Template Synthesis

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Ionothermal Materials Synthesis Using Unstable Deep-Eutectic Solvents as Template-Delivery Agents**

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The use of organic templates (also called structure-directing agents) remains one of the most successful methods of preparing new inorganic materials.[1,2] Many of the most important recent advances in porous solids in particular depend on the clever use of organic species as templates to produce new zeolites,[3–5] transition-metal phosphates[6] or oxides,[7] and to make synthetic methods more efficient.[8] Ionothermal synthesis, where an ionic liquid is both the solvent and source of the template, provides opportunities to develop new synthetic routes that are based on different chemistry to traditional hydrothermal approaches.[9–12] Herein we describe the controlled use of deep-eutectic solvents (DESs) that are unstable at high temperatures as the media for ionothermal reactions. The organic template is not added to the reaction mixture in the normal way, but is delivered to the reaction by the breakdown of one of the components of the DES itself, demonstrating how the unique solvent properties of these ionic liquids can be harnessed to produce new types of solid.

A DES is a mixture of two compounds where there is a depression in the freezing point of the mixture compared with that of the separate components. One class of DES comprises mixtures of organic halide salts with hydrogen-bond donors, such as amides, amines, alcohols, and carboxylic acids.[13,14] The freezing-point depression in the mixture results from the formation of halide ion–hydrogen-bond-donor supramolecular complexes that alter the free energy of the solid phase compared to the liquid. DESs are therefore predominantly ionic liquids, with properties that differ markedly from those of molecular liquids and salts dissolved in molecular solvents. Such DESs have features that make them excellent choices

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for use in the preparation of materials of different kinds. Their ionic nature and relatively high polarity mean that many ionic species, such as metal salts, show high solubility. They also have some significant advantages over other types of ionic liquid, particularly their ease of preparation as pure phases from easily available (and toxicologically well characterized) components and their relative unreactivity towards atmospheric moisture.[14] Our previous report on zeolite synthesis used a urea/choline chloride eutectic to prepare a new zeolitic material[9] and Liao and co-workers have used the same method to prepare a new organophosphate material.[15] Herein we report how thermal decomposition of various urea derivatives as components in DES can be used to deliver particular organic templates to the reaction mixture in a controlled manner, leading to new types of structure and providing some insight into potential synthesis mechanisms of such materials.

Several urea derivatives (structural formula in Figure 1 and 2), including 1,3-dimethyl urea (DMU), 2-imidazolindone (IMI, ethylene urea) and tetrahydro-2-pyrimidione (THP, *N*,*N*′-trimethylene urea) were investigated as eutectic mixtures with quaternary ammonium halides (choline chloride or tetraethylammonium bromide). IMI and THP are, we believe, used for the first time in deep-eutectic solvents. The expected decomposition products, and thus the expected templates delivered to the synthesis, of DMU, IMI, and THP are methylamine, ethylene diamine, and propylene diamine, respectively.

Aluminum phosphate materials can be prepared using all three urea derivatives, (Figure 1 and 2). Single-crystal X-ray diffraction, magic-angle spinning (MAS) NMR spectroscopy and elemental analysis indicate that the expected templates were occluded in the final solids (see Supporting Information). The materials vary from one-dimensional chains through to three-dimensional zeolitic-type structures and can be altered by adding suitable mineralizers, such as water or fluoride, to the systems. The dependence of final structure on mineralizer content mirrors the behavior seen in other ionothermal systems[9] and illustrates the rich potential of this system to produce different materials in a controlled manner. However, one difference between this system and other ionothermal methods is that templated materials are formed right across the range of water content from very low to very high. We have not seen any evidence for templating being stopped by intermediate water content, as is the case for imidazolium-based ionic liquids.[9]

A DMU/tetraethylammonium bromide DES can be used to prepare three different aluminophosphate solids, **1**, **2**, and **3** (Figure 1). A DMU/choline chloride DES can also be used to prepare **2**. In each case the template is the methylammonium cation as expected.

A DES containing the cyclic urea derivative IMI yields ethylene diammonium cations as the template at moderate temperatures, plus some ammonium cations above 200 °C. This approach produces two closely related aluminophosphate solids **4** and **5** (Figure 2). Using a DES with one extra carbon center in the cyclic urea component (TMP, Figure 2) leads to the crystallization of four different solids. Three of these materials, **6**–**8** have the expected propylene diammonium template. However, if a large excess of water is added to the system, breakdown of the urea derivative proceeds further at temperatures of 200 °C to produce a material **9** that has only ammonium as the templating cation.

