Zinc Silicates: Very Efficient Heterogeneous Catalysts for the Addition of Primary Alcohols to Alkynes and Allenes**

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Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

The addition of alcohols to alkynes is usually achieved in the liquid phase with mercury(II) or gold(I) catalysts under acidic conditions near room temperature. The products that are usually formed stem from a double addition (acetals).[1] With the use of a strong base like KOH as catalyst at elevated temperature only the monoaddition products are obtained (vinyl ethers, products of Reppe vinylation).[2]

Supported zinc and cadmium carboxylates, for example metal acetates supported on charcoal, have long been known as catalysts for the addition of carboxylic acids to acetylene in the gas phase.[2] However, this reaction can also be accomplished in the liquid phase with the metal carboxylates as homogeneous catalysts. The addition of acetic acid to acetylene in the gas phase was the main process for the large-scale synthesis of vinyl acetate until the late 1960s. Vinyl propionate is still being produced nowadays with zinc propionate on active charcoal as the catalyst.[3]

In contrast, the addition of alcohols to acetylenes using zinc catalysts has never been extensively investigated, although vinyl ethers are produced industrially on a large scale. In the literature, only the addition of methanol to propyne and allene in the gas phase above 250 °C with zinc oxide or zinc nitrate supported on active charcoal or silica gel as the catalyst has been described by Temkin and co-workers.[4] However, no information regarding the catalyst preparation or the reactor used was given.

Propyne and allene are formed in large amounts as by-products in the process of steam cracking for ethylene synthesis, but up to now there have not been many attempts to use them.[5] The methanol addition product 2-methoxypropene, which can be viewed as an activated acetone, is an interesting intermediate[6] and led us to investigate this chemistry in detail.

In an attempt to reproduce the results reported by Temkin and co-workers,[4a] we synthesized zinc oxide supported on commercially available, high-surface silica or active charcoal by thermal decomposition of previously deposited basic zinc carbonate.[7] However, the catalyst turned out to be inactive. In an attempt to reproduce some further results described by Temkin and co-workers,[4b] catalysts consisting of zinc nitrate or zinc acetate supported on the carriers mentioned above were prepared. However, upon testing at 275 °C the fresh catalysts showed only a small activity. Interestingly, when they were tested at lower temperatures (ca. 185 °C), the catalysts containing zinc acetate or zinc nitrate supported on silica showed a dramatic change in activity during the first few hours on stream. As shown in Figure 1 the fresh catalysts turned out to be inactive, but both the conversion and the selectivity increased sharply in the first 200 minutes.

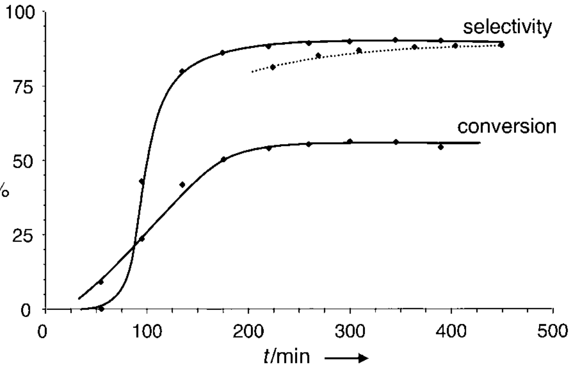

Figure 1. Variation in the conversion and selectivity (y) with time for the reaction of propyne/allene and methanol to 2-methoxypropene on stream using zinc acetate supported on silica gel as the catalyst precursor. The dotted selectivity curve was obtained by replacing propyne/propadiene by nitrogen during the first 200 minutes.

We considered this to be a clear indication that zinc acetate was not the actual catalyst, but instead the active species is formed in situ during the reaction. These preliminary results prompted us to have a closer look at both the catalyst and the mechanism of this reaction. Attempts to use other materials as supports—such as active charcoal, alumina, zirconia, titanium dioxide, silicon carbide, or silicon nitride—lead to completely inactive catalysts. We therefore concluded that silica was also involved in the formation of the active catalyst. The participation of methanol in the in situ formation of the active phase could be demonstrated by treating the freshly prepared catalyst with a propyne/propadiene mixture or with methanol alone (diluted with nitrogen) for 200 minutes at 175 °C and under normal pressure before adding the second reagent. While pretreatment with propyne/propadiene had no effect, treatment with methanol alone induced the formation of the catalytically active phase (dotted line in Figure 1).

