Amine Phosphates as Intermediates in the Formation of Open-Framework Structures

S. Neeraj, Srinivasan Natarajan, and C. N. R. Rao*

There has been intense research activity in the area of inorganic open-framework materials during this decade, partly motivated by their potential applications in catalysis and sorption and separation processes.[1] While aluminosilicates and aluminophosphates with open architectures have been known for some time, it is only recently that diverse inorganic open-framework structures, especially phosphates, of a wide range of metals were synthesized hydrothermally in the presence of structure-directing amines.[2] In spite of the progress made, one is not able to adequately rationalize the formation of such a variety of open-framework metal phosphate structures. In the case of aluminophosphates, it is proposed that linear chains of corner-sharing metal phosphate units are progressively transformed into ladder, layer, and three-dimensional structures.[3] In tin phosphates, four-rings of the metal phosphate are believed to transform into larger rings and give rise to layer and other complex structures.[4] While the variety of structures generated in a given metal phosphate system, often with the same amine, may arise because of the small energy differences amongst them or due to kinetic control of the reactions, the exact role of the amines is not fully understood, in spite of several hypotheses.[5] We consider it of great importance to understand how the initial chain or layer structures of metal phosphates are formed, and therefore investigated whether a stable reaction intermediate, formed during hydrothermal synthesis, plays a key role, and, if so, whether this intermediate can be directly used to generate novel metal phosphates.

In the hydrothermal synthesis of open-framework metal phosphates, we isolated several amine phosphates as additional products. Initial experiments showed that the amine phosphates react with metal ions under hydrothermal conditions in the absence of additional phosphoric acid to give open-framework metal phosphates. This suggested that amine phosphates could indeed act as intermediates in the formation of open-framework structures. Although amine phosphates are known to occur as by-products in the synthesis of metal phosphates,[6] they are not normally encountered because of their high solubility in water and the usual preoccupation with less soluble crystalline products. Amine phosphates themselves are readily prepared by the reaction of amines with phosphoric acid under normal conditions in an appropriate solvent.[7] Here we demonstrate how the amine phosphates react with metal ions to yield various metal phosphate structures, which were characterized by X-ray crystallography on isolated products, as well as in-situ NMR and X-ray diffraction studies.

Reaction of 1,3-diaminopropane phosphate (DAPP; Figure 1 a) with Zn^{II} ions under hydrothermal conditions[8] initially gives a zinc phosphate with a ladder structure involving edge-shared four-ring metal phosphate units (Figure 1 b). It is noteworthy that this ladder structure is also produced in the conventional hydrothermal synthesis with 1,3-diaminopropane (DAP) as structure-directing agent.[9] More significantly, DAPP reacts with Zn^{II} to give this ladder structure at much lower temperatures (30 °C for 96 h).[8] In addition, we obtained a new layer structure (Figure 1 c) when DAPP was treated with Zn^{II} for extended periods ($\geq$96 h) at moderate temperatures ($\leq$85 °C). This observation suggests that the layer structure may be a transformation product of the ladder structure.

