DALTON
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# $[CN_3H_6]_2[Zn(CO_3)_2]$, the first organically templated open-framework carbonate

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***Received 1st December 2000, Accepted 23rd January 2001***
***First published as an Advance Article on the web 15th February 2001***

$[CN_3H_6]_2[Zn(CO_3)_2]$, the first organically templated open-framework carbonate has been synthesized hydrothermally and its single crystal structure and some properties have been determined. This phase is built up from a three-dimensional framework of vertex-linked $ZnO_4$ and $CO_3$ building units encapsulating the extra-framework guanidinium cations. Template-to-framework hydrogen bonding appears to play an important role in stabilizing the structure. The zincocarbonate framework shows a surprising similarity to those of known zinc phosphates and phosphites.

## Introduction

Organically templated inorganic networks now cover a huge range of compositions and structures.[1] Conceptually, these phases may be considered to be built up from three components: a templating organic cation, a metallic cation, and an oxo-anion, with the last two moieties fusing together to form the extended inorganic framework. A great deal of attention has been paid to the structure-directing role of organic species,[2] and the structural effect of variously coordinated cations, such as vanadium[3] and tin.[4] Much less exploratory work has been carried out on the oxo-anion part of the inorganic network, and most groups reported so far invariably adopt tetrahedral coordination. In particular, the $[PO_4]^{3-}$ phosphate anion (possibly protonated) is ubiquitous in these materials.[1] We are now studying open-framework phases containing pyramidal oxo-anions including $[CN_3H_6]_4[Zn_3(SeO_3)_5]$, the first organically templated selenite,[5] and several phases[6] incorporating the phosphorus(III)-containing $[HPO_3]^{2-}$ hydrogenphosphite group.

In this paper we report the synthesis, crystal structure, and some properties of $[CN_3H_6]_2[Zn(CO_3)_2]$, the first open-framework solid templated by an organic cation to contain the essentially flat, triangular, carbonate ion as part of the inorganic framework.

## Experimental

### Synthesis

The analytical grade starting chemicals were obtained from Aldrich and used as received. 3.60 g $[CN_3H_6]_2CO_3$, 0.41 g ZnO and 25 ml deionized water were combined in a 30 ml plastic bottle, shaken well, and placed in a 90 °C oven for 42 h. Solid product recovery from the pH 12 mother liquors resulted in 0.58 g (38% yield based on Zn) of large (to 3 mm), translucent octahedral chunks of $[CN_3H_6]_2[Zn(CO_3)_2]$. The crystal quality of this initial batch was too poor for single crystal structure determination. Much better crystals were obtained from the following reaction: 0.31 g (5 mmol) $H_3BO_3$ and 3.60 g (20 mmol) $[CN_3H_6]_2CO_3$ were dissolved in 18.0 g deionized water at 90 °C in a HDPE bottle. 0.81 g (10 mmol) ZnO was added and the suspension shaken thoroughly. The bottle was placed in an oven and held at 90 °C for 68 h. The solid product, consisting of a majority of gem-like, faceted, transparent crystals (maximum dimension ≈0.2 mm) of $[CN_3H_6]_2[Zn(CO_3)_2]$ and a minority component of white powder, was recovered by filtration, washing with water, then with methanol, and dried at 90 °C. The yield was 26%, based on Zn. The boric acid is not incorporated in the crystalline product, but it may affect the nucleation rate of $[CN_3H_6]_2[Zn(CO_3)_2]$ crystals from solution, thus improving their quality.

### Characterization

Powder XRD on well ground samples from both synthetic routes described above showed the major phase to be highly crystalline $[CN_3H_6]_2[Zn(CO_3)_2]$ with a trace ZnO (zincite) impurity. The pattern was essentially unchanged after heating the sample to 130 °C for 1 hour. Elemental analysis confirmed that there was negligible boron content in the solid product. TGA/DTA showed a series of overlapping weight losses/thermal events (−4%, 140–170 °C, endothermic; −3%, 170–210 °C, endothermic; −37%, 210–300 °C, strongly endothermic; −24%, 300–850 °C, strongly exothermic at ≈800 °C). Powder XRD on the TGA end product indicated the presence of poorly crystalline zinc oxide (calculated total loss = 73.4%, observed = 68%). The IR spectrum of $[CN_3H_6]_2[Zn(CO_3)_2]$ showed bands which could be assigned to the guanidinium cation and the carbonate group based on comparison with library data. $^{13}C$ MAS NMR data were collected on a Bruker spectrometer and chemical shifts referenced to an external sample of tetramethylsilane (TMS, $\delta$ 0).

### Structure determination

Preliminary laboratory single crystal diffraction data indicated a tetragonal cell of dimensions ≈9.09 × 12.78 Å with a weak 3*c*