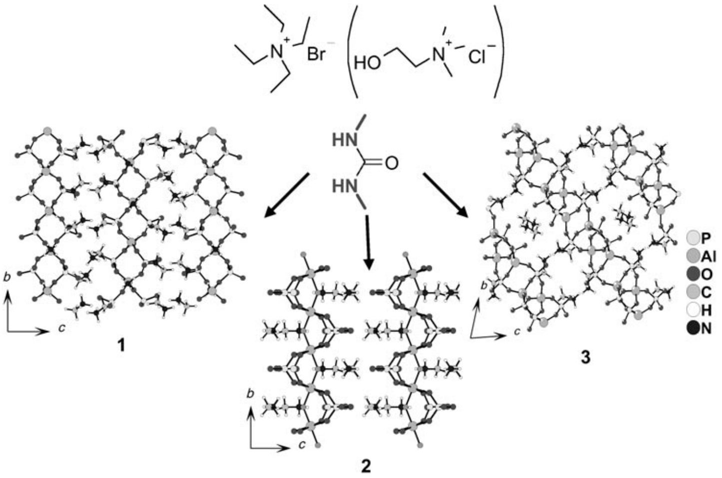

Figure 1. The synthesis of materials using dimethyl urea based eutectic mixtures. Dimethyl urea based eutectic mixtures with tetraethylammonium bromide or choline chloride decompose to give methylammonium cations as the templates for the preparation of three aluminophosphate materials, **1**–**3**. The portion of the urea derivative that delivers the template on decomposition is shown in bold in the structural formula. The conditions for the reactions are given in the Supporting Information.

The nine aluminophosphate materials prepared in this way include five previously unknown compounds, although some related topologies are known, and four known materials, **3**, **4**, **7**, and **9**. Full details of the synthesis and crystallography of these materials can be found in the Supporting Information.

Interestingly, the different structures fit rather well with some proposed mechanistic pathways postulated in previous work. Oliver et al.[16] proposed that the crystallization of aluminophosphates proceeds through the initial formation of chains. Vidal and co-workers postulated exactly such a mechanism for the synthesis of Mu-7[17] by the hydrolytic condensation of so called parent chains. However, there was no evidence for the existence of the parent chain in any experiments Vidal and co-workers carried out. In our work, compound **3** (Figure 1) has the same structure as Mu-7 and compound **1** has the structure of the parent chain, which is isolated at lower temperatures. The reason given for the non-detection of the parent chain by Vidal was that the parent chain was “probably very labile”.[17] That the parent compound can be isolated using the eutectic mixture indicates rather milder hydrolysis conditions than in the hydrothermal or solvothermal synthesis. This situation suggests that synthesis in DES may be more controllable than other synthetic methods and perhaps more compounds that are not isolable under normal conditions can be recovered. Other workers have postulated different mechanisms of framework synthesis, in particular those based on crystal growth by condensation of small clusters rather than by condensation of chains or layers as proposed by Oliver et al. Indeed, Férey, Taulelle, and co-workers have shown from very elegant in situ

