

One-dimensional void-space arrays constructed from a coordination polymer with bowl-like frameworks of cavitands†

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A one-dimensional coordination polymer of $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ bridged by new bowl-like ligands of cavitands was prepared and the crystal structure was determined by X-ray crystal analysis. Ethyl acetate molecules are necessarily included as guest molecules in each of the void-space cavities of the cavitands, and then are held by weak interaction forces.

Molecular crystals with closed inter-spaces (void-spaces) have been recognized as a novel hollow material that can perform uptake and release of small organic molecules¹ and gases like H_2 ² in the crystalline-state without open channels. Modifying the alignments of void-spaces is important for creating new hollow materials with this attractive functionality and understanding the guest-transport mechanism. Therefore, we have carried out crystal designs to control the alignments of void-spaces originating from the bowl-like frameworks of cavitands with coordination sites. The cavitands can fabricate multi-dimensional super-structures by using metal configurations.

Cavitands are supramolecular robust compounds with a bowl-shape, which are made up from four methylene-bridging portions with eight OH groups in calixresorsinane.³ They play an important role in host-guest chemistry as not only fundamental frameworks in preparation of carcerands, hemicarcerands and other large organic hosts,^{4–7} but also as cyclic host compounds taking a guest molecule into the cavity by non-covalent interactions. Furthermore, cavitands with coordination sites can construct capsules^{8–11} and cage¹² assembled by transition metal ions and their crystals have necessarily formed void-spaces. In order to control the alignments of void-spaces in the crystal, we intend to find a rational synthesis of coordination polymers bridged by cavitands with such coordination sites. Here we report the synthesis and crystal structure of a 1-D coordination polymer $\{[\text{Mn}^{\text{II}}(\mathbf{1})(\text{hfac})_2] \cdot 3\text{AcOEt}\}_n$ (**2**) with a 1 : 1 composition of **1** and $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ (hfac = hexafluoroacetylacetonate).

We have designed a new bridging ligand **1** with a cavitant framework, which can coordinate to metal ions and control the assembling structures of coordination polymers as a zero-dimensional (0-D) capsule, a one-dimensional (1-D) chain and a two-dimensional (2-D) square grid, as shown in Fig. 1. Compound **1** has a robust C–C covalent-bond with the 5-position of a pyrimidyl ring at each 2-position of four resorcinol rings. Generally, cavitands are a cone structure supported by a square framework of four alkyl chain feet (the chain feet of **1** are

phenethyl groups) as depicted in Fig. 2. The part close to the bottom of their cavity is defined by a 16-membered *meta*-cyclophane ring, whereas the open top is defined by a ring containing eight oxygen atoms within a 24-membered ring. The base angle (α) of the cone in the cavitant of **1** is nearly 60° .¹³ Two N atoms in a pyrimidyl group on **1** can coordinate to metal ions in two directions, an inner convergent **A** and an outer divergent **B**, at angles of $\sim 120^\circ$ from the cone sides. This coordination motif of **1** provides a variety of coordination modes: a discrete capsule is constructed by connecting two molecules of **1** through coordination to metal atoms using eight N atoms of **A** in pyrimidyl groups

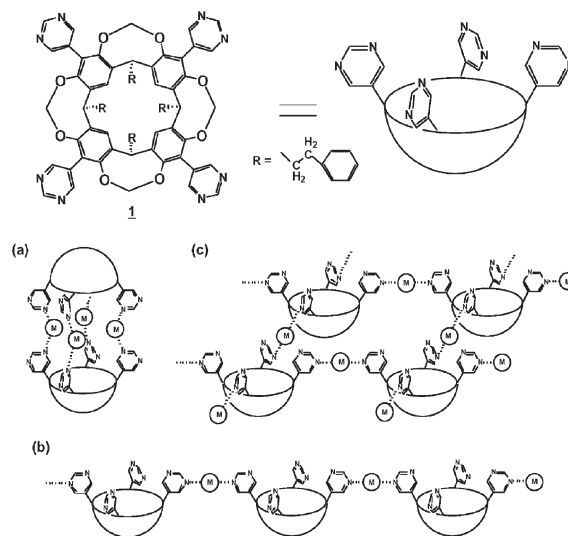


Fig. 1 Controlled crystal arrays formed from **1** and transition metal complex: (a) cage, (b) one-dimensional chain, (c) two-dimensional sheet.