The actual catalytically active phase was apparently being formed in situ by a solvothermal reaction between the zinc salt, methanol, and the silica in the solid state. Unfortunately, the true catalyst proved to be very difficult to characterize. The X-ray diffractogram showed only a diffuse band similar to that observed for the silica support, indicating that the material is more or less amorphous. The ^{29}Si CP-MAS NMR spectra of the formed catalysts showed only a broad signal at $\delta = -109$ with a small unresolved shoulder at $\delta = -99$, that is, very similar to the spectrum observed for the silica support after calcination at 900 °C (which removes all the adsorbed

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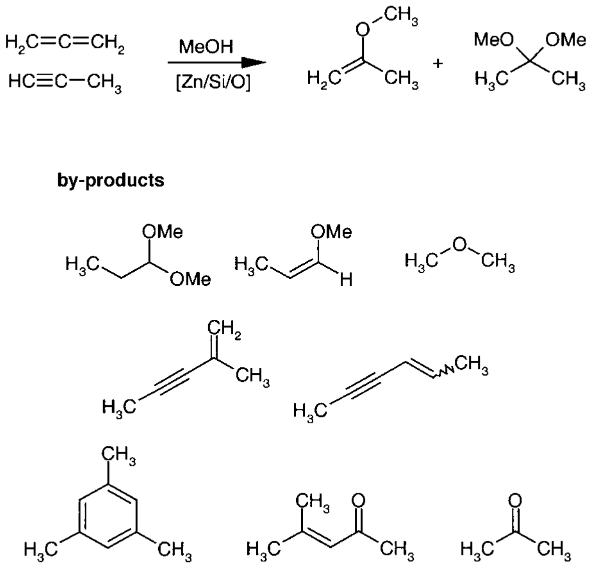
water and most of the surface SiOH groups). The spectrum shows no similarity to that of known zinc silicates.

An examination of the active catalyst with extended X-ray absorption fine structure (EXAFS) spectroscopy showed that the average coordination number of zinc was 3.9 oxygen atoms at a distance of about 1.97 Å ($\sigma^2 = 5.7 \times 10^{-3}$ Å^2). However, the EXAFS spectra of all known zinc silicates mentioned below were very similar. Comparison of the diffuse reflectance IR (DRIFT) spectra of zinc acetate deposited on silica and of the active catalyst obtained from it clearly showed that in the process of building the active phase all the acetate is decomposed. As was shown by scanning electron microscopy combined with electron probe microanalysis (SEM/EPMA), zinc and silicon were very homogeneously distributed all over the catalyst pellet, and there were no regions with isolated zinc oxide. The catalyst is quite stable even after 800 hours on stream at 175 °C and at normal pressure. No further structure changes were observed by X-ray diffraction (XRD) and ^{29}Si CP-MAS NMR spectroscopy, indicating no further catalyst aging. However, heating the catalyst at temperatures above 350 °C leads to a loss of activity.

In an attempt to independently prepare the catalytically active phase, we allowed silica gel to react with zinc acetate in the presence of liquid methanol in an autoclave at 200 °C for 24 hours. The obtained white powder was crystalline, and the reflections observed by XRD could easily be assigned to willemite, also known as α-zinc orthosilicate (α-Zn_2SiO_4), which is the most stable phase in the Zn/Si/O phase diagram.[8] Pure willemite, which was prepared according to a literature procedure,[9] proved to be catalytically inactive. In the course of our work a number of other known zinc silicates were prepared and tested as catalysts. The β form of the zinc orthosilicate (β-Zn_2SiO_4)[10] and sauconite ($Zn_3Si_4O_{10}(OH)_2 \cdot 4H_2O$)[11] both turned out to be inactive, but hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$)[12] was as active and selective as the amorphous zinc silicate obtained in situ from zinc acetate and silica.

