

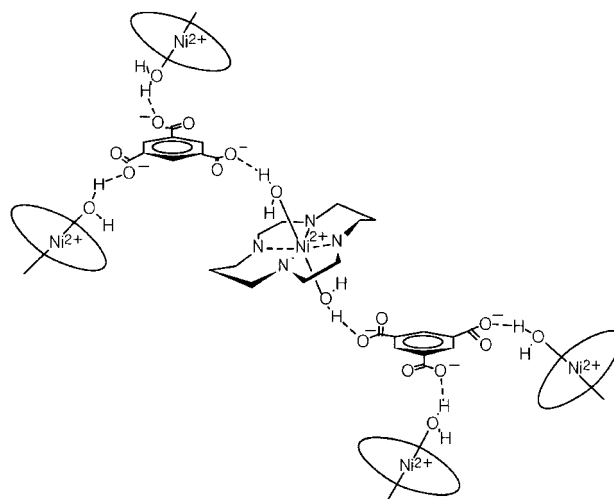
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- [29] The nuclear charges of the hydrogen link atoms have been adjusted according to the formal charge contribution of the zinc (0.5) and silicon atoms (1.0) which they replace. The link atoms have been set in the direction of the replaced atoms, with the O–H distance optimized at the DFT level. The positions of the link atoms have been kept fixed in all subsequent calculations.
- [30] This is a very simplified view. More likely the protons will be able to distribute themselves over the available surface oxygens. The reaction will only occur when the proper silanol group is carrying a proton. In the course of this work we did not investigate the activation barriers for the proton transfers.
- [31] A Gibbs energy of activation ($\Delta G^\ddagger$) will still exist because the activation entropy should be negative.
- [32] Preliminary kinetic results show the reaction to be first order in the partial pressure of methanol and lower than first order in allene. A strong inhibition by methanol, but no inhibition by 2-methoxypropene, is found, in spite of the fact that the calculated desorption energy of 2-methoxypropene is 19 kJ mol^{−1} higher than that of methanol. A possible explanation would be that product desorption occurs through an addition–elimination mechanism.
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Self-Assembly of a Molecular Floral Lace with One-Dimensional Channels and Inclusion of Glucose**

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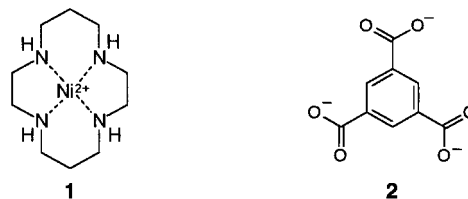
Supramolecular chemistry has advanced to a stage at which we can design and construct molecular solids with specific network topologies^[1] as well as with potentially interesting properties.^[2] Self-assembly of organic molecules and metal-ion building blocks may yield multidimensional networks containing channels or cavities of various sizes and shapes.^[3, 4] However, macrocyclic complexes have seldom been used in the construction of supramolecular networks although they could be used as the multifunctional building blocks.^[5]

Here we present a novel three-dimensional network containing one-dimensional channels, which is assembled by a nickel(II) macrocyclic complex. Our construction strategy (Scheme 1) was based on the ability of the nickel(II) complex



Scheme 1. Proposed formation of the network.

of cyclam (**1**) to bind water as the axial ligands^[6, 7] and hydrogen bond formation between the coordinated water molecules of the complex and the carboxylate oxygen atoms of 1,3,5-benzenetricarboxylate trianion (BTC^{3−}; **2**). Some