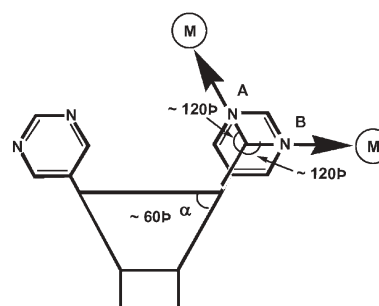


Fig. 2 Schematic representation of a conical formation with the cone structure of cavitands supported on a square framework α : the cone tilting angle, **A**: the inner convergent nitrogen atom of the pyrimidyl group and **B**: the outer divergent atom.

† Electronic supplementary information (ESI) available: experimental details, X-ray structure report and molecular structures. See <http://www.rsc.org/suppdata/cc/b4/b415374j>
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(Fig. 1a). A 1-D polymer chain can be obtained by the coordination of each N atom of **B** to metal atoms to make a diagonal line array of pyrimidyl groups. Therefore, the void-space cavities are oriented one-dimensionally (Fig. 1b). When coordination polymers are bridged by all four N atoms of **B**, a 2-D square grid is formed (Fig. 1c).

The tetrabromocavitand was prepared according to the method described in a previous report.¹⁴ The treatment of 5-bromopyrimidine with *n*-butyl lithium and trimethyl tin(II) chloride at $-78\text{ }^{\circ}\text{C}$ in THF gave trimethylstannyl tin pyrimidinate in high yield. Compound **1** was prepared by the reaction of a tetrabromocavitand and 4 equiv. of trimethylstannyl tin pyrimidinate with a small amount of $\text{PdCl}_2(\text{PPh}_3)_2$ catalyst in toluene at $110\text{ }^{\circ}\text{C}$ for six days, and purified by silica-gel column chromatography (eluent; CH_2Cl_2 : EtOH = 85 : 15) in a yield of 53.2%. We succeeded in complexation of **1** with $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ in AcOEt to yield yellow prismatic crystals of **2**. The crystals consist of an alternating chain of **1** and $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ components in a 1 : 1 ratio. A similar reaction of **1** and $[\text{Cu}^{\text{II}}(\text{hfac})_2]$ afforded **3** in green crystals, which also have a 1 : 1 composition of **1** and $[\text{Cu}^{\text{II}}(\text{hfac})_2]$, like **2**. In contrast, the reaction of **1** with $[\text{Ni}^{\text{II}}(\text{hfac})_2]$ or $[\text{Co}^{\text{II}}(\text{hfac})_2]$ gave light-green (**4**) or orange micro-crystals (**5**), respectively, and both show a 2 : 1 composition between **1** and the metal complexes. X-Ray crystal analysis was carried out on a single crystal of **2** only.

The asymmetric unit in a crystal of **2** is made up of $[\text{Mn}^{\text{II}}(\text{hfac})_2]$, **1**, an included AcOEt and two other solvated AcOEt molecules.¹⁵ The pyrimidyl groups on **2** orient by roughly $58\sim 84^{\circ}$ angles toward resorcinol rings. The corresponding angle for **1** without a guest molecule is estimated to be about 65° as an average value from MM2 theoretical calculation.¹⁶ The angles occur due to a steric repulsion between H atoms of $-\text{CH}_2-$ bridging groups of cavitands and those of a 4- or 6-position on pyrimidyl groups and their interaction is observed by NOE correlation using 2D-NMR spectra of **1** (Fig. 1S, see ESI†). Two pyrimidyl groups in a diagonal line on **1** coordinate to two different $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ at the axial positions to create coordination polymer **2** with 1-D chains. (Fig. 3) The closest intra-chain Mn–Mn distance in **2** is 17.67 \AA , and the closest inter-chain Mn–Mn distance between is 9.65 \AA . Each chain in the *ac* plane is located in the parallel arrangements to the diagonal direction. The *ac* planes stack in mirror symmetry along the *b* axis with deviations of about 8 \AA in the direction (0, 0, *c*/2). The characteristic feature of **2** is that AcOEt molecules are completely included as a guest in all cavities of cavitands (Fig. 2S, see ESI†). The precise positions of other solvated AcOEt molecules could not be determined because of the disordering. The included AcOEt are stabilized not only by $\text{CH}\cdots\pi$ interactions between a methyl group of AcOEt and four resorcinol

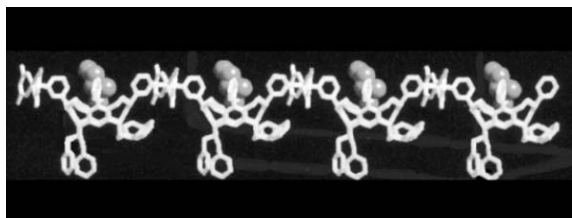


Fig. 3 The structure of coordination polymer **2** with one-dimensional chains with alternative linkage between $[\text{Mn}^{\text{II}}(\text{hfac})_2]$ and **1**.

