

Cyclam as a Structure-Directing Agent in the Crystallization of Aluminophosphate Open Framework Materials from Fluoride Media

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Two aluminofluorophosphates have been synthesized using 1,4,8,11-tetraazacyclotetradecane (cyclam) as a structure-directing agent (SDA). The two materials were synthesized hydrothermally and their structures solved by microcrystal diffraction using synchrotron radiation. In both cases, the SDA has been located crystallographically. The first material, [F, Cyclam]-AIPO-CHA, has the molecular formula $\text{Al}_6\text{P}_6\text{O}_{24}\text{F}_2 \cdot \text{C}_{10}\text{H}_{26}\text{N}_4$ and has a framework structure related to the mineral chabazite, with the cyclam molecules occluded within chabazite-like cages (space group $P-1$, $a = 9.0993(4)$ Å, $b = 9.2232(5)$ Å, $c = 9.3929(4)$ Å, $\alpha = 77.881(2)^\circ$, $\beta = 87.205(1)^\circ$, $\gamma = 87.777(1)^\circ$, $Z = 1$, $wR(F^2) = 0.1354$, $R(F) = 0.0487$). The second material, [F, Cu-Cyclam]-AIPO-SAS, has the molecular formula $\text{Al}_8\text{P}_8\text{O}_{32}\text{F}_2 \cdot [\text{CuC}_{10}\text{H}_{24}\text{N}_4 \cdot 2\text{H}_2\text{O}]$ and has a framework structure closely related to STA-6 (SAS) zeolite structure type, although the usual tetragonal symmetry has been reduced to monoclinic by the presence of the fluoride ions (space group $P2_1/n$, $a = 10.3738(4)$ Å, $b = 14.8060(5)$ Å, $c = 13.4494(5)$ Å, $\beta = 90.275(1)^\circ$, $Z = 2$, $wR(F^2) = 0.1484$, $R(F) = 0.0524$). The cyclam is occluded as a copper complex ordered within the cages of the structure. © 2002 Elsevier Science (USA)

Key Words: macrocycle; zeolite; aluminophosphate; X-ray diffraction, fluoride media.

INTRODUCTION

Many new technologies depend on the availability of solid-state materials with suitable chemical and physical properties. The rational design of new materials is thus an important goal for solid-state chemists. Microporous materials, despite being well known already in catalysis, ion exchange and adsorption applications, are one example where designer synthesis will certainly have an impact on future technologies. A recent committee constituted by the US Department of Energy identified the preparation of

tailored porous solids as a major challenge (1). They highlighted many potential future applications of novel porous solids in areas such as shape-selective gas or liquid permselective membranes, catalytic membrane reactors, energy-storage systems, molecular electronic and optoelectronic devices, as well as biomolecule separation, isolation and delivery (1).

Macrocyclic polyamines (azamacrocycles) are well-known molecules that have a number of interesting properties. Recently, there has been interest in these molecules as structure-directing agents (or templates) in the preparation of microporous materials such as gallophosphates and aluminophosphates. Usually, microporous materials are prepared using protonated or quaternary amines as templates (2), and features such as the charge density of the molecules play an important part in determining the final structure of the solid. The cyclic structure and high nitrogen to carbon ratio in azamacrocycles is different from many linear and branched polyamines and may well give different types of microporous structures in these syntheses. In addition, azamacrocycles tend to coordinate strongly to metal ions, and can be regarded as functional molecules in their own right. The possibility of incorporating the azamacrocycles as protonated amine templates and as functional metal complexes is very attractive in the quest to produce new solids with different properties compared to those that have been previously synthesized.

