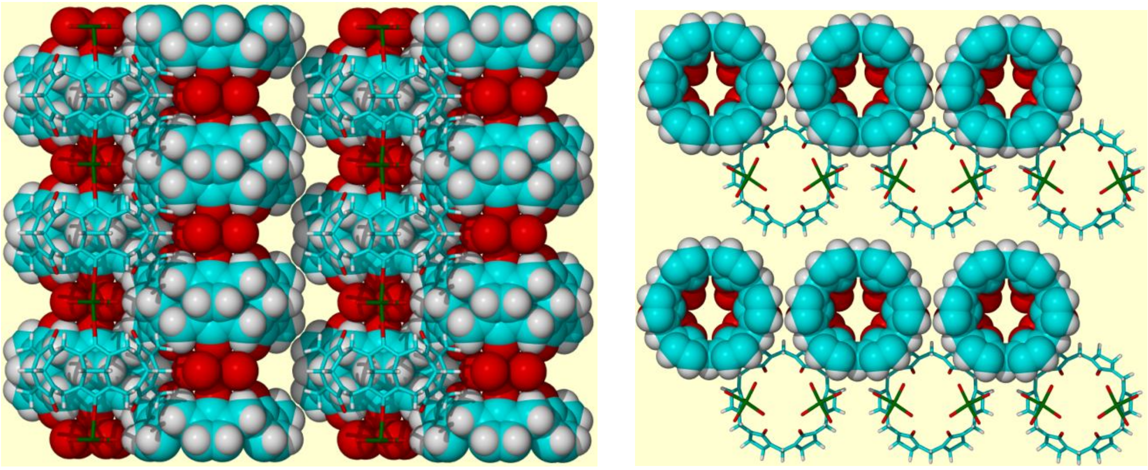

Figure 1. Packing diagrams of the complex 1.

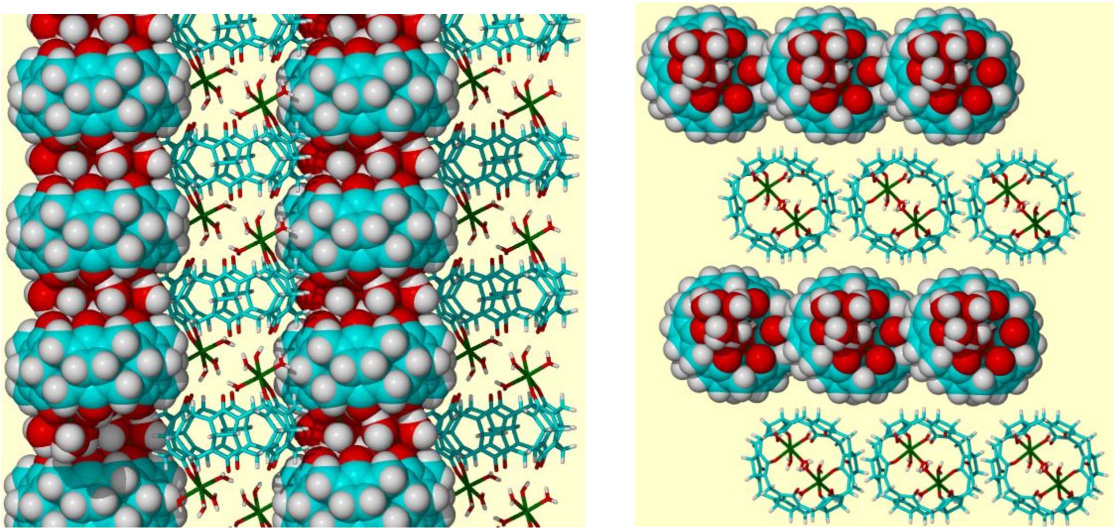

Figure 2. Packing diagrams of the complex 2.

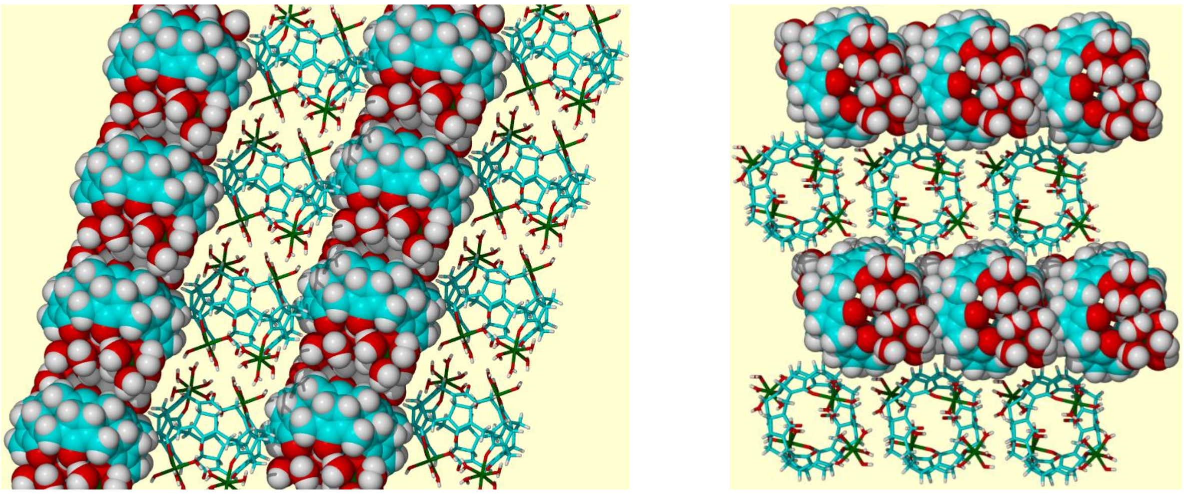

Figure 3. Packing diagrams of the complex 3.

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[i] Agilent. *CrysAlis PRO*; Agilent Technologies UK Ltd: Yarnton, U.K., 2011.

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[v] Barbour, L. J. *J. Supramol. Chem*. **2001**, *1*, 189-191.

[vi] *POV-Ray*, version 3.6; Persistence of Vision Pty. Ltd., Persistence of Vision Raytracer, 2004; available at http://www.povray.org/.