Both hemimorphite and the amorphous zinc silicate are remarkable catalysts for the addition of methanol to propyne and/or allene. Catalytic activity is observed at temperatures as low as 120 °C at normal pressure. The reaction rate increases between 120 and 250 °C with an apparent activation energy of about 70 kJ mol^{-1}. In contrast to homogeneous Hg^{II} or Au^{I} catalysts, where propyne reacts about an order of magnitude faster than allene, with hemimorphite or amorphous zinc silicate as the catalyst allene reacts about 1.6 times faster than propyne. The addition of methanol to propyne and/or allene proceeds very selectively, the main products being 2-methoxypropene and 2,2-dimethoxypropane with a combined selectivity of about 96 % (Scheme 1).



Scheme 1. Main and by-products of the zinc silicate catalyzed addition of methanol to propyne and/or allene.

The relative amounts of 2-methoxypropene and 2,2-dimethoxypropane formed depend strongly on the reaction conditions, because the zinc silicates also catalyze the reversible addition of methanol to 2-methoxypropene very effectively. Although the substrate spectrum has not yet been studied exhaustively, it is known that these silicates also catalyze the addition of water to propyne/allene to yield acetone as well as the reaction of ethanol, propanol, and 1-butanol with acetylene to give mainly the corresponding enol ethers.

Since the addition of methanol to propyne or allene is a rather simple reaction and the structure of the catalytically active phase (hemimorphite) is known in detail,[13] we tried to develop a plausible mechanism for this reaction using ab initio calculations. In view of the nature of the active metal (Zn^{2+} with a d^{10} closed shell) and of the small difference in reactivity between propyne and allene, an activation of the hydrocarbon seems improbable. On the other hand, cases where tetrahedrally coordinated zinc(II), as found in hemimorphite, is used to activate water or lower alcohols are known in homogeneous catalysis.[14c] The best examples are probably the carbonic anhydrases, a family of ubiquitous enzymes which catalyze the reaction between water and CO_2 to form carbonic acid.[14] The zinc-bound water molecule in a carbonic anhydrase is quite acidic, and it is the zinc hydroxide species formed after ionization that will react with CO_2. A network of water molecules provides for the necessary proton scrambling.[14e, f, 15]

The question was which zinc atoms in hemimorphite could serve as active centers. Electron diffraction measurements with a transmission electron microscope on single crystals of hemimorphite obtained from our synthesis showed the preferred facet orientation in our crystals to be the (0,1,0) plane. Inspection of a model of the dehydrated hemimorphite (Figure 2) clearly shows that the lowest energy (0,1,0) facet is obtained by cutting the crystal along the [0,2,0] Miller plane.

The surface thus generated looks very promising from the view point of catalysis since it contains many tetrahedrally coordinatinated zinc atoms for which one of the coordination sites is occupied by water. Calculations showed that this water molecule is loosely bound and can easily be exchanged with methanol.

However, there are not enough properly coordinated zinc atoms to produce an active catalyst. Once again, the analogy with the carbonic anhydrase gave us the decisive hint: A key

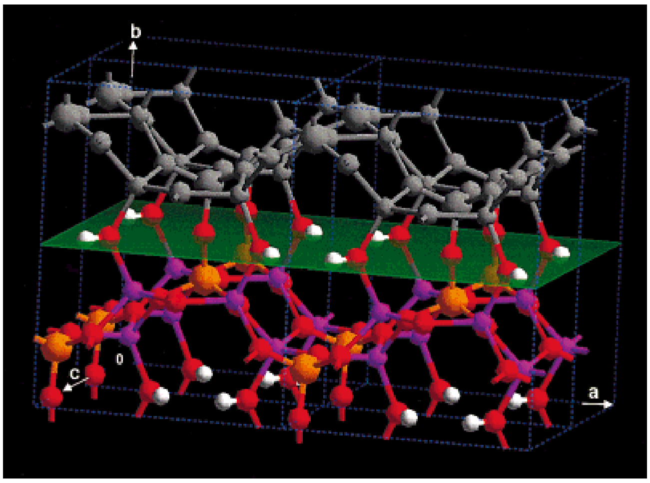


Figure 2. View of the expanded unit cell ($2a \times 2b \times c$) of hemimorphite showing the [0,2,0] Miller plane (green). On cleavage this plane gives the lowest energy (0,1,0) facet.