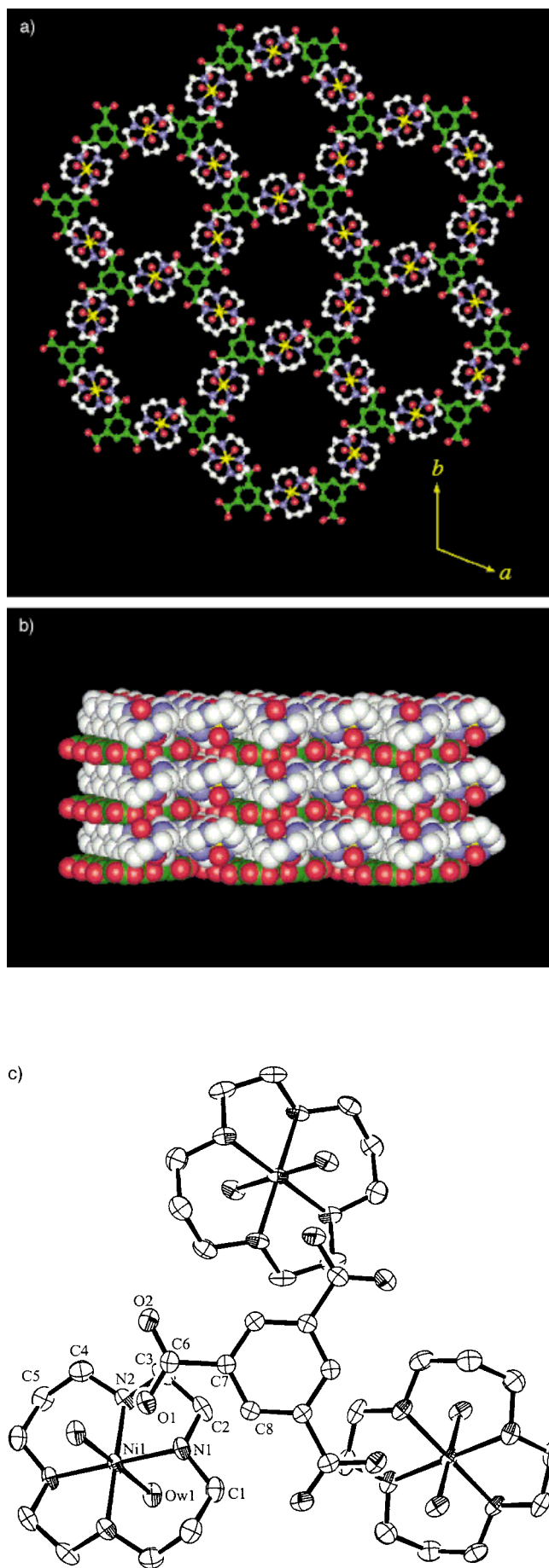
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nickel(II) macrocyclic complexes with a square-planar coordination geometry are in equilibrium in aqueous solution with the six-coordinated species that binds two water molecules at the *trans* position, with cyclam being the best ligand known to produce the six-coordinated species.^[6] In addition, **2** can be used as trigonal three-connectors in the construction of supramolecular assemblies.^[3b, 5, 8] Although H₃-**2** itself forms two-dimensional infinite honeycomb grids, their pores are usually filled by interpenetration or catenation of other grids and thus extremely few uncatenated structures of H₃-**2** are reported in which the cavities are occupied by some organic guests.^[9] Therefore, if **1** and **2** are self-assembled in water, each nickel(II) macrocycle will interact with two units of **2** up and down with respect to its macrocyclic plane and each unit of **2** will interact with three nickel(II) units since **2** contains three carboxylate groups. Based on this building scheme, the assembly will lead to a three-dimensional network.

A three-dimensional supramolecular network [Ni(cyclam)(H₂O)₂]₃[C₆H₃(COO)₃]₂·24H₂O (**3**), which can be regarded as a molecular floral lace, has been assembled by **1** and **2** in water. The supramolecule **3** is extremely stable. It is insoluble in common organic solvents or in cold water and it maintains its crystal morphology even after the crystal is heated at 140°C. Single crystal X-ray analysis of **3**^[10, 11] revealed the structure shown in Figure 1. Viewed down the *c* axis, it is composed of rings, each of which consists of six nickel(II) macrocyclic complexes and six of the anions **2**, each being related with *S*₆ symmetry. Every nickel(II) macrocyclic complex is shared by two rings and every anion **2** is shared by three rings, which corresponds to the stoichiometry of the network Ni^{II}/2 = 3/2. The network generates prominent channels parallel to the *c* axis. In the three-dimensional network, nickel(II) macrocyclic complexes lie in a layer extending along the *ab* plane. The anions **2** lie on the other layer parallel to the *ab* plane. These positively charged inorganic and negatively charged organic layers are alternately packed. The distance between the centers of the positive and negative layers is 3.70 Å, so there is no open space on the *bc* or *ac* plane. Every nickel(II) complex of cyclam forms hydrogen bonds with two of the anions **2** located up and down with respect to its coordination plane with an inversion center at its nickel(II) ion.^[11] In addition, every anion **2** forms hydrogen bonds with three of the cyclam units. The macrocyclic coordination planes are tilted with respect to the benzene plane of the interacting anion **2** with a dihedral angle of 40.7°. The planes of the three macrocyclic rings linked to the anion have dihedral angles of 69.1° between them. The effective void of the channels is 10.3 Å in diameter, as measured by the distance between van der Waals surfaces of opposing macrocyclic walls. The channels are filled with guest water molecules, some of which are hydrogen bonded with oxygen atoms of **2**.^[12]

Figure 1. a) View of the *ab* plane in **3**. Water molecules included in the channels are omitted for clarity (yellow: nickel(II), red: oxygen, blue: nitrogen, white: carbon of macrocycle, green: carbon of **2**). b) CPK representation of the *ac*–*bc* plane of **3**. c) ORTEP drawing of the asymmetric unit of **3** showing the numbering scheme. The bond distances and angles are listed in ref. [11]. The atoms are represented by thermal ellipsoids at 30% probability. The center of symmetry is at the Ni^{II} atom.