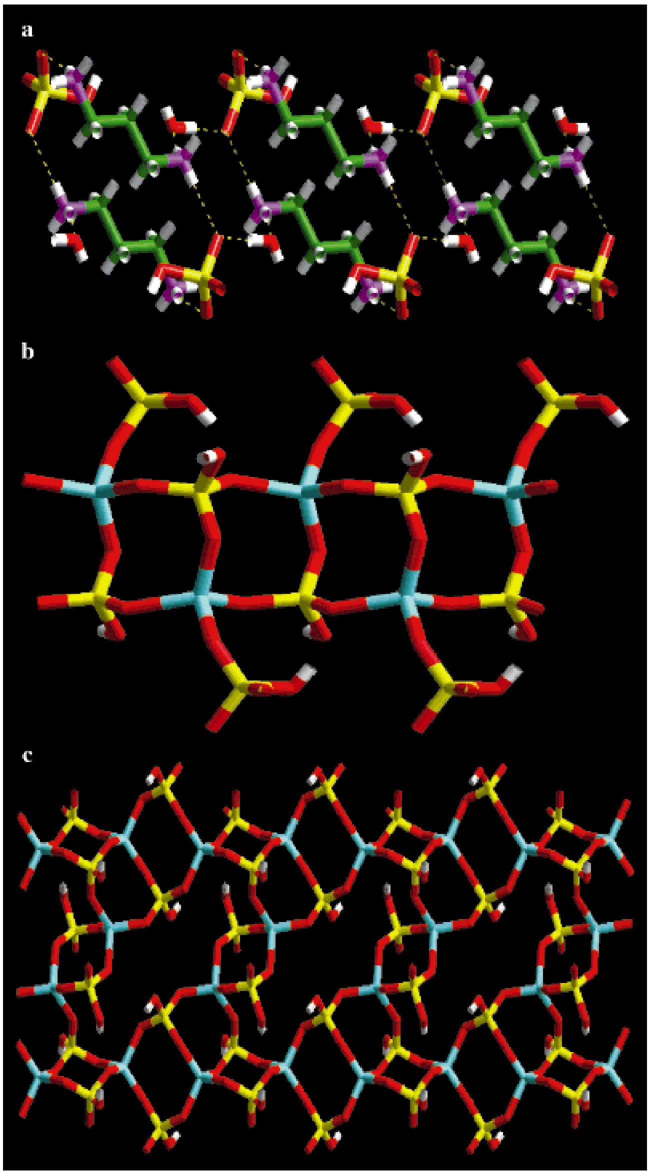

Figure 1. a) Structure of diaminopropane phosphate (DAPP) showing its hydrogen-bonded assembly (blue: Zn, yellow: P, red: O, green: C, pink: N, white: H). b) The one-dimensional zinc phosphate ladder structure. Replacement of the water molecules in (a) by Zn ions gives this structure. c) Layered zinc phosphate.

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[*] Prof. Dr. C. N. R. Rao, S. Neeraj, Dr. S. Natarajan
Chemistry and Physics of Materials Unit and
CSIR Centre of Excellence in Chemistry
Jawaharlal Nehru Centre for Advanced Scientific Research
Jakkur P.O., Bangalore 560 064 (India)
Fax: (+91) 80-846-2766
E-mail: cnrrao@jncasr.ac.in

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Reaction of piperazine phosphate (PIPP) with Zn^{II} ions under hydrothermal conditions gave a new linear ladder structure of corner-sharing metal phosphate units, along with a new three-dimensional structure (Figure 2); two known three-dimensional structures[10] were also obtained. Reaction of PIPP with Zn^{II} ions at 85 °C also yielded the three-dimensional structures. Similarly, the phosphate of 1,4-diazabicyclo[2.2.2]octane (DABCOP) reacted with Zn^{II} ions at around room temperature to give the same three-dimensional structure that was obtained at 150 °C or by direct hydrothermal synthesis.[11] Reaction of ethylenediamine phosphate (ENP) with Zn^{II} ions at 150 °C gave new ladder, layer, and three-dimensional structures. The last two were also obtained from a reaction carried out at 50 °C. Table 1 lists the various open-framework zinc phosphates obtained by the reactions of amine phosphates with Zn^{II} ions at different temperatures.

