Elusive Double-Eight-Ring Zeolitic Secondary Building Unit

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Ⓢ *Supporting Information*

ABSTRACT: The double-eight-ring (D8R), an elusive secondary building unit of zeolites, has been stabilized for the first time, both in solution and solid-state. The present study further establishes that any of the three double-ring building blocks of zeolites, viz. D4R, D6R and D8R ($[ArPO_3Zn(L)]_n$ ($n = 4, 6$ or 8)), can be preferentially isolated (over the other two) through a careful choice of metal source, aryl phosphate and ancillary ligand, apart from maintaining a meticulous control on the reaction conditions.

Enduring widespread interest in porous solids dates back to 1756 when Cronstedt discovered a class of compounds then known as "zeolithe".[1] Since then, zeolites have bourgeoned due to their widespread applications in a variety of fields.[2–4] The complex structures of zeolites have been comprehended by breaking them down to smaller structural units that periodically repeat in the 3-D lattice.[1] Precise determination of their 3-dimensional structures has led to the realization that the entire zeolite family can be built by using just 23 "secondary building units" (SBUs), by edge sharing or corner sharing hierarchical architectural fusion.[1] Due to this comprehension, chemists began to synthesize many of these SBUs as independent entities. Isolation of $[RSiO_{1.5}]_n$ ($n = 8$) and $[Si_8O_{16}]^{4-}$ anions (D4R) was an early step in this direction.[5] It turns out that the most common and stable molecular entity among the zeolite building blocks is the doube-4-ring (D4R) unit,[6,7] although in a few instances double-6-ring (D6R) silicates and phosphonates have also been isolated.[8,9] In contrast, there are no known molecular species with a double-8-ring (D8R) core structure. Theoretical studies carried out to determine the possible structure of $[RSiO_{1.5}]_n$[10] reveal three possible isomers in case of $n = 16$, but none of them display a D8R core.[10a–c] The relative stability of some of the SBUs has been a subject of extensive investigations because D8R units do occur in the frameworks of zeolite type MER, PAU, RHO, SBE and TSC.[1] The absence of independent D8R clusters either has been understood on the basis that such large rings are too floppy to be stable to any degree.[11]

While engaging a lipophilic organophosphate as the synthon to resolve issues related to hierarchical structure building in zeolite science,[6a,b,d,12] we have shown that it is possible to form extended structures such as 1-dimensional polymers in preference to the well-known D4R structures.[13] The occurrence of zigzag polymers seemed to suggest that it should be possible to fold these chains into larger double rings by proper choice of starting materials and reaction conditions (Figure 1). Experi-

ments designed in our laboratory to validate this suggested pathway has now resulted in the isolation of first ever examples of D8R molecular species.
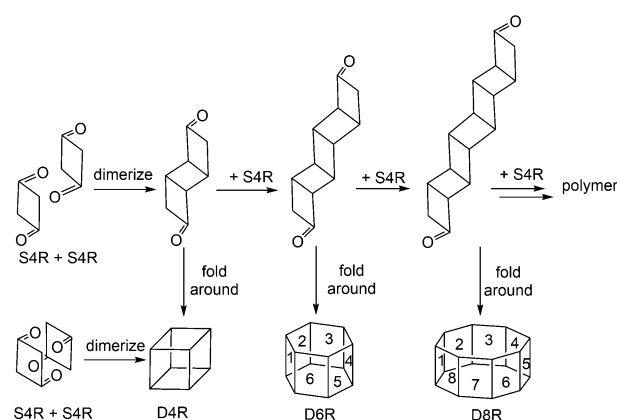
**Figure 1.** Suggested pathway for assembling elusive D6R and D8R SBUs.

