Channel Structures in a Simple Inorganic Salt − An Open Framework Formed through Structural Integration of Distinct Sodium Acetate and Sodium Perchlorate Domains

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The novel mixed salt of sodium acetate and perchlorate reported herein, $Na_4(OAc)_3(ClO_4)$, has a distinctive lattice structure formed from sodium acetate planes linked together by sodium perchlorate cylinders. In total contrast to the component salts, the structure contains channels parallel to the *c* axis. The integration of the two molecular-level structural motifs of the two component salts thus leads to a supramolecular/macromolecular-level structure which is very different from those of the components. A template mechanism is implicated in the formation.

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Introduction

The design of new porous materials is a field of much current activity driven by the plethora of applications based around zeolite chemistry.[1] Much of the work has focused on crystal engineering approaches based on organic ligands or metallo-organic coordination frameworks in which supramolecular assembly principles are extended to polymeric solid-state materials.[2] However, relatively simple inorganic salts can also be used to create porous materials - the encapsulation of fullerene molecules inside the pores of a silver nitrate framework is a particularly striking example.[3] We have fortuitously prepared a remarkable mixed inorganic salt of sodium acetate and perchlorate, which has a distinctive lattice structure containing porelike channels (that hold a small amount of disordered solvent), and we report this finding herein.

Results

The mixed salt $Na_4(OAc)_3(ClO_4)\cdot 0.25(MeOH)$ was obtained serendipitously in the course of our studies on aggregation of supramolecular units into larger polymeric solid-state arrays[4] during the attempted preparation of the Ag complex of a chiral bispyridylimine ligand.[5] A methanolic solution of 5-hydroxypyridine-2-carboxaldehyde and (*S*)-(−)-1,1′-binaphthalene-2,2′-diamine was heated at reflux and then treated with silver acetate. Following further heating, the solution was treated with excess sodium perchlorate. Crystals were observed 4 days after addition of diethyl ether. It appears that the presence of the organic ligand or its constituents are significant in this preparation (possibly by a templating/nucleating mechanism) as extensive attempts to prepare the material from mixtures of sodium acetate and perchlorate were unsuccessful, generally leading to the formation of either hydrated sodium acetate or sodium perchlorate. The crystal structure determination indicates that Ag is absent from the crystals.

A search of the Cambridge Crystallographic Database[6] indicates that the complex is the only known simple, mixed acetate-perchlorate salt. The crystal structure determination reveals a remarkable supramolecular structure in a large high-symmetry cell, and channels run through the structure parallel to the *c* axis (Figure 1). These channels are lined with inward-pointing methyl groups. The channel diameters are about 8 Å (H···H) and contain a small amount of highly disordered solvent.

The presence of the channels is particularly striking since the structures of neither of the individual component salts contain cavities: Structures of two polymorphs of anhydrous sodium acetate have been reported.[7] Both forms contain two-dimensional layers in which a sodium carboxylate framework is lined on each side by the acetate methyl groups. In each form, the sodium ions are six-coordinate and bound to one bidentate acetate and four unidentate acetate groups with Na−O distances in the range

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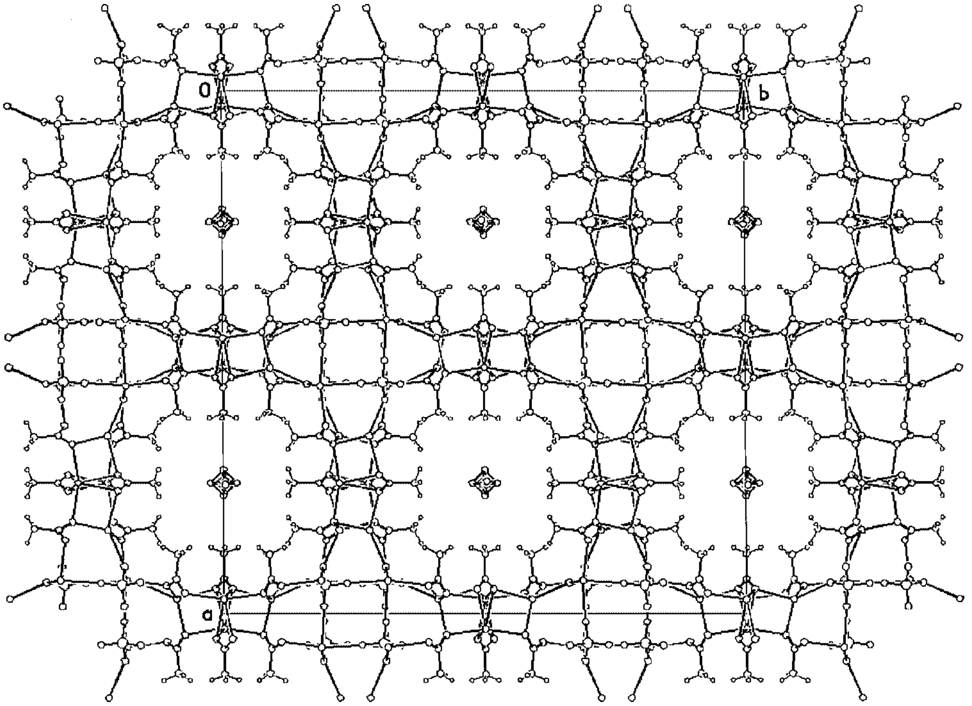

Figure 1. The $Na_4(OAc)_3(ClO_4).0.25(MeOH)$ structure viewed down the *c* axis, showing the channels through the structure