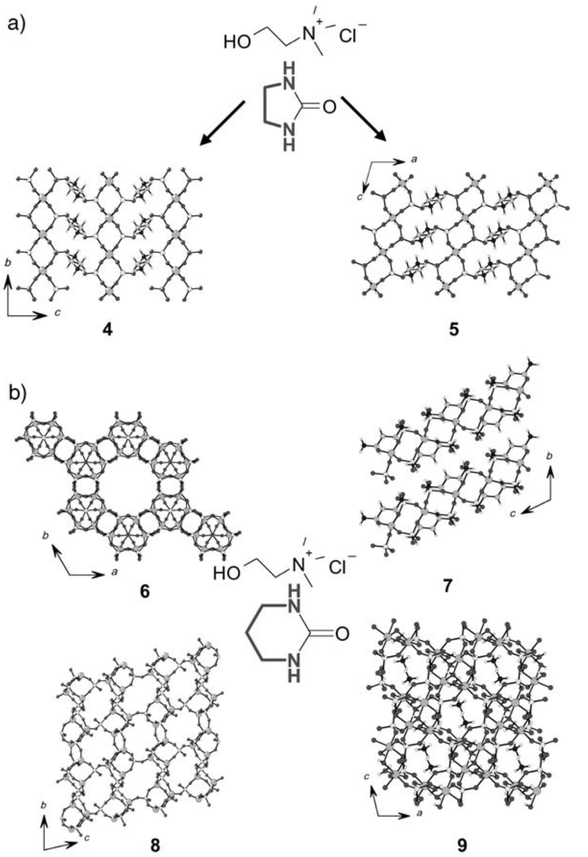

Figure 2. The synthesis of aluminophosphate materials from cyclic urea-based eutectic mixtures. a) Materials prepared from 2-imidazolindone-based eutectics templated by ethylene diammonium cations b) Four materials prepared from tetrahydro-2-pyrimidone. In compounds **6**–**8** the template is a propylene diammonium cation while in compound **9**, prepared at higher temperature, the template is ammonium. For clarity the location of the templates in **6** and **8** are not shown. The key is as for Figure 1 The portion of the urea derivative that delivers the template on decomposition is shown in bold in the structural formula. The Conditions for the reactions are given in the Supporting Information.

NMR spectroscopy in real time that the mechanism proposed by Oliver et al. is certainly not possible in all cases.[18] The isolation of the parent chain in our work is not evidence of the mechanistic pathway (since we only characterize the final products) but does raise some interesting points that may require further work.

Time studies using X-ray diffraction indicate that the crystallinity of the products reaches its maximum between 12 and 48 h after the reactions started, with overall yields of 50–70% after 48 h (see Supporting Information). Interestingly, ^{1}H NMR spectra of the DESs recovered after the reactions show that at 12 h the breakdown products are only just visible above background. However, after six days the DESs show quite complex ^{1}H NMR spectra indicating extensive degradation of the solvent systems. Clearly the nucleation and crystallization of the materials takes place at relatively low levels of solvent degradation under conditions where the concentration of the template species is slowly increasing as more of the DES decomposes.

While aluminophosphates are of special interest because of their close relationship to zeolites, other materials are also attractive targets for various reasons. Using a DES we have successfully synthesized **10**, the gallium phosphate version of the zeolite-A framework (Figure 3). Zeolite-A is an important industrially used framework with emerging applications in, for example, gas storage for medical applications.[19] This material was prepared using a fluoride-free synthetic route, and is unusual in that it is, we believe, the first time this material has been prepared without fluoride at the center of the double four-ring secondary building units (SBUs) present in the structure.[20,21] We believe the only previous double four-ring unit occluding an atom other than fluorine are not linked into three-dimensional structures but are isolated anions.[22,23]

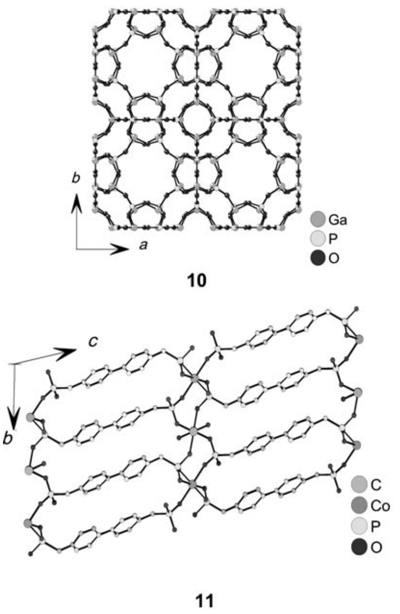

Figure 3. Phosphate and phosphonate and metal–organic solids prepared from eutectic mixture or related systems. Compound **10** is a gallium phosphate with the zeolite-A framework, and **11** is a cobalt organophosphonate material prepared from a chlorine chloride/succinic acid DES.

Carboxylic acid/quaternary ammonium eutectic mixtures seem to be more stable and do not contribute decomposition products as templates to the reactions. Using this approach a succinic acid/choline chloride DES can be used simply as a solvent to prepare the new transition-metal dibenzyldiphosphonate solid **11** (Figure 3) that contains no template. Such inorganic hybrid materials are of particular interest for their structural architectures[24–28] and potentially useful gas-adsorption characteristics.[29] Liao et al.[15] have recently shown that a choline chloride/urea mixture can be used to prepare a zinc organophosphate where ammonium acts as the temple. Our work herein shows that we can control whether or not templating takes place by judicious choice of the eutectic solvent.