An equimolar reaction of 2,6-di-isopropylphenyl phosphate ($dippH_2$) with $Zn(OAc)_2 \cdot 2H_2O$ in methanol in the presence of 3-pyridinecarboxaldehye (py-3-CHO) leads to the isolation of $[Zn_6(dipp)_6(py-3-CH(OMe)_2)_2(py-3-CHO)_4(H_2O)_2]$ (**1**) (Figure 2). Although the use of py-3-CHO as ancillary ligand assists the formation of high nuclearity SBU, other pyridine ligands employed previously for corner-capping purposes have yielded D4R clusters.[6a,b,d,12b–d] The hexameric nature of **1**, built around a D6R core, is established by both spectroscopic and single-crystal X-ray diffraction studies (see ESI). The ^1H NMR spectrum of **1** exhibits a singlet δ 9.88 for the formyl proton whereas the ^{31}P NMR spectrum displays two resonances at δ -2.8 and -3.4 ppm (Figure S2 and S3). Four ESI-MS signals appear at m/z 1995.44, 1981.43, 1965.43 and 1949.42 corresponding to the hexanuclear cluster minus peripheral ligands (Figure S10) with the expected isotopic pattern.

Compound **1** crystallizes as its dihydrate. Unlike the previously known $dippH_2$ derived zinc phosphates,[6a,b,12b,c] **1** is made up of a drum-like $Zn_6P_6O_{18}$ core that resembles the D6R SBU (Figure S13).[1] Although no metal or nonmetal molecular phosphate displaying a D6R core has been previously known, a few examples of D6R boron and aluminum phosphonate clusters and silsesquioxanes have been reported.[8,9]

The phosphate dianion binds to three zinc centers in a [3.111]
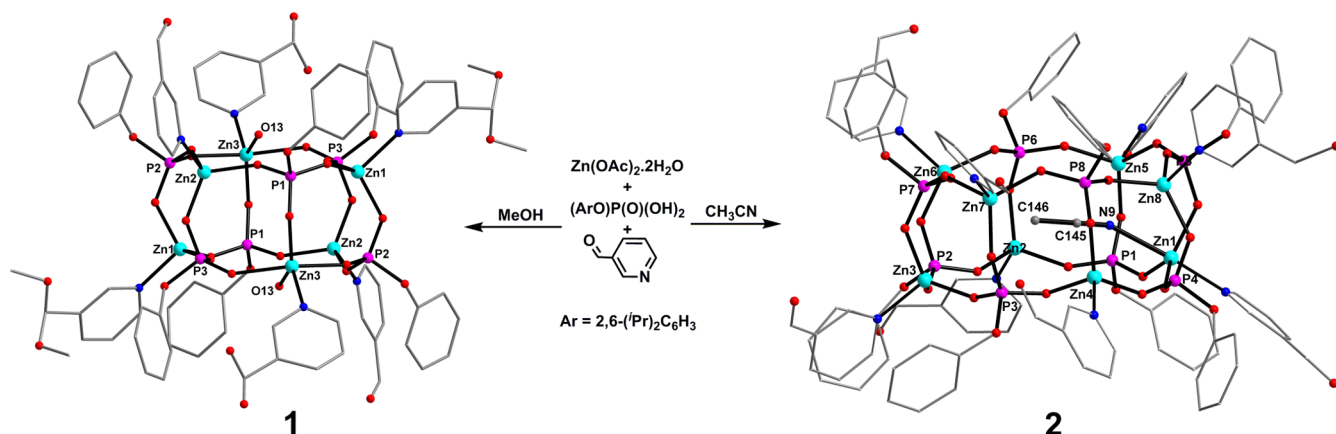
Figure 2. Schematic representation of the syntheses and crystal structure of hexanuclear and octanuclear zinc organophosphate clusters **1** and **2**. Isopropyl groups on the aryl rings have been removed for the sake of clarity.

fashion[14] assisting the formation of D6R core (Figure 2). The three zinc cations in the asymmetric part exhibit three different coordination environments. The four-coordinate tetrahedral Zn1 and Zn2 differ from each other by the ancillary pyridinic ligand, where the py-3-CHO on Zn1 has transformed to the corresponding acetal; Zn3 exhibits trigonal-bipyramidal geometry as a result of coordinated water molecule. Although all the pyridinic ancillary ligands point away from the drum-like cluster, the coordinated water on Zn3 (and Zn3′) points inward, contributing for the conversion of the usual D4R core into a D6R core. The hydrogens of the coordinated water are involved in intramolecular H-bonding with O7 and O11 of the framework, aids the assembly of a D6R core (Figure S15).