rings, but also by $\text{CH}\cdots\text{O}$ hydrogen bonds between two O atoms in AcOEt and H atoms at a 4- or 6-position in four pyrimidyl groups (Fig. 3S, see ESI†). The $\text{CH}\cdots\text{O}$ hydrogen bonds have $\text{C}\cdots\text{O}$ distances in the range of about $3.41\text{ \AA}\sim 3.71\text{ \AA}$ ($\text{O}(13)\text{--C}(34) = 3.51(2)\text{ \AA}$, $\text{O}(13)\text{--C}(38) = 3.68(2)\text{ \AA}$, $\text{O}(14)\text{--C}(44) = 3.41(2)\text{ \AA}$, $\text{O}(14)\text{--C}(48) = 3.71(2)\text{ \AA}$) (Fig. 4S, see ESI†). Practically, NMR spectra on **1** in d^8 -AcOEt solvent has revealed that the singlet peak (8.46 ppm) for protons in the 4- and 6-positions of pyrimidyl groups separates to two peaks at low temperature due to hydrogen bonding interactions with the guest molecule. The coalescence temperature at $-75\text{ }^{\circ}\text{C}$ corresponds to an activation energy of *ca.* 40 kJ mol^{-1} for a rotational motion (Fig. 5S, see ESI). The included AcOEt in **2** would have such a motion in the cavities in a solid, but solid-state NMR on **2** can not identify its motion because of the paramagnetic Mn(II) complex.

In this report, we have for the first time characterized **2** as a 1-D chain of **1** bridged by $[\text{Mn}^{\text{II}}(\text{hfac})_2]$. The alignments of the void-space cavities can be modified within crystals by formation of coordination polymers such as a capsule, a chain like **2** and a grid structure, which are controlled by metal configurations with the linear didentate coordination and rotational directions of pyrimidyl groups of **1**. Each void-space of **2** incorporates an AcOEt molecule held by $\text{CH}\cdots\text{O}$ hydrogen bonds with the pyrimidyl groups and $\text{CH}\cdots\pi$ interactions with the resorcinol rings. The included AcOEt molecules would be able to move rotationally in the crystal. The obtained **3** may possess a 1-D linear coordination polymer structure like **2** because **3** shows an analogous IR spectra and a 1 : 1 composition ratio of $[\text{Cu}^{\text{II}}(\text{hfac})_2]$ and **1**. In contrast, **4** and **5** would probably be formed from coordination polymers composed of 2-D square grids or capsules because of different compositions, with a 1 : 2 ratio of $[\text{M}^{\text{II}}(\text{hfac})_2]$ ($\text{M} = \text{Ni}, \text{Co}$) to **1**.

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- 15 Crystal structure determination of **2**: C₁₀₂H₉₀O₁₈N₈F₁₂Mn, $M_t = 1998.79$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.689(4)$, $b = 44.935(6)$, $c = 16.354(4)$ Å, $\beta = 108.50(2)^\circ$, $V = 9539(4)$ Å³, $Z = 4$, $T = -70$ °C, $\rho_{\text{calcd}} = 1.392$ g cm⁻³, $F(000) = 4140.00$, 1034 parameters, Sift/Error = 0.011, and $R_1 = 0.082$ and $R_w = 0.122$ and GOF = 1.31 for all 5503 data ($I > 3\sigma(I)$), values of minimum and maximum residual electron density 1.27 and -0.64 e Å⁻³. Diffractometer, Rigaku AFC7R; $\mu(\text{MoK}\alpha) = 2.35$ cm⁻¹; Lp collected; 16524 reflections collected; computing structure solution, SIR 92; computing structure refinement, DIRDIF92; reflections were refined based on F_o by full matrix least squares. C–F bond distances on two hexafluoroacetylacetonate ligands were restricted to 1.31 Å and each F atom using the distributed occupancy factors, C(81), C(83), C(86) and C(90) was fixed and excluded from the final refine. EtOAc molecules without the inclusion into the cavitands were also calculated isotropically to fix the respective atom positions and bond distances of C–O (1.45 Å), C=O (1.35 Å) and C–C (1.65 Å). CCDC 251793. See <http://www.rsc.org/suppdata/cc/b4/b415374j/> for crystallographic data in .cif or other electronic format.
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