The use of deep-eutectic mixtures reported herein allows the ionic nature of the liquid, with the advantages this brings in terms of solvent chemistry and control of mineralizer concentration to be retained while also providing a new mechanism by which the template is delivered to the reaction mixture. The synthesis technique has proved to be very versatile, delivering a number of different templates to aid in the preparation of a number of types of material. Several hundred functionalized ureas are commercially available and many of these will be suitable for this type of work, illustrating the scope of this method. The ease of preparation of eutectic mixtures and the different chemistry involved, as evidenced by, for example the non-fluoride preparation of gallium phosphate zeolite-A, indicate that this route may be useful for targeting materials that are difficult to prepare in traditional hydrothermal synthesis. This work also shows beyond doubt that the template comes from the urea part of the DES, as this is the only way in which the chemical structure of the templates can be explained. In work based on urea/choline chloride mixture there was the possibility that the ammonium ions could originate from the urea or the choline chloride. Thus this issue is now resolved. Further work aimed at preparing other types of material are currently underway to explore more fully the potential of this synthesis method.

Experimental Section

Synthesis of DESs: The required amount of as bought amide and quaternary ammonium salt was measured out in a 2:1 ratio (or 1:1 in the case of the succinic acid based DES) and ground in a mortar. Melting points of the different DES are given in Table 1.

Table 1: Melting points of the deep-eutectic solvents and their constituent compounds.

H-bond donor (m.p. [°C])	Ammonium salt (m.p. [°C])	DES m.p. [°C]
1,3-dimethyl urea (101–105)	tetraethylammonium bromide (285–290)	20–25
1,3-dimethyl urea (101–105)	choline chloride (298–305)	69–71
tetrahydro-2-pyrimidione (264–266)	choline chloride (298–305)	150–155
2-imidazolindone (129–132)	choline chloride (298–305)	69–73
urea (134)	choline chloride (298–305)	12
succinic acid (183–187)	choline chloride (298–305)	73–77

Aluminophosphates **1**–**9**: A Teflon-lined autoclave (volume 23 mL) was charged with eutectic mixture, $Al[OCH(CH_3)_2]_3$ (Aldrich), and H_3PO_4 (85 wt% in H_2O, Aldrich). HF (48 wt% in H_2O, Aldrich) and distilled water were added if required. The stainless steel autoclave was then heated in an oven to the required temperature. The reagent masses, temperatures, and length of time left in oven are as detailed in the Supporting Information. After cooling the autoclave to room temperature the product was suspended in distilled water, sonicated, filtered by suction, and washed with acetone. The products were white, crystalline solids.

Gallium phosphate zeolite-A **10**: The method was followed as for the aluminophosphates but the $Al[OCH(CH_3)_2]_3$ was replaced by $Ga_2(SO_4)_3$ (0.105 g, Aldrich). Tetrahydro-2-pyrimidione (2.0 g, 0.020 mol, Fluka)/Choline Chloride (1.4 g, 0.010 mol, Avocado) constituted the DES. H_3PO_4 (0.173 g, 85 wt% in H_2O), molar ratio of $Ga_2(SO_4)_3$:H_3PO_4 was 1:6.1. The reaction was heated at 170 °C for 72 h.

11: A Teflon-lined autoclave (23 mL) was charged with the urea/choline chloride eutectic mixture (4 g), (4,4′-biphenylylenedimethylene)diphosphonic acid (0.12 g, 3.51×10^{-4} mol) and cobalt acetate tetrahydrate (0.22 g, 8.83×10^{-4} mol) The autoclave was heated at 150 °C for three days. After cooling to room temperature the eutectic mixture was dissolved in distilled water and the resultant powder recovered by filtration, washed with distilled water and acetone then air dried. An isostructural material using nickel as the metal salt (nickel acetate tetrahydrate (0.23 g, 9.24×10^{-4} mol) can be prepared in a similar way using a 1:1 molar DES of succinic acid and choline chloride

Single-crystal X-ray diffraction data for all materials except **3** were collected using $Mo_{K\alpha}$ radiation using a Rigaku rotating anode single-crystal X-ray diffractometer at the university of St Andrews or using a wavelength of ≈ 0.7 Å station 9.8 at the Synchrotron Radiation Source (SRS), Daresbury Laboratories, Cheshire, UK. The structures were solved using standard direct methods and refined using least-squares minimization techniques against F^2. When ordered template molecules could not be refined the program SQUEEZE was used to remove the scattering from the channels/voids in the structures before the final cycle of least-squares refinement. Framework phase identification for **3** (which has the Mu-7 structure) was accomplished from the unit cell given by single crystal X-ray diffraction. 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 numbers CSD-416132 (**10**), CSD-416133 (**1**), CSD-416134 (**2**), CSD-416135 (**6**), and CSD-416132 (**9**). CCDC-295436, CCDC-295437, CCDC-295438, CCDC-295439 and CCDC-295440 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.

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