The controlling factors in deciding which of the two types of behavior that is seen are the conditions of synthesis (such as the pH) and the presence of ions of the correct size and chemistry to coordinate to the macrocycle. For example, Ga^{3+} ions are of a good size to coordinate to 1,4,8,11 tetraazacyclotetradecane (cyclam) and the use of this macrocycle in the synthesis of a gallium phosphate material leads to a new type of inorganic–organic hybrid material where the cyclam is present as a complex, coordinated to gallium, which is covalently bound to the

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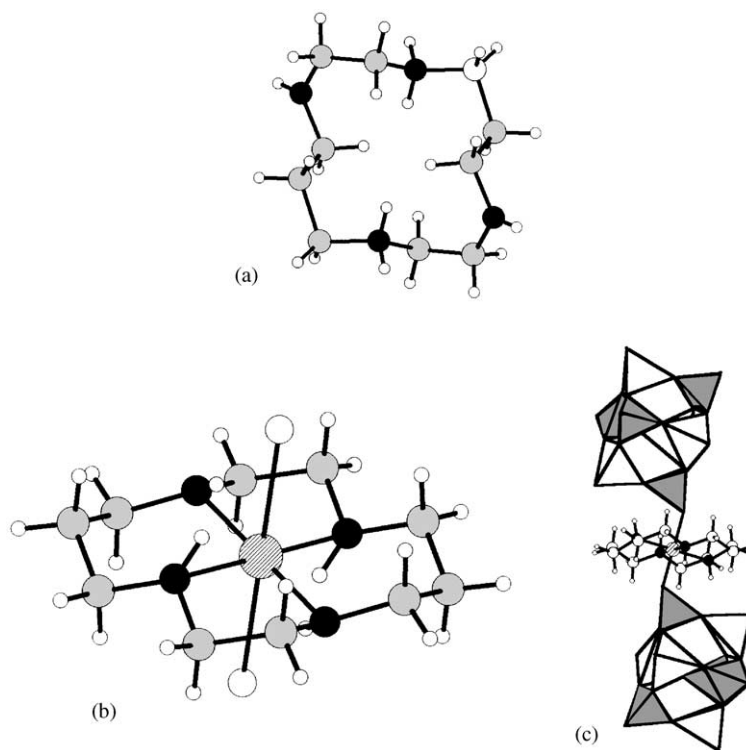


FIG. 1. The three possible 'templating' modes for the azamacrocycle cyclam in microporous materials; protonated cyclam (a), cyclam complex not bound to the framework (b) and metal cyclam complex covalently bonded to the framework (c).

zeolite-like gallium phosphate framework (3). The gallium at the center of the cyclam complex can be replaced by other metal ions that form strong complexes with the macrocycle, such as Cu^{2+} (4). Similar situations can be found in other compounds (5). In contrast, when no metal ions of the correct size are available to form complexes to the macrocycle, and the pH conditions are such that at least one of the nitrogen atoms is protonated, macrocycles can be incorporated into the structure as a free ligand, not bound to the framework. This situation occurs when the size of the macrocycle is increased, for example to the larger 1,4,7,10,13,16-hexaazacyclooctadecane, where the gallium ion is now too small to be effectively coordinated inside the macrocycle (6). In certain situations, when the ratio of metal:azamacrocycle is correct, both types of behavior can be seen in the same material (7). One other possible situation that has not been explicitly identified, at least unambiguously by crystallography, is a metal-macrocycle complex directing the structures (i.e., a metal complex not connected covalently to the framework). The three situations are depicted schematically in Fig. 1.

In this paper, we report the use of the fluoride method to synthesize two microporous aluminophosphate materials using cyclam (1,4,8,11 tetraazacyclotetradecane) with and without Cu^{2+} ions present. We have prepared frameworks based on the CHA and SAS zeolite structure types (8). We have shown that the macrocycles can be incorporated as

either the protonated amine, in the absence of metal ions, or as the Cu^{2+} complex. In all cases, the crystal structures of the materials have been solved using single-crystal X-ray diffraction, and in both cases the fluoride ions cause a lowering of the high symmetry, which allows the location of the macrocycle to be identified crystallographically.

EXPERIMENTAL

The two materials prepared in this work have been designated [F,Cyclam]-AIPO-CHA and [F,Cu-Cyclam]-AIPO-SAS, indicating the SDAs used (e.g., [F,Cu-Cyclam]), the chemical composition of the framework (AIPO) and the type of zeolite framework prepared (e.g., SAS).

Synthesis

A summary of the synthesis conditions and major products is given in Table 1. Specific syntheses for the two materials reported here are as follows.