Intrigued by the role of coordinated water (and py-3-CHO) in stabilizing a D6R SBU, the role played by solvent in stabilizing even larger SBUs was investigated. The change of solvent to acetonitrile was crucial for the isolation of the most elusive zeolite SBU "D8R" in the form of discrete cluster $[Zn_8(dipp)_8(Py-3-CHO)_8(CH_3CN)]$ (**2**) (Figure 2). The structural change in this case has been brought about by expansion of the coordination sphere of one of the zinc centers through the ligation by CH_3CN. The ESI-MS of **2** in CH_3CN indicates the stability of the D8R core (Figure 3 and S11). The ^{31}P NMR spectrum displays three resonances at δ −3.4, −3.7

and 4.0 ppm, indicating dissymmetry (Figure S5). Single crystal X-ray structure further confirms this dissymmetry. The stand-out structural feature of **2** is its wide drum-like $Zn_8P_8O_{24}$ core that resembles the D8R SBU (Figure 2 and S16). **2** represents the first example of an independent molecular model for D8R SBU, which is the essential building block in zeolite frameworks MER, PAU, RHO, SBE and TSC.[1]

The dissymmetry in **2** arises because one of the eight zinc centers (Zn1) adopting a trigonal-bipyramidal coordination (Figure 2 and S18). Thus, each of the eight zinc centers in the cluster are bound by three phosphate oxygen atoms and an exocage py-3-CHO coligand,[15] whereas Zn1 alone is further loosely coordinated by acetonitrile (Zn1-N9 (2.349(5) Å)[16] in the endocage position (Figure S17). The coordination of CH_3CN in **2** is very similar to the coordination of water molecule in **1**. Thus, the formation of D6R and D8R structures for **1** and **2** is an essential outcome of the endobinding of small molecules around at least one of the metal centers of the cluster. While smaller H_2O in **1** templates the formation of D6R, the larger CH_3CN dictates the formation of D8R core. Thus, it appears that the combination of a solvent template along with py-3-CHO leads to the stabilization of the larger clusters in the present case.

The above findings throws open the challenge of stabilizing the more common D4R for the present set of reactants. Since endoligation appears to be the means to stabilize D6R and D8R SBUs, it is desirable to use a ligand system that can interact all metal ions to isolate D4R cage. Our recent report on post encapsulation of fluoride ion inside D4R cages suggests the possibility of obtaining D4R cage through a template approach.[12c] The introduction of fluoride (as $^nBu_4NF$) in the reaction mixture leads to the formation of $[^nBu_4N][F@\{Zn-(dipp)(Py-3-CHO)\}_4]$ (**3**), irrespective of the solvent used (Figure 4). The structure of **3** displays anionic core similar to D4R SBUs with an encapsulated fluoride, similar to the fluoride containing silsesquioxane.[17] The Zn1-F1 (2.3731(15) Å) and Zn2-F2 (2.2641(15) Å) distances reveal that the fluoride anion weakly interacts with all the four zinc cations This weak Zn···F interaction is however sufficient to convert the tetrahedral zinc centers to trigonal bipyramidal.