feature of these enzymes is the presence of a suitably located proton donor. Preliminary calculations on a simple model system[16] indicated that the proton-donating atom should be located above the zinc methoxide. Such a geometry cannot be found within a single crystal plane. The next obvious place to search is at a step in the (0,1,0) surface, and indeed at this step a sterically unencumbered zinc and a silanol group, as the proton donor, are present in an adequate geometry (Figure 3).

The model system was created as follows: A crystal containing $3 \times 3 \times 7$ unit cells was built, and half of the top (0,1,0) layer removed. With this procedure, all of the surface Zn and Si atoms kept the oxygen atom to which they were bonded. The remaining free valences of the dangling oxygen atoms or hydroxyl groups were then saturated by adding protons to ensure overall electroneutrality. This produced terminal OH groups on the silicon atoms and both OH and H_2O moieties on the zinc atoms.[17] To create the reactive site, one of the zinc-bound OH groups at the step was removed, producing a cationic zinc center. All the water molecules in the crystal channels were also removed since they are lost during catalysis, which has only a little effect on the crystal structure.[13b]

The resulting model system (Figure 3) contains 2150 atoms. Since this is too large to be treated entirely with quantum-mechanical (QM) methods, we have defined a cluster around the reactive center which was treated using quantum mechanics, while the rest of the model is handled by simpler molecular mechanics (MM).

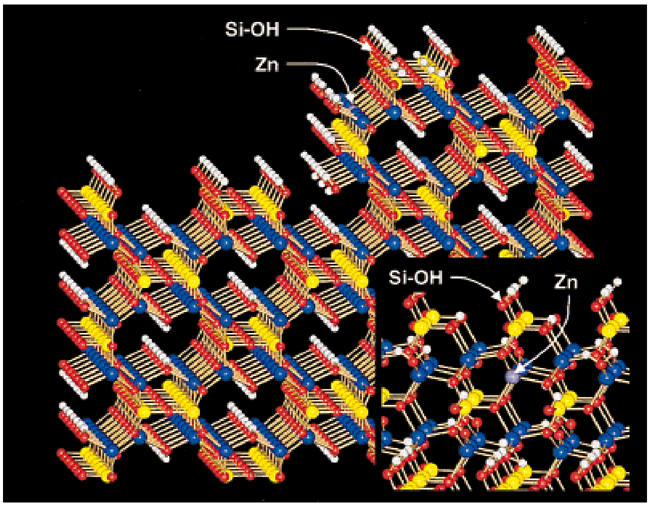
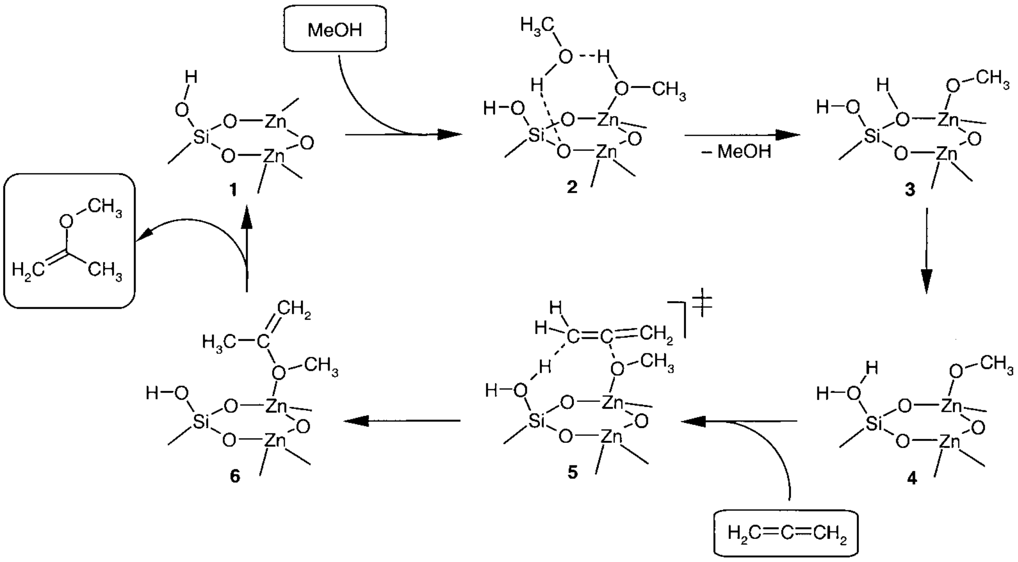