[F,Cyclam]-AIPO-CHA. The aluminum source, 1.67 mmol of aluminum hydroxide hydrate or aluminum isopropoxide (Aldrich), was dispersed into 10 ml of distilled water and 0.19 g of phosphoric acid (85 wt% in H_2O , Aldrich) and the mixture was stirred until homogeneous. Hydrofluoric acid (0.03 g, 48 wt% in H_2O , Aldrich) was

TABLE 1
Synthesis Details

Aluminium source	SDA	M ²⁺	pH	Products
Aluminium hydroxide or + isopropoxide	Cyclam	None	5–6.5	major—CHA Minor—unknown
Aluminum isopropoxide	Cyclam	Cu ²⁺	5	major—CHA minor—SAS
Aluminum hydroxide	Cyclam and trimethylamine	Cu ²⁺	5	LTA

added, followed by 0.08–0.12 g of cyclam (Aldrich) to fix the initial pH in the range 5–6.5. This mixture was aged for 1 h at 25°C, transferred to a polytetrafluoroethylene-lined acid digestion bomb (23 ml, Parr) and heated at 170°C for 96 h. The resultant colorless crystalline product was recovered by sonication, filtration, washed with distilled water and acetone and then dried in air. This synthesis produced two phases, the major one was [F, Cyclam]-AlPO-CHA and a trace phase which is unidentified.

[F,Cu-Cyclam]-AlPO-SAS. Aluminium isopropoxide (0.60 g, Aldrich) was dispersed into 10 ml of distilled water and 0.34 g of phosphoric acid (85 wt% in H₂O, Aldrich) and the mixture was stirred until homogenous. Copper acetate hydrate (0.1 g, Aldrich) and 0.07 g of hydrofluoric acid (48 wt% in H₂O, Aldrich) were added to the mixture and stirred until homogenous. Cyclam (0.21 g, Aldrich) was added to adjust the initial pH to 5. This mixture was aged for 1 h at 25°C, transferred to a polytetrafluoroethylene-lined acid digestion bomb (23 ml, Parr) and heated at 170°C for 72 h. The resultant pink crystalline product was recovered by sonication, filtration, washed with distilled water and acetone and then dried in air. Powder X-ray diffraction showed that three phases were present. The major phase was identified as [F, Cyclam]-AlPO-CHA and the second as [F,Cu-Cyclam]-AlPO-SAS. The third unknown minor phase has not yet been identified.

Characterization

Powder X-ray diffraction was carried out on a STOE STADIP diffractometer operating on monochromated CuK α_1 radiation. Powder data were collected in Debye-Scherrer geometry using 0.5 mm quartz capillaries over 14 h. Single-crystal X-ray diffraction was carried out with a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK. Data reduction was carried out using the Bruker AXS SAINT and SADABS packages (9). Both structures were solved by direct methods (SHELXS-97) (10) and refined with full-matrix least-squares technique (SHELXL-97) (10). Full details of the X-ray diffraction experiments are given in Table 2 and in the

TABLE 2
Crystal Structure and Refinement Details

Sample title	[F, Cyclam]AlPO-CHA	[F, Cu-Cyclam]AlPO-SAS
Chemical formula	C ₁₀ N ₄ H ₂₆ ·Al ₆ P ₆ O ₂₄ F ₂	[CuC ₁₀ H ₂₄ N ₄ ·2H ₂ O]·Al ₈ P ₈ O ₃₂ F ₂
Formula weight	972.05	1313.51
Temperature (K)	293(2)	150(2)
Wavelength	0.69300	0.68870
Unit cell (Å)		
A	9.0993(4)	10.3738(4)
B	9.2232(5)	14.8060(5)
C	9.3929(4)	13.4494(5)
α	77.881(2)	90
β	87.205(1)	90.275(1)
γ	87.777(1)	90
Cell volume (Å ³)	769.48(6)	2065.73(13)
Z	1	2
Symmetry,	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> ₂ /n
Spacegroup		
Density (calculated) (Mg/m ³)	2.0298	2.112
Absorption coefficient (mm ⁻¹)	0.519	0.955
<i>F</i> (000)	492	1318
Crystal size (mm)	0.03 × 0.02 × 0.01	0.05 × 0.03 × 0.02
θ range (°)	2.2–29.42	1.98–29.35
Unique reflections	4033	5587
Observed reflections	3740	4574
Parameters/restraints	271/0	304/0
Goodness-of-fit (<i>F</i> _{all data} ²)	1.124	1.12
Final <i>R</i> indices		
[<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.1354	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1484
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0522, <i>wR</i> ₂ = 0.1382	<i>R</i> ₁ = 0.060, <i>wR</i> ₂ = 0.1515

supplementary material. In both cases, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed. Atomic coordinates and equivalent isotropic displacement parameters for [F, Cyclam]-AlPO-CHA and [F, Cu-Cyclam]-AlPO-SAS are given in Tables 3 and 4, respectively.