The above experiments demonstrate the power of using a suitable template (fluoride, water or acetonitrile) as a tool to stabilize SBUs of different size. It is important to note that this requires the entry of the templating ligand inside the cage and wrapping the fused S4R SBUs polymers postulated in Figure 1.
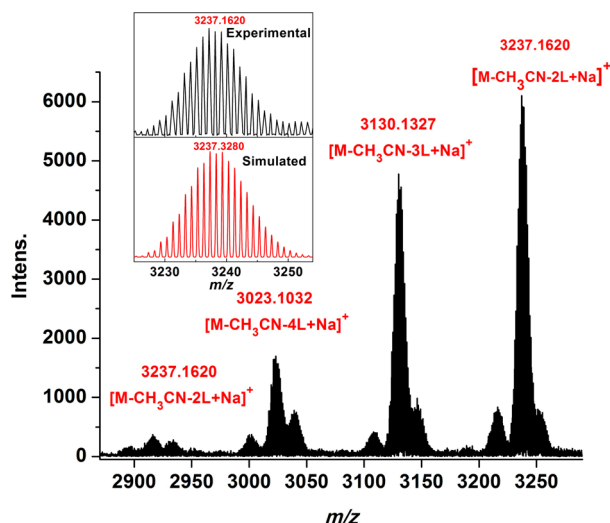
Figure 3. ESI-MS of **2** in acetonitrile.
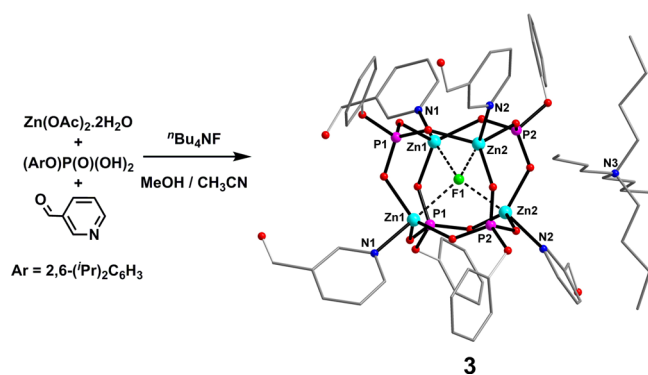
Figure 4. Schematic representation showing the role of fluoride as template in the formation of **3** that is built around D4R SBU. Isopropyl groups on the aryl rings have been removed for the sake of clarity.

This also provides clues for the stabilization of even larger SBUs if appropriate templates were to be utilized. To glean further information on these possibilities, DFT calculations have been carried out on model systems (see ESI) to estimate the energetics involved in stabilizing these SBUs in the presence of different templates (Table 1). To rationalize the absence of a smaller D4R system, the first set of calculations addressed the stability of various SBUs in the untemplated form where all zinc centers in the cluster are tetra-coordinate (Table S8). The gas phase calculations for $[ArPO_3Zn(py\text{-}3\text{-}CHO)]_n$ (n = 4, 6, 8 and 10) indicate that when py-3-CHO is used as the corner capping ligand, the most preferred form of aggregation is D8R whereas the least preferred is D4R. Thus, the D8R structure is stabilized by −67.0 kJ mol^{-1} relative to D4R. The second most stable form is D6R, which is stabilized by −37.4 kJ mol^{-1} relative to D4R, whereas the yet to be isolated D10R structure is still lower in energy (−23.5 kJ mol^{-1}). These results corroborate the isolation of D6R and D8R in the present study and the isolation of a D10R could be a possibility in future.

The second set of calculations was carried out to identify the preferred template for stabilizing a particular structure (Table 1). Although the calculations were restricted to unsolvated and fluoride ion encapsulated forms for D4R, additional possibilities were considered for the higher SBUs. In the case of D4R, the results clearly indicate that fluoride incorporation at the center of the cubane stabilizes the system enormously both in gas phase (−156.7 kJ mol^{-1}) and in methanol (−88.0 kJ mol^{-1}) with respect to no encapsulation. Among various possibilities considered for D6R structures, the solvent coordinated structures have been found to be more stable than the simple D6R structure. Water stabilizes the D6R most, in view of the smaller endohedral cavity, consistent with the experimental isolation of **1**. As the cavity size increases, there are further

possibilities for the D8R. Clearly, the acetonitrile binding to one of the zinc centers seems to be the best endohedral fit both in gas phase and in solvent. Although the ligands such as water, methanol and acetonitrile offer almost similar stabilization for D6R structures in view of their partial encapsulation inside the cage (Figure S26), the larger cavity in D8R completely encapsulates the entire guest molecule. Calculations carried out for possible stabilization of D10R indicate that although it may be possible to isolate these species, clearly these are less preferred than D6R and D8R (Table 1).