Figure 3. Structure of the catalyst model used in the calculations. Presented is a side view (along the c axis) of a step on the (0,1,0) surface showing the reactive zinc atom (purple) and proton-donating SiOH group. The inset is an enlarged front view (along the a axis) of the reactive center. Zn: blue, Si: yellow, O: red, H: white.

Within this QM/MM hybrid, or embedding approach, we have combined density functional theory (DFT)[18] in the TURBOMOLE program suite[19] for the QM part with the universal force field (UFF)[20] in the Cerius^2 software package[21] for the MM part.[22] The QM cluster includes the reactive zinc atom and the first shell of zinc and silicon atoms surrounding it, which are connected and terminated by O atoms or OH groups (33 atoms in total, without reactants). In the QM calculations, the bonds of the QM cluster to the MM part of the crystal have been saturated by 14 hydrogen atoms.[29] Only the QM atoms were relaxed within the structure optimizations.

The proposed reaction mechanism is shown in Scheme 2. The Langmuir–Rideal-type catalytic cycle starts at a zinc atom with a vacant coordination site (**1**). This zinc atom coordinates to a methanol molecule in an exothermic reaction



Scheme 2. Overview of the mechanism computed for the addition of methanol to allene. The species shown are all cationic.

(-171 kJ mol^{-1}). For geometrical reasons it is unlikely that the hydrogen atom of the methanol ligand is transferred directly to the silanol group. More likely the hydrogen transfer occurs by a hopping mechanism promoted by a second methanol molecule (**2**).[30] The overall reaction of **1** to **2** is computed to be exothermic (-343 kJ mol^{-1}). A proton is first transferred to the bridging oxygen atom (**3**) and in a second step to the silanol group (**4**). The transformation of **2** into **4** is endothermic ($+134$ kJ mol^{-1}). The key intermediate **4** has the appropriate geometry to react with allene to produce 2-methoxypropene, which is coordinated to the zinc center (**6**). This reaction is exothermic (-117 kJ mol^{-1}) with no apparent activation barrier.[31] Thus, the experimentally observed activation energy (70 kJ mol^{-1})[32] is needed either for the desorption of the product, which is computed to be endothermal ($+190$ kJ mol^{-1}), or more likely for the dissociation of methanol. This result parallels the behavior of the enzyme carbonic anhydrase, where the rate-determining step is a proton transfer and not the attack of the zinc-bound hydroxide on CO_2.[14d–f]

These calculations demonstrate the existence of one energetically viable pathway for the activation of methanol. The astonishing parallel between the catalytic pathways in hemimorphite and in the zinc enzyme carbonic anhydrase supports the suggested and calculated mechanism.