Molecular-based materials that are stable even after removal of guests are important in view of the development of a new class of porous substances. Hydrogen-bonded organic networks are generally less robust than the inorganic analogues that are held together by covalent bonds. However, there are a number of open networks that are stable enough to sustain the frameworks upon partial or complete removal of guests.^[4b, 13] Thermal gravimetric analysis (TGA) data for the crystalline sample **3** indicate three stepwise losses of weight at 54, 85, and 135 °C, which correspond to the loss of 12 simple guests, 12 hydrogen-bonded water guests, and then two coordinated water molecules, respectively, per formula unit. The remaining compound can be heated to 210 °C without any additional weight loss. Differential scanning calorimetry (DSC) data show the phase changes at 95, 106, and 130 °C. The crystal morphology of **3** is maintained throughout the heating processes up to 140 °C.

X-ray diffraction (XRD) patterns of the dried solids are compared with those of **3** in Figure 2. The solid obtained by heating the crystals of **3** to 55 °C shows XRD patterns in which the positions and intensities of some lines are slightly changed

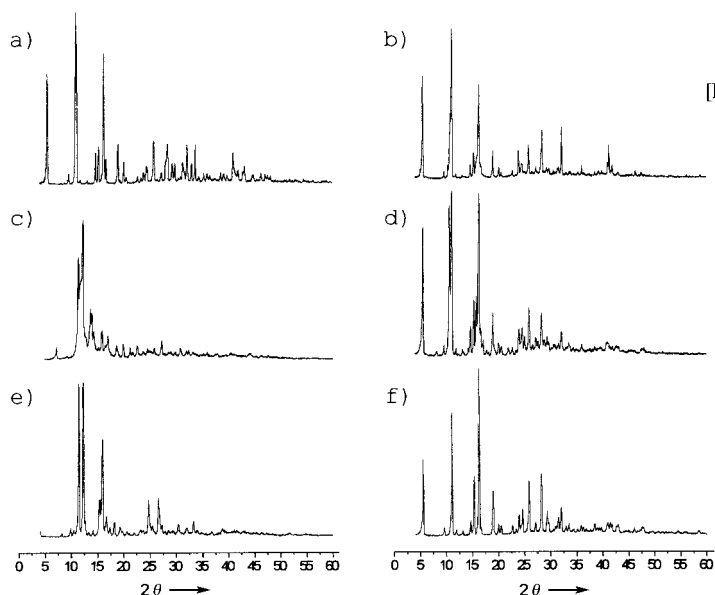


Figure 2. X-ray diffraction patterns for: a) the original crystal **3**, b) solid heated to 55 °C, c) solid heated to 90 °C for 2 h, d) solid obtained by immersing (c) in H₂O, e) solid heated to 135 °C, f) solid obtained by immersing (e) in H₂O.

relative to those of the original sample. When crystals of **3** are heated at 90 °C for 2 h, they show XRD patterns in which the lines are broadened and their positions are moved relative to those of **3**. However, when this solid is suspended in water the same XRD patterns as those of the original crystal are regenerated. Further heating of the dried solid to 135 °C results in sharp XRD lines whose positions are different from those of the original solid. The same XRD pattern as for **3** is, however, also regenerated when this solid is immersed in water for a few minutes.

D-Glucose and maltose, a dimer of glucose, were examined for inclusion into **3**.^[14] The binding experiments were carried

out in methanol containing 5 % water at 30 °C with the host dried at 90 °C for 2 h.^[15] D-Glucose was chosen as the guest molecule for **3** in view of its compatible molecular dimensions with the channel size and possibility to form hydrogen bonds with **2** in the channels. On the other hand, maltose is too large to be included in the channels.^[14]

The formation constant K_f for the complex formed between a guest molecule (G) and a binding site (BS) of an insoluble host can be defined as k_{ad}/k_{de} for Equation (1) by analogy with the Langmuir isotherm for adsorption of gas molecules on solid surfaces.^[16]