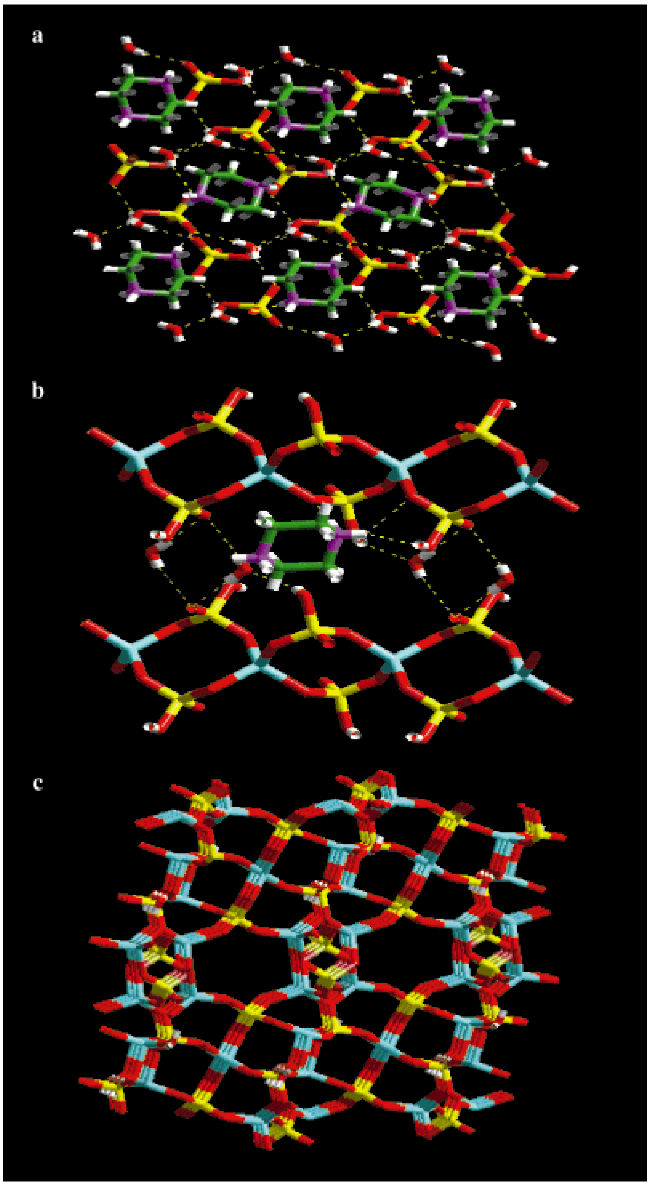

Figure 2. a) Structure of the hydrogen-bonded piperazine phosphate (PIPP) assembly. b) A new corner-shared zinc phosphate structure. This is the simplest chain structure. c) Structure of a new three-dimensional open-framework zinc phosphate. This structure can be derived from the chain structure.

The above results suffice to indicate the key role of amine phosphates in the formation of open-framework phosphates. Furthermore there is a close similarity between the structures of DAPP (Figure 1 a) and the zinc phosphate ladder structure (Figure 1 b). The former consists of a hydrogen-bonded network with water molecules and resembles the loosely hydrogen bonded structures involved in the synthesis of aluminosilicates.[12] The mechanism of formation of the initial ladder phosphate can be understood in terms of the displacement of the water molecules from the amine phosphate by Zn^{II} ions (Figure 3).

To further substantiate that the amine phosphates undergo facile reactions with metal ions, we monitored the reaction between DAPP and Zn^{II} ions at 85 °C in an aqueous medium by in situ ^{31}P NMR spectroscopy. The intensity of the signal of

