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Zeolite Analogues

Ionothermal Synthesis of Unusual Choline-Templated Cobalt Aluminophosphates**

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Crystalline porous solids, such as zeolites and metal–organic frameworks, are of interest in a number of areas of modern science, particularly in those associated with catalysis[1] and gas adsorption.[2–4] Recently, we developed a new method of preparing aluminophosphate molecular-sieve analogues,[5–10] as well as other materials,[11–13] based on the use of ionic liquids as both the solvent and the structure-directing agent (or template). This new method, which we call ionothermal synthesis, has some interesting features and potential advantages over the traditional methods of molecular-sieve synthesis. For example, most ionic liquids have vanishingly small vapor pressures, which means that no autogenous pressure is produced on heating and that ionothermal synthesis can take place at ambient pressure. In addition, altering the solvent system from a molecular solvent (e.g. water) to an ionic liquid also changes the chemistry involved. One particularly attractive feature of the method is that the cation of the ionic liquid can also act as the structure-directing agent, around which the final solid material forms during the reaction process. It should be noted that, while ionothermal synthesis takes place in a predominantly ionic environment, it does not preclude the presence of small, reactant quantities of molecular species, such as water. In fact, this property can be beneficial, as it allows precise control over the water content in the reaction, leading to more subtle control over the hydrolysis occurring in the reaction process.

Deep-eutectic solvents (DESs) are ionic liquids comprising mixtures of compounds for which there is a depression in the freezing point compared with that of the separate components. One class of such DESs comprises mixtures of organic halide salts, such as choline chloride, with hydrogen-bond donors, such as amides, amines, alcohols, and carboxylic acids.[14,15] Choline itself is a very attractive template, as it is cheap and toxicologically very benign. However, in our recent work using a choline chloride–urea DES,[5,8] the urea portion of the liquid acted as the template. Clearly, in a competition between choline and urea-derived ammonium cations, it is the latter that provide the better templating. To remove this competition, it is necessary to replace the urea in the DES with a component that is not likely to act as a template. Herein, we report the use of choline chloride–carboxylic acid DESs in the ionothermal synthesis of cobalt aluminophosphate (CoAlPO) materials. Two of the materials we report are a CoAlPO zeolite analogue with the levyne (LEV) framework topology, and a novel and unusual zeolite-related layered material in which the cobalt atoms are ordered and form terminal Co−Cl bonds. These Co−Cl units are normally not accessible using traditional routes, because they are sensitive to hydrolysis in the presence of excess water. This work illustrates how changing the chemistry of the synthesis system from molecular to ionic can lead to novel types of materials.

Three different choline chloride–carboxylic acid DESs were used in this study. Succinic acid, glutaric acid, and citric acid were each mixed with choline chloride to form three DESs, all with melting points less than 150 °C, making them potentially useful solvents for ionothermal synthesis. When the solvents were used for the attempted preparation of aluminophosphates, only dense phases, such as berlinite, were formed. However, it is important to find the right conditions, and control over the acid–base properties of the solvent seems particularly important. To control these properties, we added bases, such as 1,4,8,11-tetraazacyclotetradecane (cyclam) or pyridine, to the acidic DESs. Using these modified DESs, a novel CoAlPO, SIZ-13, was prepared at 150 °C. All three carboxylic acids gave this product under the same conditions.

The blue crystals of SIZ-13 recovered from the reaction mixture were large enough for single-crystal X-ray diffraction experiments. Unfortunately, the crystals were of relatively poor quality, and the resulting agreement factors after structure solution and refinement were still relatively large ($R_1 = 0.18$). Data collected at a synchrotron source failed to improve the quality of the refinement. However, the refinement was good enough to locate all the non-hydrogen atoms, and the structure was subsequently confirmed using Rietveld refinement of the model against powder X-ray diffraction data (see the Supporting Information). The addition of a small amount of base to the DES is necessary for SIZ-13 to form, but the nature of the base seems to be unimportant, as cyclam and pyridine are both suitable.