RESULTS AND DISCUSSION

The use of cyclam as a templating agent in the absence of any divalent metal ions produces the material [F,Cyclam]-AlPO-CHA (Figs. 2 and 3). This material has essentially the same framework as the UT6 material first prepared by Ozin and co-workers (11) and reported in gallium phosphates subsequently (12), although this is the first time this framework has been prepared using a macrocyclic SDA. The structure consists of double six-membered rings (D6R), which are linked through four membered rings to produce a cage structure (Figs. 2 and 3) and is topologically equivalent to the structure of the mineral chabazite, although the symmetry is reduced to triclinic. The cyclam molecule sits inside the cages formed at the intersection of eight-membered ring pores. The cyclam molecule is incorporated into this structure as a diprotonated species, as would be expected from the conditions of synthesis. The X-ray diffraction clearly reveals two resolvable orientations of the template inside the cages, the four nitrogen atoms

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$) for [F, Cyclam]-AlPO-CHA

Atom	x	y	z	U(eq)
P(1)	1176(1)	8650(1)	6775(1)	10(1)
P(2)	-3136(1)	8864(1)	8929(1)	11(1)
P(3)	-1449(1)	3275(1)	8603(1)	11(1)
Al(4)	-1318(1)	11036(1)	6553(1)	11(1)
Al(5)	-623(1)	6317(1)	9090(1)	10(1)
Al(6)	-3353(1)	11270(1)	10727(1)	11(1)
F(1)	1080(2)	5073(2)	9216(2)	13(1)
O(1)	131(2)	7428(2)	7386(2)	17(1)
O(2)	2512(2)	8619(2)	7694(2)	16(1)
O(3)	1766(2)	8474(2)	5264(2)	16(1)
O(4)	409(2)	10174(2)	6640(2)	18(1)
O(5)	-2363(2)	7369(2)	9119(2)	16(1)
O(6)	-2857(2)	9616(2)	10193(2)	21(1)
O(7)	-2652(2)	9881(2)	7493(2)	19(1)
O(8)	-4786(2)	8661(2)	8870(2)	21(1)
O(9)	-1462(2)	4957(2)	8122(2)	13(1)
O(10)	-274(2)	2650(2)	9676(2)	15(1)
O(11)	-2965(2)	2775(2)	9313(2)	17(1)
O(12)	-1249(2)	2640(2)	7214(2)	18(1)
C(1)	-5407(7)	5357(8)	7896(6)	70(2)
N(2) ^a	-4201(11)	5863(12)	6813(13)	64(2)
C(3) ^a	-4515(15)	7282(14)	5712(14)	62(3)
C(4)	3015(16)	12421(15)	5113(12)	147(6)
N(5) ^a	2134(14)	13463(18)	5720(30)	122(7)
C(6) ^a	3037(9)	4575(10)	6124(12)	46(2)
C(7)	3820(13)	4079(8)	7388(10)	125(5)
C(2) ^a	-4848(17)	6653(16)	6578(16)	71(4)
N(3) ^a	-3407(12)	6183(13)	5955(11)	67(2)
C(5) ^a	3510(80)	12330(50)	6370(40)	430(60)
N(6) ^a	4640(40)	3360(110)	6400(60)	580(80)

^aFractional occupancy fixed at 50%. The two orientations of the cyclam SDA are coincident at C(1), C(4), and C(7).

being almost coincident in the two orientations. In both cases the macrocycle adopts the trans-III conformation. However, a number of atoms (as can be seen in Table 3) have relatively large anisotropic displacement parameters, indicating that the disorder may in fact be even more complicated than that described above. However, no further chemically sensible disordering schemes could be resolved.