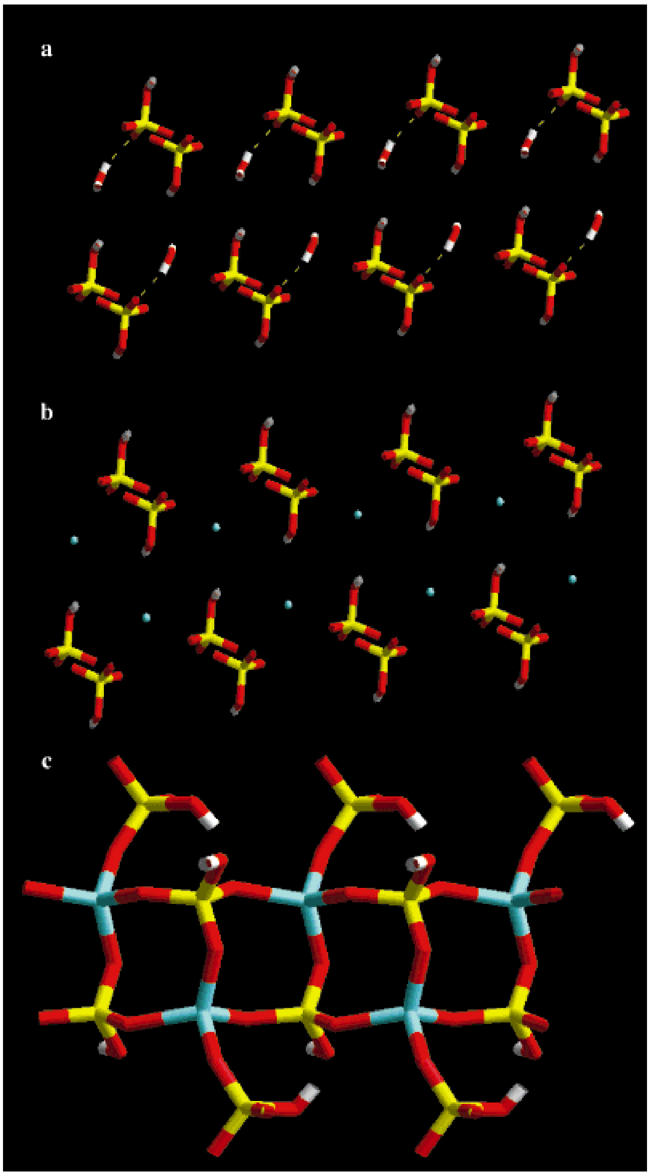

Figure 3. a) Structure of the hydrogen-bonded DAPP assembly (amine molecules omitted for clarity). b) Schematic replacement of water molecules by Zn^{II} ions. c) Edge-shared zinc phosphate ladder structure.

Table 1. Open-framework zinc phosphates obtained from amine phosphates.