The asymmetric unit of SIZ-13 (empirical formula $[Al_3CoClP_4O_{16}][C_5H_{13}NOH]_2$) contains 2 cobalt, 6 aluminum, 8 phosphorus, 32 oxygen, and 2 chlorine atoms (Figure 2).

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Four crystallographically independent choline cations could also be located. The material contains $[Al_3CoClP_4O_{16}]^{2-}$ layers, with the choline cations filling the interlayer space. The structure of SIZ-13 is very closely related to that of the gallium phosphate (GaPO) solid DMAP–GaPO (DMAP = 4-dimethylaminopyridine),[16] and to those of the microporous zeolites SSZ-51[17] and SAPO-40,[18] which all contain a similar building unit. This building unit, shown in Figure 1, is closely related to the double-four-ring (D4R) units found in other phosphate-based solids.[19–21] However, unlike in many other zeolite-related materials, the cobalt ions in the SIZ-13 structure are ordered in one crystallographic position at the corner of the building unit, and are coordinated to three oxygen atoms and one chlorine atom, rather than to four oxygen atoms, as is normally the case. Under normal circumstances, using more traditional synthetic methodologies in the presence of water, Co–Cl bonds like those present in SIZ-13 are extremely sensitive to hydrolysis. Such metal–chlorine bonds have, therefore, not been found previously in this type of compound when made hydrothermally.

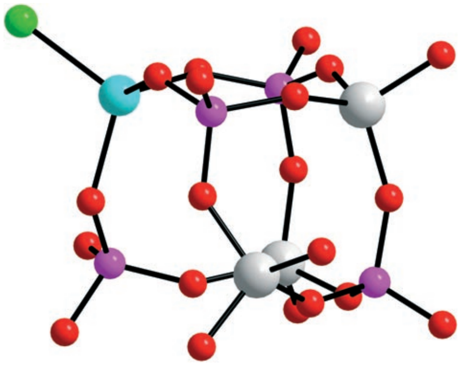

Figure 1. The ring-opened D4R unit in SIZ-13. Co cyan, Al gray, P purple, O red, Cl green.

The main question arising is why a material like SIZ-13 can be made using ionic liquids. The answer is probably found in the deactivation of water through its strong interaction with the anions in the DES.[22,23] It is now relatively well-known that "wet" ionic liquids (containing as much as 7 M water, depending on the ionic liquid) behave as if the water is less reactive than one would expect it to be. Yasaka et al. showed, using hydrogen–deuterium exchange reactions, that water is significantly deactivated in ionic liquids,[24] and Hardacre and co-workers showed that highly sensitive molecules like PCl_3 can be stored for extended periods in various ionic liquids without hydrolysis.[25] The reason for this deactivation of water is that, even at significant concentrations, the water is molecularly dispersed or present only as small clusters, and the strong water–anion interactions reduce the nucleophilicity of the water and decrease its hydrolysis activity. In contrast, water in organic solvents often phase segregates on a microscopic scale to form hydrophilic regions that show normal water reactivity.

In essence, ionic liquids act as if they are "dry" solvents, allowing hydrolysis that is much slower, and hence more controllable, than for other solvents. That a compound such as SIZ-13 can be isolated from an ionothermal synthesis demonstrates the extra control over the hydrolysis conditions that is possible using such non-aqueous preparative routes.

The ring-opened D4R units are connected together through Al-O-P linkages to form sheets in the structure of SIZ-13 (Figure 2). The mode of connectivity is very similar to that seen in DMAP-GaPO,[16] but in SIZ-13 the ordered Co–Cl units point into the interlayer spaces. The choline template molecules are also ordered between the layers in the SIZ-13 structure. That the template is choline was confirmed by dissolving the structure in hydrochloric acid and using ^{1}H NMR spectroscopy to identify the choline resonances in the resulting solution.