The fluoride ions are incorporated, as for other fluoride CHA-type structures (12), as part of six coordinate AlO_4F_2 octahedra. Two of these octahedra share one edge and link the D6R units into chains running through the structure. In the other directions the D6R units are linked by 4MRs, as in the chabazite structure.

Hydrogen bonding plays an important role in this structure, with relatively short hydrogen bonds from the nitrogen of the cyclam to the framework oxygens (see supplementary material for details). Adding some Cu^{2+} ions to the synthesis mixture results in the recovery of a pale pink powder containing very small crystals with two different types of morphology. Single-crystal data collec-

TABLE 4
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$) for [F, Cu-Cyclam]-AlPO-SAS

Atom	x	y	z	U (eq)
Cu(1)	0	0	0	15(1)
Al(1)	7655(1)	1053(1)	3492(1)	8(1)
Al(2)	2296(1)	1006(1)	3870(1)	7(1)
Al(3)	5075(1)	1041(1)	7278(1)	6(1)
Al(4)	9978(1)	2320(1)	6158(1)	6(1)
P(1)	2327(1)	1045(1)	6198(1)	7(1)
P(2)	7592(1)	1079(1)	5973(1)	7(1)
P(3)	4858(1)	1058(1)	2647(1)	7(1)
P(4)	-5(1)	2350(1)	3784(1)	6(1)
F(1)	7909(2)	917(2)	2204(2)	22(1)
O(1)	8562(2)	1748(2)	6431(2)	12(1)
O(2)	8037(3)	131(2)	6311(2)	14(1)
O(3)	7525(3)	1168(2)	4869(2)	16(1)
O(4)	5954(2)	1217(2)	3365(2)	14(1)
O(5)	4978(2)	1630(2)	1713(2)	11(1)
O(6)	4787(3)	69(2)	2313(2)	13(1)
O(7)	3602(2)	1320(2)	3163(2)	13(1)
O(8)	985(2)	1638(2)	3475(2)	14(1)
O(9)	108(2)	2516(2)	4901(2)	12(1)
O(10)	301(2)	3245(2)	3275(2)	11(1)
O(11)	-1341(2)	2038(2)	3486(2)	15(1)
O(12)	2625(3)	1233(2)	5103(2)	15(1)
O(13)	1823(3)	98(2)	6340(2)	17(1)
O(14)	1310(2)	1714(2)	6563(2)	11(1)
O(15)	3557(2)	1213(2)	6794(2)	14(1)
O(16)	6264(2)	1267(2)	6417(2)	13(1)
O(17)	183(3)	-50(2)	1872(2)	30(1)
N(1)	-1638(3)	724(2)	142(2)	15(1)
C(2)	-1369(4)	1635(3)	-260(3)	22(1)
C(3)	-45(4)	1913(3)	87(3)	23(1)
N(4)	873(3)	1199(2)	-224(3)	20(1)
C(5)	2180(4)	1334(3)	187(3)	23(1)
C(6)	3107(4)	597(3)	-150(3)	23(1)
C(7)	-2827(4)	321(3)	-286(3)	20(1)

tion of the "block" crystals, which are by far the minor product, showed them to have the same structure as the copper-free [F,cyclam]-CHA described above. Unfortunately, the remaining crystals were intergrown together and could not be used for single-crystal X-ray diffraction and their structure remains unknown at present, although powder XRD does show them to have a different structure compared to either of the two materials described here.

Using a more acidic source of aluminum, in combination with slightly less macrocycle and more fluoride ions, produced another pink powder. Single-crystal X-ray diffraction, of the minor phase, in this case revealed the structure as being a highly distorted version of the SAS structure first reported by Wright and co-workers (13,14). The template in this case, as shown by the beautifully ordered crystal structure, is the Cu-cyclam complex, incorporated unbound into the cages of the SAS structure. As in the cyclam-GaPO and Cu-cyclam-GaPO materials, the four nitrogen atoms of the cyclam take the four