The plot of the concentration of G bound to BS ($[\text{BS} \cdot \text{G}]$) against total concentration of G ($[\text{G}]_0$) is illustrated in Figure 3 for complexation of glucose to **3**. Analysis of the

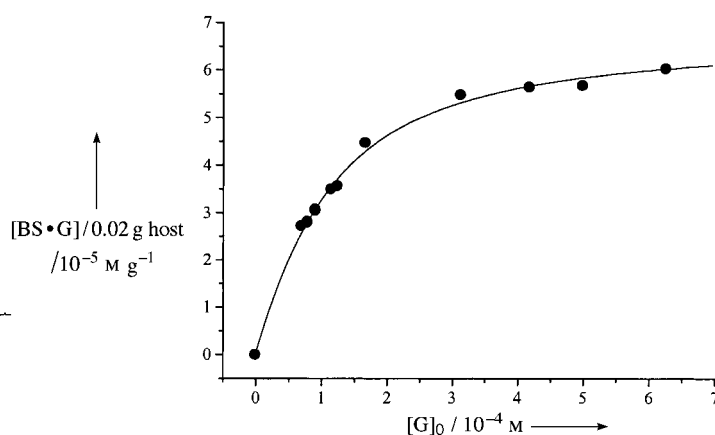


Figure 3. Binding of D-glucose to **3**.

data for glucose complexation according to a method described previously^[17] led to $K_f = (1.38 \pm 0.01) \times 10^4 \text{ M}^{-1}$.^[18, 19] The number of glucose binding sites occupied in **3** for the particular solids used in the binding experiment was estimated as $0.405 \pm 0.004 \text{ mol \%}$ relative to the formula unit of $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]_3[\text{C}_6\text{H}_3(\text{COO})_3]_2$. The small number of the binding sites occupied suggests that inclusion of a glucose molecule effectively blocks succeeding inclusion of glucose molecules into the deeper side of the channels of **3**. In contrast to glucose, complexation of maltose to **3** was not detected, which suggests that the sugar binding is made through the inclusion into the channels rather than adsorption on the surface.^[15] The selective binding of **3** with glucose must be attributable to the size fit for glucose into the channels.

In conclusion, we have showed that we were able to create a molecular artwork by crystal engineering. We also demonstrated that a macrocyclic complex was utilized in the construction of hydrogen-bonded three-dimensional networks with one-dimensional channels. We are now extending this result by the preparation of some open frameworks with pore channels of various hole sizes through variation of the macrocycles and the bridging molecules.

Experimental Section

3: An aqueous solution (5 mL) of Na₃BTC (0.21 g) was added to a hot aqueous solution (15 mL) of [Ni(cyclam)](ClO₄)₂^[20] (0.52 g) and the solution allowed to stand at room temperature for several hours to give a good yield (ca. 75 %) of long rod-shaped pale-purple crystals.^[21, 22] Compound **3** is insoluble in common organic solvents or in cold water and maintains its crystal morphology except in alcohol where it turns into powder.

Binding experiments: Crystals of **3** were ground in a mortar until they became microcrystalline and then dried in an oven at 90 °C for 2 h.^[15] The transparent pale purple sample lost its transparency. The dried solid was preserved in a desiccator containing 4 Å molecular sieves. A stock solution of glucose was made in water and diluted with a 5 % solution of H₂O in MeOH. The glucose solution (1.00 mL) of various concentrations was added to each tube containing 0.020 g of dried host, and incubated at 25 °C in a shaker for 3 h. The amount of uncomplexed glucose was determined with glucoseoxidase.^[23, 24] The binding of maltose to **3** was studied under identical conditions. For determination of uncomplexed maltose, the maltose was converted into glucose with α -glucosidase and the resulting glucose was quantified by the aforementioned method.

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- [11] Relevant bond lengths [Å] and angles [°]: Ni1–N2 2.057(3), Ni1–N1 2.070(3), Ni1–OW1 2.160(3), O1–C6 1.266(4), C6–O2 1.249(4), C7–C8 1.383(5); N1–Ni1–N2 85.50(12), N2–Ni1–OW1 87.66(12), N1–Ni1–OW1 91.39(11), O2–C6–O1 124.9(3), C8–C7–C6 120.6(3). Hydrogen bonding interaction: O1–OW1' 2.701 Å, O1–HW1A–OW1' 171°.
- [12] Among the 24 water guest molecules per formula unit, 12 are hydrogen bonded with carboxylate oxygen atoms of **2** that are uninvolved in the hydrogen bonding with coordinated water molecules. O–O 2.743–2.748 Å.
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