Looking ahead, compounds **1** and **2** are not just "molecular cut-outs" of many of the well-known zeolites, but they represent a promising starting point for a new chapter in building zeolite-like porous solids. Recent work from our laboratory has already explored how D4R zeolite building blocks can be combined with ditopic connectors to prepare several isomeric forms of 4-connected hybrid structures.[6d,12d] Compounds **1** and **2**, with six and eight Lewis acidic zinc centers, would offer numerous possibilities for 6- and 8-connected networks with newer network topologies. Currently, our laboratory is engaged in generating other D6R and D8R structures to take this chemistry forward; the second example of an isolated D8R structure **4** has already been realized.[18]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11156.

> Synthesis, ^1H, ^{31}P and ^{19}F NMR spectra, FTIR spectra, TGA profile, ESI-MS spectra, crystallographic details, computational details, and DFT-optimized geometries (PDF)
> CIF files for **1**−**4** (CIF)

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Notes
The authors declare no competing financial interest.

Table 1. Relative Energies (kJ mol^{-1}) of Various DXR (X = 4, 6, 8 and 10) Zinc Phosphates in the Gas and Solution Phases

D4R-SBUs	gas	solution	D6R-SBUs	gas	solution	D8R-SBUs	gas	solution	D10R-SBUs	gas	solution
D4R	0	0[a]	D6R	0	0[b]	D8R	0	0[c]	D10R	0	0[c]
F@D4R	−156.7	−88.0[a]	2H$_2$O@D6R	−143.8	−79.2[b]	CH$_3$CN@D8R	−58.1	−24.7[c]	CH$_3$CN@D10R	−16.6	1.6[c]
			2CH$_3$CN@D6R	−125.6	−72.8[c]	CH$_3$OH@D8R	−18.9	194.9[a]	C$_2$H$_2$@D10R	55.6	53.9[c]
			2CH$_3$OH@D6R	−150.0	66.1[a]	C$_2$H$_2$@D8R	4.4	6.0[c]	C$_4$H$_2$@D10R	52.2	54.0[c]
						C$_4$H$_2$@D8R	−23.0	−15.7[c]	C$_4$N$_2$@D10R	−11.9	6.2[c]
						HCN@D8R	−38.6	−9.3[c]			

^{a}Methanol as solvent. ^{b}Water as solvent. ^{c}Acetonitrile as solvent.

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(15) Unlike in **1**, the 3-pyridinecarboxaldehyde ligands in **2** do not undergo transformation to the corresponding hemiectal or acetal forms due to lack of methanol in the reaction medium.

(16) Although the Zn-N(py) distance of the tetra-coordinated zinc ions varies from the 2.044(4)−2.097(5) Å, the Zn1-N8 distance is longer than the remaining Zn-N distances (2.176(5) Å). The Zn1-N9 distance involving acetonitrile ligands is still longer (2.349(5) Å).

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(18) Compound **4** is formed from the reaction of zinc acetate and 4-chloro-2,6-diisopropylphenyl phosphate with 4-cyanopyridine in acetonitrile. Although most structural features of **4** are similar to **2**, the acetonitrile molecule is not symmetrically oriented within the cage. The coordinated N22 atom forms a weak interaction with Zn8 (2.894 Å) in the apical position, giving rise to a pseudo-trigonal-bipyramidal coordination (see Figure S23; Table S2 and S3 for details).