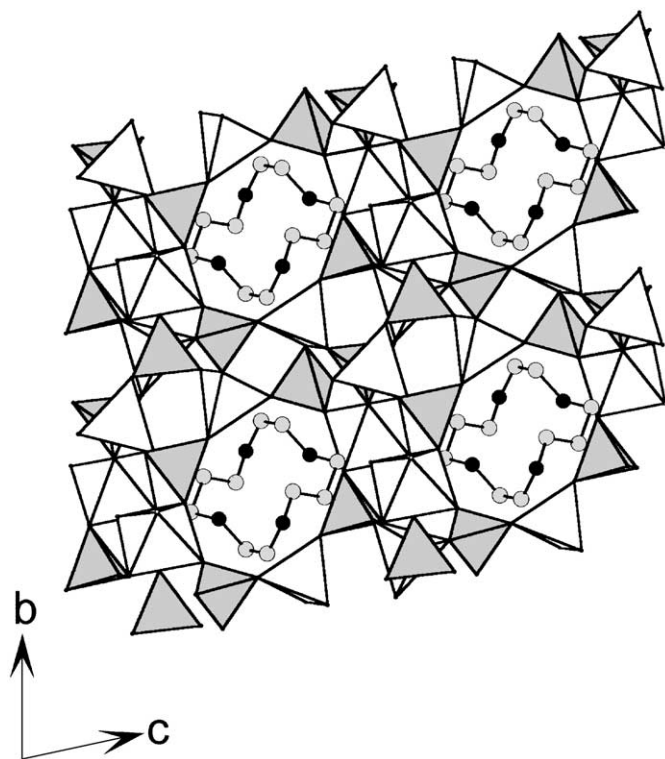


FIG. 2. View of [F,Cyclam]-AlPO-CHA down the crystallographic *a*-axis. AlO_4 tetrahedra and AlO_4F_2 octahedra are depicted as open polyhedra, PO_4 tetrahedra as shaded polyhedra. Carbon and nitrogen atoms are shown as empty and filled spheres, respectively.

equatorial positions of the octahedral complex. However, unlike cyclam GaPO, the axial oxygen atoms are not part of the inorganic framework, but are instead water molecules. This is the first example of this type of templating by a metal azamacrocycle complex that has been proven crystallographically (Figs. 4 and 5).

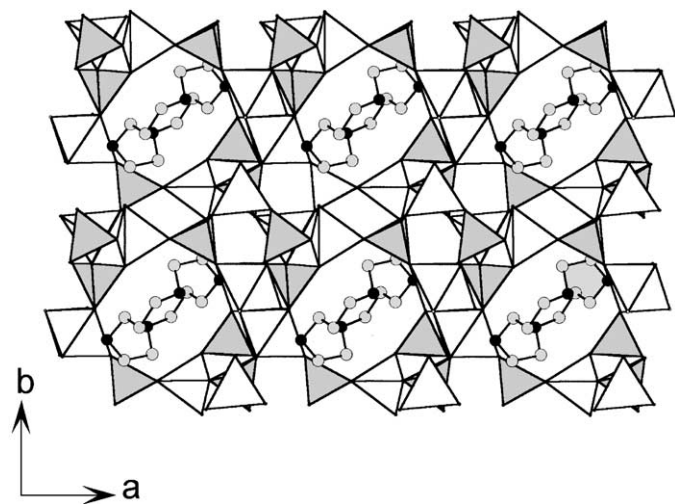


FIG. 3. View of [F,Cyclam]-AlPO-CHA down the crystallographic *c*-axis. Key as for Fig. 2.