Experimental Section

Typical procedure for the addition of methanol to propyne/allene mixtures: The reported results were obtained using a C_3 fraction with the following approximate composition (vol %): propyne (32), allene (24), propene and propane (44), C_4 hydrocarbons (<2). The reaction was conducted in a stirred tank reactor designed for reactions in the gas phase on heterogeneous catalysts.[33] The products were analyzed by on-line gas chromatography with cyclohexane as the internal standard. A typical experiment was conducted at 170 °C and 1.15 bar with hemimorphite (57.2 g; extrudate, pellet size 2 mm) as the catalyst. The feed contained propyne/propadiene (1.58 mmol min^{-1}), methanol (2.95 mmol min^{-1}), and cyclohexane (0.3 mmol min^{-1}; gas hourly space velocity 140 h^{-1}). The conversions of propyne and allene were 72 and 85 %, respectively. The selectivities were as follows: 2-methoxypropene (77 %), 2,2-dimethoxypropane (19 %), *cis-* and *trans*-1-methoxypropene (2 %), acetone (1 %), propyne/allene dimers and trimers (hex-2-en-4-yne, 2-methylpent-1-en-3-yne, mesitylene (1,3,5-trimethylbenzene); together 0.3 %), dimethyl ether (0.05 %), and 1,1-dimethoxypropane (0.1 %).

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[10] β-Zinc orthosilicate was prepared as described in reference [33d] (example 4). The observed XRD lines were identical to those in card number 14-0653 of the JCPDS-ICDD data base (**1995**).

[11] Sauconite was prepared as described in reference [33d] (example 6). The observed XRD lines were identical to those in card number 29-1393 of the JCPDS-ICDD data base (**1995**).

[12] Hemimorphite was prepared by allowing sodium silicate to react with zinc nitrate (molar ratio Zn:Si = 2) in aqueous solution, which resulted in the formation of an amorphous white precipitate, and subsequently heating this suspension to 90 °C for 24 hours as described in detail in reference [33d] (example 1). The observed XRD lines were identical to those in card number 5-0555 of the JCPDS-ICDD data base (**1995**).

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[15] The analogy goes even further since CO_2 and allene are isoelectronic.

[16] We calculated as a model system the path of the reaction between tris(pyrazolyl)hydroboratezinc(II) methoxide, allene, and NH_4^+ as the proton donor to give zinc-bound 2-methoxypropene and NH_3. This reaction is computed to occur with no activation barrier. The angle between zinc, the methoxide oxygen, and the proton-donating atom should be around 12 ± 3° and the distance between zinc and nitrogen around 5.4 ± 0.2 Å.

[17] The positions of the hydrogen atoms were optimized using the universal force field.[20]

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[22] The DFT calculations were done within the RI approximation,[23] using functions of Becke and Perdew (B–P),[24] TURBOMOLE's grid m3,[25] split valence basis sets[26] with polarization functions on non-hydrogen atoms for the structure optimizations, and triple zeta valence basis sets[27] with polarization functions on all atoms for the final energy calculations. Charges for the UFF calculations were determined with the charge equilibration method.[28]

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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 ($\Delta G^{\neq}$) 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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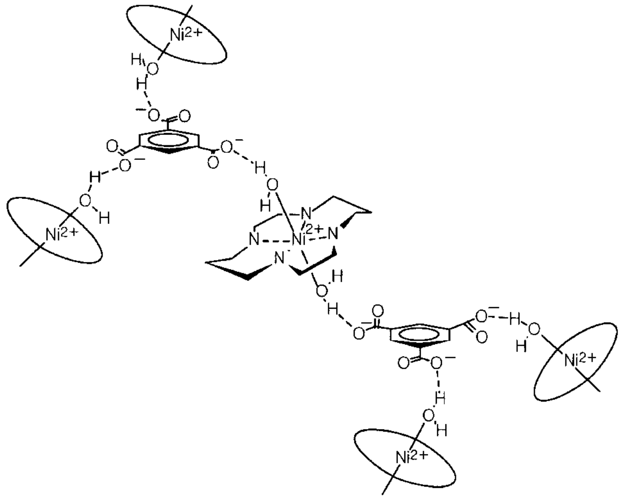
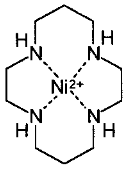
Supramolecular chemistry has advanced to a stage at which we can design and construct molecular solids with specific network topologies[1] as well as with potentially interesting properties.[2] Self-assembly of organic molecules and metal-ion building blocks may yield multidimensional networks containing 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 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



Scheme 1. Proposed formation of the network.



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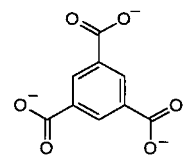

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