Composition	T [°C] (t [h])	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	Space group	$R(F)$[a]	Framework type
DAPP: $[\mathrm{dapH_2}][\mathrm{HPO_4}]\cdot\mathrm{H_2O}$[b]		7.009(9)	16.775(8)	7.845(9)	90.00	113.78	90.00	$P2_1/c$	7.8	(Figure 1 a)
$[\mathrm{Zn(HPO_4)_2}][\mathrm{dapH_2}]$	150 (40), 95 (40), 50 (48), 30 (96)	5.222(0)	12.756(1)	15.674(1)	90.00	90.00	90.00	$P2_12_12_1$	2.2	chain[9] (Figure 1 b)
$[\mathrm{Zn_2(HPO_4)_3}][\mathrm{dapH_2}]$	150 (40), 85 (96)	8.614(5)	9.618(7)	17.037(8)	90.00	93.57	90.00	$P2_1/c$	4.5	layer[c] (Figure 1 c)
$[\mathrm{SnPO_4}]_2[\mathrm{dapH_2}]$	180 (24), 85 (48), 50 (96)	18.096(7)	7.888(6)	9.150(7)	90.00	111.84	90.00	$C2/c$	2.6	layer (Figure 4)
$[\mathrm{Al_5Co_2(OH)(HPO_4)_4(PO_4)}][\mathrm{dapH_2}]$	180 (96), 110 (300)[d]	9.177(4)	9.250(5)	13.175(4)	93.07	92.31	112.06	$P\bar{1}$	13.0	3-D[c]
PIPP: $[\mathrm{pipH_2}][\mathrm{HPO_4}]\cdot\mathrm{H_2O}$[b]		6.425(6)	12.296(8)	11.220(8)	90.00	97.14	90.00	$P2_1/n$	6.4	Figure 2 a
$[\mathrm{Zn(HPO_4)_2(H_2O)}][\mathrm{pipH_2}]$	180 (36)	8.930(6)	14.025(4)	9.310(7)	90.00	95.41	90.00	$P2_1/n$	4.0	chain[a] (Figure 2 b)
$[\mathrm{Zn_4(PO_4)_3(OH)}][\mathrm{pipH_2}]$	180 (36)[e]	16.104(8)	8.256(4)	22.997(9)	90.00	104.00	90.00	$C2/c$	2.0	3-D[a] (Figure 2 c)
$[\mathrm{Zn(H_2O)Zn(HPO_4)(PO_4)}]_2[\mathrm{pipH_2}]$	180 (36), 85 (300)	12.075(5)	14.888(7)	11.835(8)	90.00	97.72	90.00	$C2/c$	3.0	3-D[10]
$[\mathrm{Zn_2(PO_4)(H_2PO_4)_2}][\mathrm{pipH_2}]$	180 (36), 85 (300)	13.388(3)	12.838 (6)	8.224(6)	90.00	94.77	90.00	$C2/c$	–	3-D (10)
DABCOP: $[\mathrm{dabcoH_2}][\mathrm{HPO_4}]\cdot\mathrm{H_2O}$[b]		6.906(2)	9.018(4)	9.271(2)	92.21	104.51	111.76	$P\bar{1}$	3.9	–
$[\mathrm{Zn_2(HPO_4)_3}][\mathrm{dabcoH_2}]$	150 (20), 95 (20)	9.528(4)	9.948(3)	9.996(4)	107.65	98.04	114.86	$P\bar{1}$	5.5	3-D[11]
$[\mathrm{Zn_4(PO_4)_2(HPO_4)_2}][\mathrm{dabcoH_2}]\cdot 3\,\mathrm{H_2O}$	150 (20), 95 (20), 50 (48), 30 (60)	9.475(1)	9.524(9)	12.312(4)	93.73	91.044	98.70	$P\bar{1}$	6.1	3-D[11]
ENP: $[\mathrm{enH_2}][\mathrm{HPO_4}]$[b]		7.507(1)	11.816(4)	8.055(4)	90.00	110.13	90.00	$P2_1/c$	3.0	–
$[\mathrm{Zn(HPO_4)_2}][\mathrm{enH_2}]$	150 (36)	5.161(1)	15.842(2)	12.027(2)	90.00	92.36	90.00	$P2_1/c$	6.0	ladder
$[\mathrm{Zn_2(HPO_4)_2(H_2PO_4)_2}][\mathrm{enH_2}]$	150 (36), 50 (40)	16.420(2)	7.826(1)	14.640(1)	90.00	116.47	90.00	$P2_1/c$	5.0	layer
$[\mathrm{Zn_6(PO_4)_4(HPO_4)}][\mathrm{enH_2}]$	150 (36)	19.182(0)	5.036(0)	21.202(4)	90.00	103.29	90.00	$C2/c$	3.6	3-D

[a] $R(F)=\frac{\sum ||F_o|-|F_c||}{\sum |F_o|}$, where $F_o > 4.0\,\sigma(F)$. [b] The amine phosphates were recovered initially from the hydrothermal syntheses and later synthesized by using the composition amine:1.2 H_3PO_4:5 H_2O at 110 °C for 12 h. [c] New structure found in this study. [d] Synthesis was carried out in ethylene glycol. [e] Different composition of the starting gel.

the amine phosphate ($\delta = 0.056$) decreases, while that of a zinc phosphate precursor[13] at $\delta = 3.82$ increases (Figure 4). The intensity of the signal of the phosphate precursor decreases after some time due to the formation of more complex open-framework phosphates. This suggests that the unidentified intermediate reported recently[14] in an in situ energy dispersive X-ray diffraction (EDXRD) study on the formation of the gallophosphate ULM-5 may be an amine phosphate. Heating the intermediate with gallium salts is reported to yield the gallophosphate.[14] Our time-dependent XRD studies[13] on the DAPP–Zn^{II} reaction lend credence to this suggestion (see inset of Figure 4).