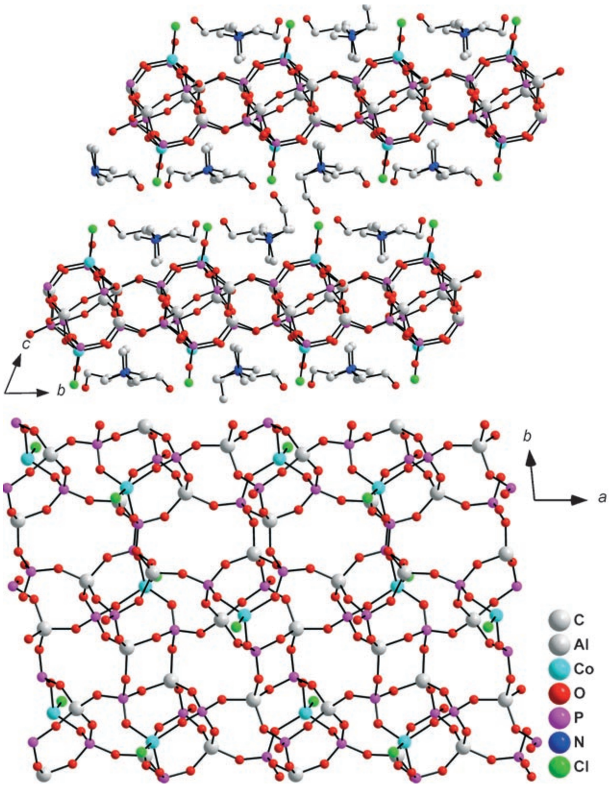

Figure 2. The layered structure of SIZ-13 viewed parallel to the *a* axis (top; hydrogen atoms are omitted), and a single $[Al_3CoClP_4O_{16}]^{2-}$ layer viewed parallel to the *c* axis (bottom; choline template molecules are omitted).

A general rule of thumb in the synthesis of aluminophosphates is that increased synthesis temperature tends to favor three-dimensional structures over layered materials, if all other synthesis conditions remain constant. The synthesis temperature was, therefore, increased to 180 °C, and the resulting blue crystalline solid was characterized by single-crystal X-ray diffraction at a synchrotron source. The diffraction experiment revealed that the new material, called SIZ-14, is a CoAlPO with the levyne (LEV) framework topology (Figure 3). The LEV topology was first prepared as an aluminosilicate zeolite by Barrer and Kerr in 1959,[26] but has subsequently been prepared as a CoAlPO material (called Co-DAF4) using 2-methylcyclohexylamine as the

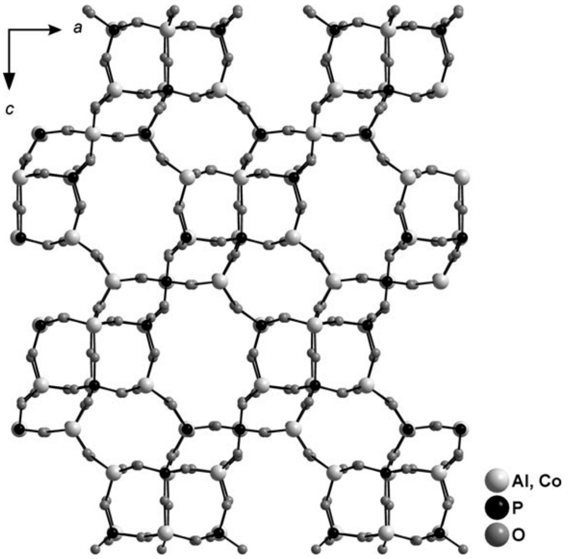

Figure 3. The structure of the framework of SIZ-14 viewed parallel to the *b* axis.

template,[27] as well as in several other compositions.[28,29] Unlike SIZ-13, where the Co^{2+} ions are perfectly ordered on one particular site, in SIZ-14 they are disordered through the structure, substituting for aluminum. This type of disorder is the usual situation in zeolitic materials and can most likely be traced back to the higher synthesis temperature.