2.34−2.67 Å. Sodium perchlorate has orthorhombic symmetry and contains eight-coordinate sodium cations bound to two bidentate and four unidentate perchlorate ions with Na−O distances in the range 2.38−2.71 Å.[8] Above 581 K it undergoes a phase change and adopts a cubic structure (as NaCl) with rotating perchlorate anions.[9]

Inspection of the structure of the present mixed acetate-perchlorate salt reveals that the structure is made up of discrete domains of sodium acetate linked by domains of sodium perchlorate: the four sides of the channels are formed from planes containing six-coordinate sodium ions surrounded by acetate ions. The sodium atoms have two environments within these planes: one sodium atom [Na(1)] is bound to one bidentate acetate and four unidentate acetate groups (Na−O 2.36−2.56 Å), while the other [Na(3)] binds one bidentate and three unidentate acetate groups and its coordination sphere is completed by a unidentate perchlorate group (Na−O 2.34−2.80 Å) that links the planes to the sodium perchlorate domains. The structure of the planes is very similar to the two-dimensional layers in polymorph (I) of sodium acetate, but is approximately 8.5 Å in width (corresponding to three sodium atoms and three acetate groups) in one direction (rather than infinite).

These sodium acetate planes are held together by cylindrical sodium perchlorate domains that form the corners of the square channels and are very similar to the cubic phase of sodium perchlorate (without the perchlorate orientational disorder associated with that phase). The sodium [Na(2)] in this domain is bound to four perchlorate and two unidentate acetate groups to give an apparent coordination number of 6 (Na−O 2.39−2.50 Å). However two of the perchlorate groups form additional long contacts (Na−O 2.98 Å) and, if regarded as bidentate, increase the coordination number to eight. The different coordination spheres of the three types of sodium(I) centres in the structure are illustrated in Figure 2, and figures illustrating the structural similarities between the discrete domains and the corresponding bulk materials (sodium acetate and sodium perchlorate) are included in the Supporting Information.

The perchlorate domains act as four-way connectors linking linear sodium acetate planes into the grid-like framework. It is significant that this can be achieved without major distortions to the known structural motifs of the individual salts. While the molecular-level structures are retained, their integration gives rise to a very different (cavity containing) supramolecular-level structure from the components. Although open-frame network structures have been prepared by combining ligands and metals,[2] and ligands and salts,[1] this appears to be the first example in which discrete salt domains are linked by other discrete salt domains to give rise to such structures.

Although a serendipitous finding, the structure herein represents a remarkable example of a porous network assembled from very simple inorganic components. Guest-framework interactions have previously been identified as key factors in the creation of porous materials from simple inorganic salts. For example, silver···fullerene interactions appear significant in the formation of the remarkable fullerene-encapsulated silver nitrate network mentioned above.[3] However, no such interactions seem to be at work herein (indeed the solvent is disordered, consistent with a lack of specific interactions, and the channels only partially occupied). Nevertheless, the inability to recreate the network simply by mixing the individual components implicates

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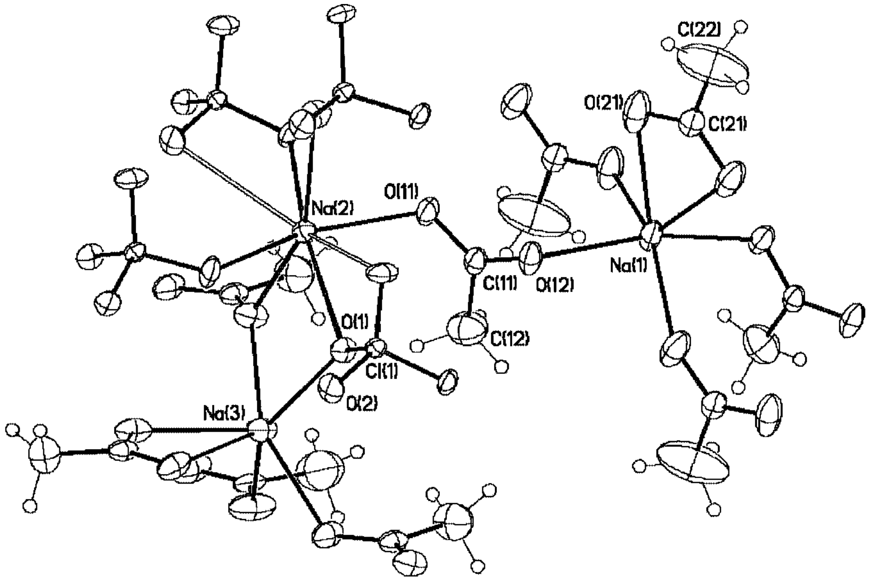

Figure 2. View of the complex, showing the full environment of each sodium ion; displacement ellipsoids are drawn at the 50% probability level

some form of templated nucleation in its formation. Indeed the size of cavity is defined by the length of the sodium acetate domains, which the template nucleation might affect or determine. Organic ligands and metal complexes have been used to direct formation of open-framework structures;[10] however, the template is usually included in the resulting structure. We can also suggest a relationship between the formation of this unusual structure and the nucleation of simple inorganic salts to afford complex and differing structures, which is a common theme in biological systems, particularly with regard to biomineralisation of calcium phosphate and carbonate salts, and which has also been exploited in chemical systems.[11]

CCDC-230080 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also the footnote on the first page of this article): Figures illustrating the structural similarity between the discrete domains and the corresponding bulk materials (sodium acetate and sodium perchlorate), synthetic and crystallographic experimental details.

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