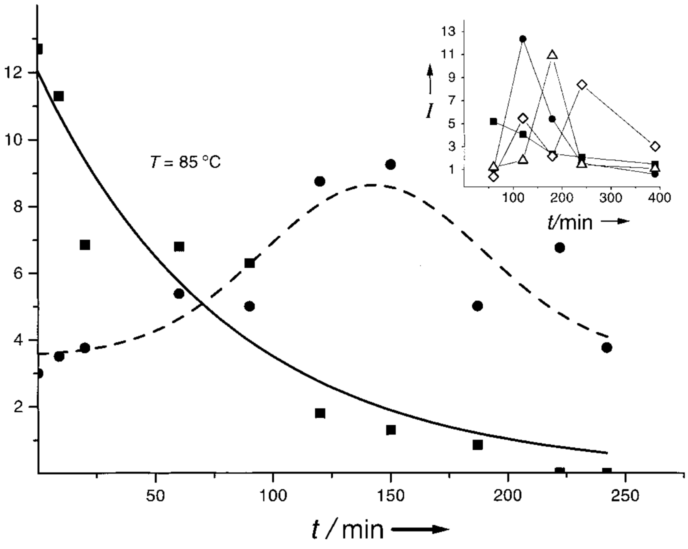

Figure 4. Plots of ^{31}P NMR signal intensity I (in arbitrary units) of DAPP (——) and of the precursor zinc phosphate (– – –) against reaction time. The inset shows the variation in the relative intensities (arbitrary units) of the low-angle reflections in the XRD patterns of the amine phosphate and of the products of its reaction with Zn^{II} ions (■ amine phosphate, ● precursor, △ chain (edge-shared) phosphate, ◇ layer phosphate).

To demonstrate the universality of the amine phosphate route to open-framework structures, we carried out the reaction of DAPP with tin(II) oxalate and obtained the layer structure shown in (Figure 5). This structure is obtained at temperatures as as low 50 °C (see Table 1). The reaction of DAPP with Co^{II} and Al^{III} ions, gave a new three-dimensional cobalt aluminum phosphate that belongs to a recently described family of materials.[15]

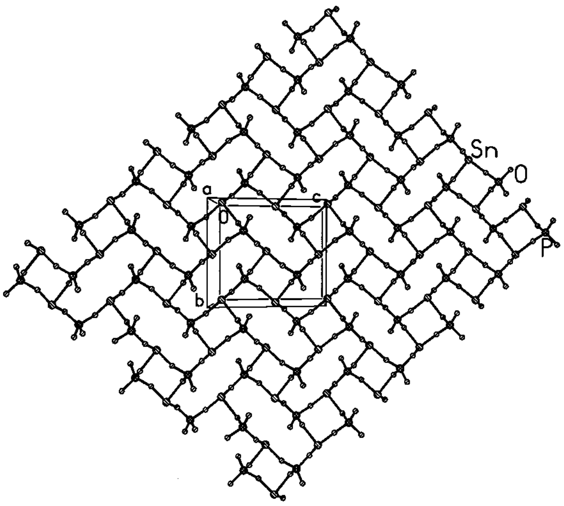

Figure 5. Layered tin(II) phosphate structure formed by the reaction of DAPP with tin(II) oxalate at around room temperature.

In conclusion, the present study demonstrates that open-framework metal phosphates can be generated under relatively mild conditions by treating amine phosphates with metal ions and that amine phosphates are intermediates in hydrothermal syntheses. The amine phosphates initially give chain or ladder structures that give rise to more complex structures, depending on time and temperature.

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[8] In a typical synthesis, 0.5 mmol of ZnO was stirred in 100 mmol of water, to which 1 mmol of HCl (35%) was added. After stirring the mixture for a few minutes, 2.7 mmol of amine phosphate (e.g., DAPP) was added, and the mixture was stirred for 30 min. The homogenized mixture was sealed in a 23-mL teflon-lined Parr autoclave and heated at the given temperature and for the given duration (see Table 1). The product was collected by filtration, and X-ray analysis of the crystals was carried out on a Siemens SMART X-ray diffractometer with a CCD detector.