The asymmetric unit of the SIZ-14 framework (empirical formula $Co_xAl_{1-x}PO_4^{x-}$, where $x \approx 0.17$ from crystallography and atomic absorption experiments) contains two aluminum/cobalt sites, two phosphorus atoms, and six independent oxygen atoms. The framework structure consists of large cages with dimensions of approximately 3.6×4.8 Å^2, which are linked through eight rings (8Rs) or four rings (4Rs) and capped by double six rings (D6Rs). The relatively large cages in the structure are, therefore, only accessible through relatively small windows, allowing free movement of small molecules through the structure and into the cages, where interesting catalytic reactions can then occur.

For Co-DAF4, Barret and Jones used resonant (anomalous) scattering of X-rays to show that the cobalt ions preferentially occupy aluminum sites that minimize the number of Co-O-P-O-Co linkages.[27] Without such complex experiments, it is difficult to say with certainty whether such preferential siting of cobalt is also present in SIZ-14. However, careful scrutiny of the bond lengths around the aluminum/cobalt sites in SIZ-14 indicates that the average Al1(Co1)−O distance of 1.750 Å (range 1.741(3)–1.772(4) Å) is slightly longer than the average Al2(Co2)−O distance of 1.713 Å (range 1.704(3)–1.723(3) Å), indicating that there might be a slight preference of cobalt for the Al1(Co1) site.[30] However, this is a very small effect, and for the final refinement both sites were restrained to have equal amounts of cobalt. The refined occupancy for Co1 and Co2 was 0.173(5), with the balance made up by aluminum. The preferential siting of metals in zeolite frameworks is connected to the location of the template, as it is the electrostatic interaction between the positively charged template and the negative charge on the framework that dominates. Since different templates were used to produce Co-DAF4 and SIZ-14, we might not expect the same ordering, in any case.

Because of the high rhombohedral symmetry of SIZ-14, the template in the structure could not be found using diffraction. The presence of paramagnetic Co^{2+} ions in the framework also means that solid-state NMR spectroscopy, the technique usually used to identify the nature of templates, is not helpful for these materials. The presence of choline as the template in SIZ-14 was, however, confirmed by dissolving the CoAlPO framework in concentrated hydrochloric acid and using ^1H and ^{13}C NMR spectroscopy to detect the resonances expected for choline, in a similar manner to that used for SIZ-13. The thermogravimetry (TG)–mass spectrometry (MS) traces for SIZ-13 and SIZ-14 also revealed very similar fragmentation patterns for removal of the organic components of the structure, further confirmation that the template is choline in both cases. These experiments are extremely important, because a base, such as cyclam or pyridine, is required for the successful synthesis of both SIZ-13 and SIZ-14, but could, in theory, compete with choline to template the final solid.

In many of our preparations using cyclam, a small amount of an impurity phase, which we call SIZ-15, was present. Single-crystal X-ray diffraction experiments revealed that this material is a chain CoAlPO templated not by choline but by cyclam. There is clearly the possibility of competition between the choline component of the DES and the added cyclam, which must be protonated to act as a template. This result is important in itself, as it confirms that a template can, in principle, be added to a DES, in the same way that templates are normally added to water in hydrothermal synthesis. For this to be an effective strategy, the components of the DES itself should preferably be poorer templates than the added compounds, although if the templating ability of the DES and the added compounds are similar, there is the intriguing possibility of cooperative templating effects.