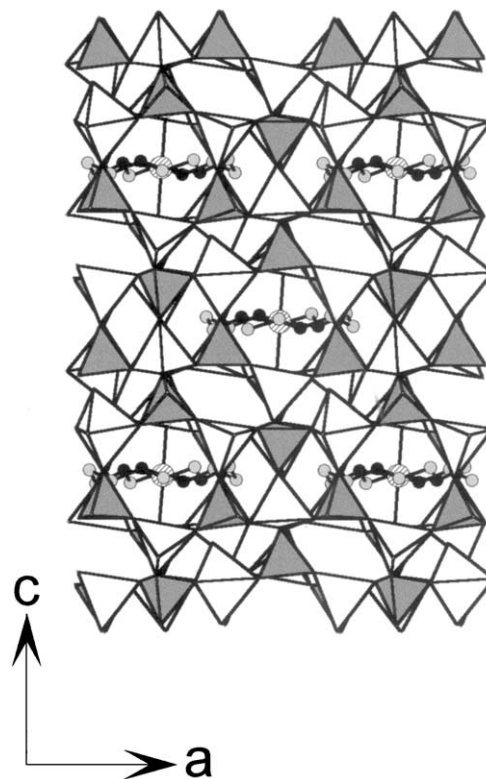


FIG. 4. [F,Cu-Cyclam]-AlPO-SAS viewed down the crystallographic *b*-axis. Al- and P-centered tetrahedra are unhatched and hatched, respectively. C, N, O, and Cu atoms are depicted as gray, black, white, and hatched spheres, respectively.

Changing the relative amounts of macrocycle and fluoride further, as well as when other bases (such as triethylamine) are used to control the pH of the synthesis mixture, leads to a material with the framework structure of zeolite LTA being the easiest to prepare. This structure has high symmetry (cubic) and can be described as containing only the D4R secondary building unit. This cage is smaller than the D6R unit and the fluoride ions are incorporated at the center of the cages, as is well known in many other D4R-containing solids (4). Again, as with [F,Cyclam]-AlPO-CHA and [F,Cu-Cyclam]-AlPO-SAS, the macrocycle would be expected to be located in the center of the large cages found in the structure. However, the high symmetry of the materials necessarily leads to many equivalent orientations of any low-symmetry template within these cages, making template location by X-ray diffraction almost impossible. Electron spin resonance studies do, however, indicate that the macrocycle is included as the metal complex in the cages.

An interesting aspect of the work is the reason why the SAS framework prepared in this work occluded the macrocycle as the copper complex, whereas Wright and co-workers prepared the aluminophosphate materials SAS (STA-6) and SAV (STA-7) (13,14) incorporating uncomplexed macrocycles. The answer is probably due to the

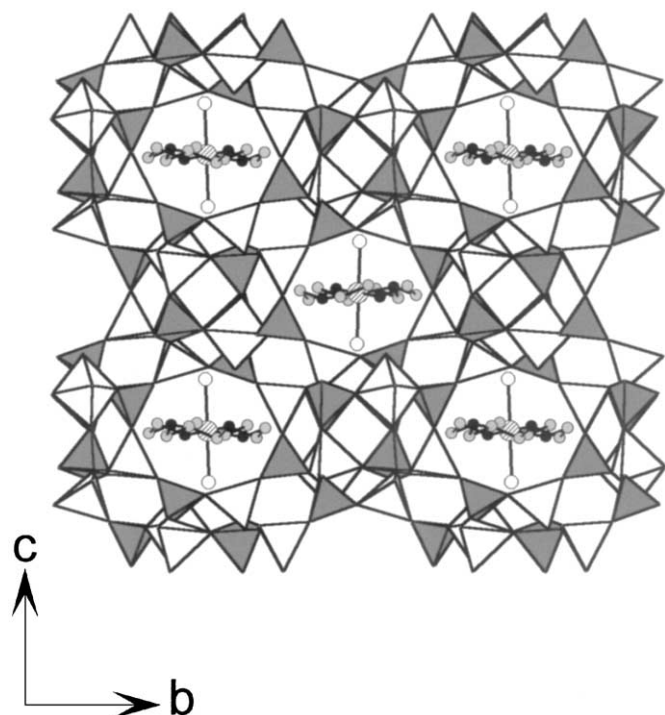


FIG. 5. [F,Cu-Cyclam]-AlPO-SAS viewed down the crystallographic *a*-axis. Key as for Fig. 4.

nature of the macrocycle used; in Wright's work the cyclam molecules were methylated on the nitrogen atoms. The alkylation of macrocycle nitrogen atoms, to produce tertiary species, reduces the binding constant of macrocycles with most metals significantly. For example, in the case of cyclam the equilibrium constant for complexation with Cu^{2+} is reduced from $\log K \sim 30$ to $\log K \sim 17$ magnitude by methylation on all four nitrogens (15). Therefore, methylation on the nitrogen reduces the probability of incorporating the macrocycle into a microporous solid as a metal complex. However, the reduction in binding constant is not enough to preclude the inclusion of a metal complex as an SDA in the structure. Wright *et al.* have used a Ni-tetramethylcyclam complex as an SDA in the preparation of metal aluminophosphates (16). The Ni complex could not, however, be located using X-ray diffraction.