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[13] Reaction of the amine phosphate with Zn^{II} at all temperatures first yields a fine particulate open-framework zinc phosphate with a low-angle XRD line ($d_{hkl} = 11.8$ Å). Time-dependent XRD studies show that the low-angle line due the precursor decreases in intensity when the characteristic reflections of the ladder, layer, and three-dimensional structures start to appear. The aqueous dispersion of the particulate material shows a ^{31}P NMR signal ($\delta = 3.82$) whose intensity first increases with time and then decreases due to the formation of a edge-shared ladder or layer structures. We consider the initial phosphate material formed to be the precursor, since on further reaction or passage of time it gives the more complex ladder, layer, or three-dimensional structures. It seems likely that the precursor is a corner-shared linear ladder phosphate which we have isolated from some reactions of the amine phosphates. Accordingly, the Zn:P ratio in the precursor phosphate is 1:1 (in contrast to the edge-shared ladder phosphates, in which it is 1:2).

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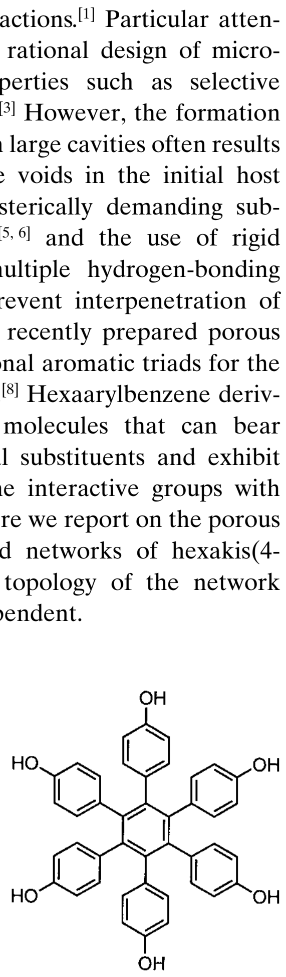
Self-Assembly of a Radially Functionalized Hexagonal Molecule: Hexakis(4-hydroxyphenyl)benzene[**]

Kenji Kobayashi,[*] Toshiaki Shirasaka, Azumi Sato, Ernst Horn, and Naomichi Furukawa

Supramolecular approaches to self-assembly of molecular solids rely in a predictable manner on directional and complementary noncovalent interactions.[1] Particular attention has recently focused on the rational design of microporous solids with specific properties such as selective adsorption[2] and catalytic activity.[3] However, the formation of hydrogen-bonded networks with large cavities often results in self-interpenetration to fill the voids in the initial host structure.[4] The introduction of sterically demanding substituents into trigonal molecules[5, 6] and the use of rigid hexagonal macrocycles[7] with multiple hydrogen-bonding sites are potential methods to prevent interpenetration of networks. Aoyama and ourselves recently prepared porous networks of bis-resorcinol orthogonal aromatic triads for the preorganization of host molecules.[8] Hexaarylbenzene derivatives[9] are highly symmetrical molecules that can bear diverse and multifunctional radial substituents and exhibit an orthogonal arrangement of the interactive groups with respect to the core moiety.[10, 11] Here we report on the porous two-dimensional hydrogen-bonded networks of hexakis(4-hydroxyphenyl)benzene (**1**); the topology of the network structures is flexible and guest-dependent.



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Host **1** was prepared by the $[Co_2(CO)_8]$-catalyzed cyclotrimerization[9] of bis(4-methoxyphenyl)acetylene (81% yield) followed by deprotection of the resulting hexakis(4-methoxyphenyl)benzene (**2**) with BBr_3 (92% yield). Recrystallization of **1** from various solvents afforded inclusion cocrystals, the stoichiometries of which were evaluated by ^1H NMR spectroscopy in CD_3OD: $\mathbf{1} \cdot 3\,C_6H_5COOCH_3$ from a

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[*] Dr. K. Kobayashi, T. Shirasaka, A. Sato, Prof. Dr. N. Furukawa
Department of Chemistry and
Tsukuba Advanced Research Alliance Center
University of Tsukuba, Tsukuba, Ibaraki 305–8571 (Japan)
Fax: (+81) 298-53-6503
E-mail: kenjinor@staff.chem.tsukuba.ac.jp

Prof. Dr. E. Horn
Department of Chemistry, Rikkyo University
Nishi-Ikebukuro, Toshima-ku, Tokyo 171–8501 (Japan)

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