The structure of SIZ-15 (empirical formula $[Al_{2-x}Co_xP_4O_{16}][C_{10}N_4H_{29}]$, where $x \approx 0.04$ as determined crystallographically) contains CoAlPO chains consisting of tetrahedrally coordinated aluminum atoms connected to four different phosphate groups (Figure 4). Two of the oxygen atoms of the phosphate groups are connected to aluminum atoms, but two form hanging P−O bonds, which are involved in hydrogen bonding to the cyclam template molecule. The cyclam molecule is in the *trans*-IV conformation and sits between the CoAlPO chains. Cyclam has been seen before both as a template[31,32] and as part of the framework itself.[33]

The work reported herein is further evidence of the richness of possible phases available from ionothermal synthesis. The unusual ordering of cobalt, together with the Co−Cl bond, in SIZ-13 can be traced back to the deactivation of water and the milder hydrolysis conditions, thereby, present in ionic liquids. In ionothermal synthesis, water is only present in reactant quantities, rather than in vast excess, as in hydrothermal synthesis. Raising the temperature of the reaction increases the reactivity of the water in the DES and promotes the formation of a fully connected zeolite framework, SIZ-14. Both these materials are templated by choline,

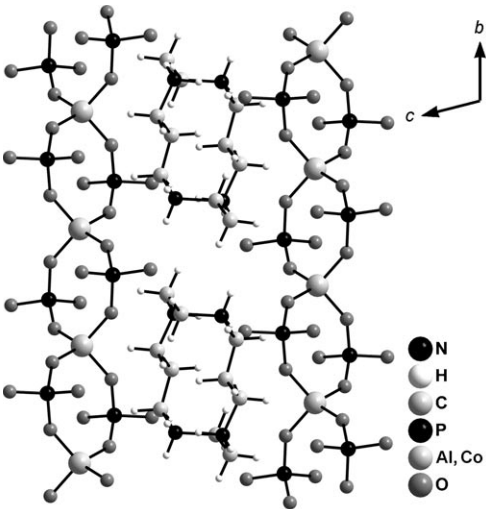

Figure 4. The structure of SIZ-15 viewed parallel to the *a* axis.

indicating that we now have control over which component of the DES provides the templating cations. The structure of SIZ-15, which includes cyclam as the template, indicates that it is possible to add external templates to DESs to produce novel materials. The scope of this reaction methodology is the subject of further study in our laboratory.

The most important aspect of the work reported herein is the preparation of materials with chemical compositions that are unlikely to be accessible using traditional hydrothermal methods. SIZ-13, with ordered Co–Cl units, is a prime example of such a material. This result points to ionothermal synthesis being somewhat milder than hydrothermal synthesis, in terms of the hydrolysis that occurs during the reaction. A publication by Harrison after the submission of this paper indicates that such metal–chlorine bonds can also be prepared in zinc phosphates using ionothermal synthesis with choline chloride–urea as the ionic liquid.[34]

Clearly, the accessibility of new types of chemistry opens up many new possibilities in the synthesis of zeolites and zeolite analogues, as well as in other areas. We are particularly interested in applying this methodology to inorganic–organic hybrid materials, such as metal–organic frameworks[35,36] and metal phosphonates,[37,38] where new chemistry could lead to exciting solids. Such work is continuing in our laboratory.

Experimental Section

Synthesis of DESs: The carboxylic acid (as bought) and choline chloride were measured out, in a 1:1 ratio for succinic acid and glutaric acid, and in a 2:1 ratio for citric acid, and ground in a mortar.

Synthesis of SIZ-13: The choline chloride–succinic acid eutectic mixture (4 g), aluminum isopropoxide (0.23 g, 1.26×10^{-3} mol), phosphoric acid (0.31 g, 85 wt% in water, 2.69×10^{-3} mol), cobalt acetate tetrahydrate (0.20 g, 8.03×10^{-4} mol), and cyclam (0.13 g, 6.49×10^{-4} mol) were loaded into a teflon-lined autoclave. The reaction mixture was heated at 150 °C for 6 days. The blue solid product was recovered by dissolving the eutectic mixture in distilled water and subsequent filtration. The solid was then washed with distilled water and acetone, and dried in air. SIZ-13 could also be prepared under the same conditions, except using the choline chloride–glutaric acid or choline chloride–citric acid eutectic mixtures as solvent.