The results of this work show that careful control over the reaction conditions and a judicious choice of mineralizer and metal ion can lead to the incorporation of the (un-methylated) cyclam complex as either the protonated amine or an unbound metal complex. This control over structure is vital if new applications of microporous materials are to be developed based on designer syntheses. It is, however, also instructive to examine the incorporation of the fluoride ions into the structures.

Fluoride ions have been known for a number of years to be excellent mineralizing agents in the preparation of microporous materials of different types (17). In silica

based zeolites, aluminum phosphates and especially gallium phosphates are also incorporated into the framework and can act to balance the charge of the template (18, 19). The use of fluoride ions, in combination with macrocycles containing secondary amines, minimizes the chances of the metal ions being incorporated into the framework while maximizing the chances of them being coordinated to the macrocycle. The choice of a metal cation (e.g., Cu^{2+}) with a high binding constant to cyclam and with a preference for octahedral coordination also reduces the chances of the metal being incorporated into the framework.

Recently, it has become evident from single-crystal diffraction experiments that fluoride can lower the symmetry of highly symmetric systems, sometimes leading to ordering of templates inside seemingly high-symmetry cavities. The most startling example of this effect of fluoride is on the purely siliceous zeolite IFR (ITQ-4) (20). In the case of IFR, the framework is topologically centrosymmetric, but the location of fluoride in the structure reduces the symmetry to non-centrosymmetric and allows ordering of the organic templating cations. The breaking of symmetry occurs because the fluoride ions bond to the silicon or aluminum atoms (in addition to four oxygen atoms), removing local tetrahedral symmetry. The structure of [F,Cu-Cyclam]-AlPO-SAS is also an excellent example of this. Metal-aluminophosphate SAS crystallizes in a tetragonal spacegroup, and the methylated cyclam template used to prepare the material is grossly disordered inside the high-symmetry cages. However, the fluoride ions

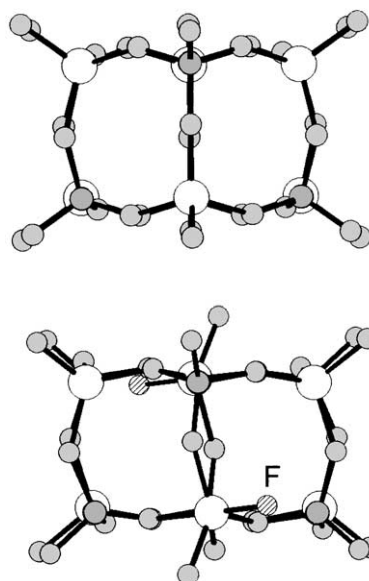


FIG. 6. The high-symmetry D6R cage from the tetragonal SAS framework (top) and the lower symmetry cage formed when fluoride ions are connected at two opposite corners of the cage, as in the [F,Cu-Cyclam]-AlPO-SAS structure (bottom). One of the fluoride ions (hatched circles) is labelled. Key: Al, White; P, dark gray; O, light gray.

are incorporated into the SAS framework as $[\text{AlO}_{4/2}\text{F}]^-$ units (Fig. 6), and the symmetry of the material is lowered to monoclinic, allowing the hydrated Cu-cyclam template to be beautifully ordered in the structure. The distortion from tetragonal is marked, one of the previously equivalent cell edges increasing by $\sim 0.8 \text{ \AA}$, the other decreasing by almost the same amount. The fluoride ions are located in the structure so that two of them point into the cages containing the Cu-cyclam template, exactly balancing the dipositive charge of the complex.

CONCLUSION

Careful design of reaction conditions has allowed the incorporation of an azamacrocycle template (cyclam) in both diprotonated and copper (II) complex forms into three different microporous structures. Characterization of the materials was carried out using a number of techniques. Microcrystal X-ray diffraction at a synchrotron source enabled the structures to be solved from relatively small crystals. The use of such synthetic methods opens up the possibility of preparing new materials with functional templates for novel applications.

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