Synthesis of SIZ-14: The choline chloride–succinic acid eutectic mixture (4 g), aluminum isopropoxide (0.22 g, 1.08×10^{-3} mol), phosphoric acid (0.32 g, 85 wt% in water, 2.78×10^{-3} mol), cobalt acetate tetrahydrate (0.21 g, 8.43×10^{-4} mol), and cyclam (0.15 g, 7.49×10^{-4} mol) were loaded into a teflon-lined autoclave. The reaction mixture was heated at 180 °C for 3 days. The blue solid product was recovered by dissolving the eutectic mixture in distilled water and subsequent filtration. The solid was then washed with distilled water and acetone, and then dried in air. SIZ-14 could also be prepared under the same conditions, except using pyridine instead of cyclam.

Synthesis of SIZ-15: In samples of SIZ-13 prepared using cyclam, small single crystals of SIZ-15 could be identified as a minor impurity by their different morphology from SIZ-13.

X-ray diffraction: The crystal-structure data for SIZ-13 were collected using $\mathrm{Cu}_{\mathrm{K}\alpha}$ radiation at the University of St. Andrews. Data sets using $\mathrm{Mo}_{\mathrm{K}\alpha}$ and synchrotron radiation were also collected, but owing to the relatively poor crystallinity of these samples the first data set was the best. While the agreement factors for this data set are relatively poor, the bond distances and angles in the structure indicate reasonable chemistry. The correctness of the structural connectivity was subsequently confirmed by Rietveld refinement against powder data. The crystal-structure data for SIZ-14 and SIZ-15 were collected using $\mathrm{Mo}_{\mathrm{K}\alpha}$ and synchrotron radiation (SRS, Daresbury, UK), respectively. All structures were solved using direct methods, and the refinements were carried out against F^2.

SIZ-13: $C_{20}H_{56}Al_6Cl_2Co_2N_4O_{36}P_8$, triclinic, $P\bar{1}$, $a=14.167(7)$, $b=15.045(5)$, $c=15.104(3)$ Å, $\alpha=67.69(6)$, $\beta=75.26(6)$, $\gamma=89.65(6)°$, $V=2865.6(18)$ Å^3, $Z=2$, $0.1\times0.05\times0.01$ mm^3, $T=173(2)$ K, 9538 independent reflections ($\lambda=1.54056$ Å, $3.19<\theta<68.06°$), $R_1=0.1869$, $wR_2=0.4371$, max. residual electron density = 1.93 e Å^{-3}.

SIZ-14: $Al_{44.66}Co_{9.34}O_{216}P_{54}$ (framework only), rhombohedral, $R\bar{3}$, $a=13.097(1)$, $c=45.627(6)$ Å, $V=6778.0(11)$ Å^3, Z = 1, $0.05\times0.05\times0.05$ mm^3, $T=93(2)$ K, 9538 independent reflections ($\lambda=0.71073$ Å, $2.01<\theta<30.99°$), $R_1=0.0787$, $wR_2=0.2681$, max. residual electron density = 2.301 e Å^{-3}.

SIZ-15: $C_{10}H_{29}Al_{1.96}Co_{0.04}N_4O_{16}P_4$, triclinic, $P\bar{1}$, $a=7.8215(13)$, $b=8.7905(15)$, $c=8.9928(15)$ Å, $\alpha=102.253(2)$, $\beta=97.237(3)$, $\gamma=102.486(3)°$, $V=580.27(17)$ Å^3, $Z=2$, $0.075\times0.05\times0.005$ mm^3, $T=150(2)$ K, 3473 independent reflections ($\lambda=0.6910$ Å, $2.38<\theta<30.05°$), $R_1=0.0703$, $wR_2=0.2281$, max. residual electron density = 2.364 e Å^{-3}.

CCDC-638575 (SIZ-13) and CCDC-638576 (SIZ-15) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-417835 (SIZ-14).

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