DOI: 10.1039/b009641p

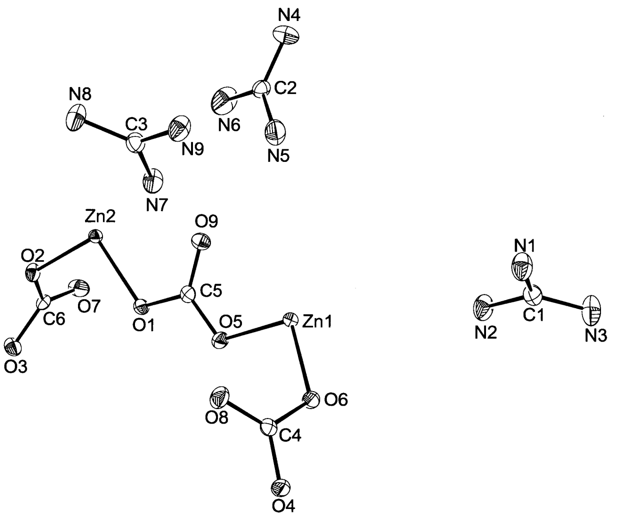

**Fig. 1** Asymmetric unit of $[CN_3H_6]_2[Zn(CO_3)_2]$ (50% thermal ellipsoids).

supercell. Structural models based on the smaller unit cell appeared to indicate massive disorder. The existence of the supercell was fully confirmed by the use of synchrotron X-ray diffraction methods at SRS beam line station 9.8 at Daresbury Laboratory.[7] Intensity data from a colourless octahedron of $[CN_3H_6]_2[Zn(CO_3)_2]$ were collected on a Bruker SMART CCD diffractometer[8] [31785 reflections scanned, 4206 of 4546 merged reflections ($R_{\mathrm{Int}} = 0.035$) with $I > \sigma(I)$ considered observed]. An absorption correction (min./max. transmission coefficients = 0.834/0.872) was made with SADABS.[8] The systematic absences ($00l$, $l = 4n$, $0k0$, $k$) indicated the enantiomorphic pair of space groups $P4_12_12$ (no. 92) and $P4_32_12$ (no. 96) and the structure was solved by direct methods and successfully refined by full-matrix least squares methods using CRYSTALS[9] in the former of these. The H atoms were located geometrically and refined by riding on their N atoms with $d(\mathrm{N–H}) = 0.95$ Å. Refinement of the Flack absolute structure parameter[10] indicated that the particular crystal studied consisted of a single enantiomer (absolute structure). Crystal data are summarized in Table 1.

CCDC reference number 154055.

See http://www.rsc.org/suppdata/dt/b0/b009641p/ for crystallographic data in CIF or other electronic format.

## Results

The inorganic framework of $[CN_3H_6]_2[Zn(CO_3)_2]$ (Table 2, Figs. 1 and 2) is built up from $ZnO_4$ tetrahedra [$d_{\mathrm{av}}(\mathrm{Zn–O}) = 1.959$ Å] and almost flat $CO_3$ triangles (for each carbonate group, maximum atomic deviation from the best least-squares plane < 0.01 Å), fused together *via* Zn–O–C links ($\theta_{\mathrm{av}} = 118.7°$ for six O atom contributors). Both Zn atoms make four links to nearby carbon atoms, and each C atom makes two links to zinc neighbors. There is a pendant, terminal C–O bond associated with each carbonate species, which is significantly shorter [$d_{\mathrm{av}}(\mathrm{C–O_T}) = 1.250$ Å] than the bridging bonds to zinc [$d_{\mathrm{av}}(\mathrm{C–O_{Zn}}) = 1.302$ Å]. Zn1 occupies a special position with twofold symmetry.

The connectivity of the strictly alternating $ZnO_4$ and $CO_3$ groups results in an infinite, three-dimensional network. Spiral columns of vertex-sharing polyhedral units propagate in the polar *c* direction of the unit cell. The unit-cell periodicity is 24 units (12 $ZnO_4$ and 12 $CO_3$), which corresponds to *three* complete turns of the basic spiral. Each spiral sub unit (Fig. 3) consists of eight units (four $ZnO_4$ and four $CO_3$) which correlates with the strong *c*/3 subcell observed in the single crystal experiments. In the particular crystal examined, all the spirals propagate in a counterclockwise sense when the structure is viewed down [001], although, since the starting materials are non-chiral, we assume that the overall sample contains a random, 50 : 50 mixture of crystals of each enantiomer. Interestingly, the essentially flat, achiral, guanidinium cation has also templated a chiral, tetragonal, three-dimensional, tin(II) phosphate framework,[4] although, as seen here, both enantiomers of $[CN_3H_6][Sn_4(P_3O_{12})]$ are formed in equal proportion.

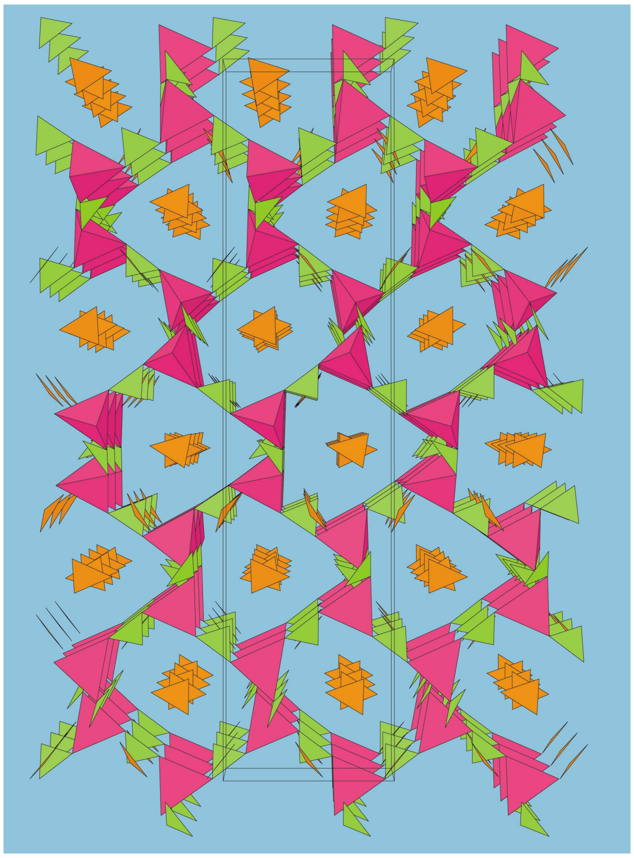

**Fig. 2** Polyhedral view down [100] of the $[CN_3H_6]_2[Zn(CO_3)_2]$ structure showing the network of $ZnO_4$ tetrahedra (maroon) and $CO_3$ triangles (green) templated by guanidinium cations (brown).

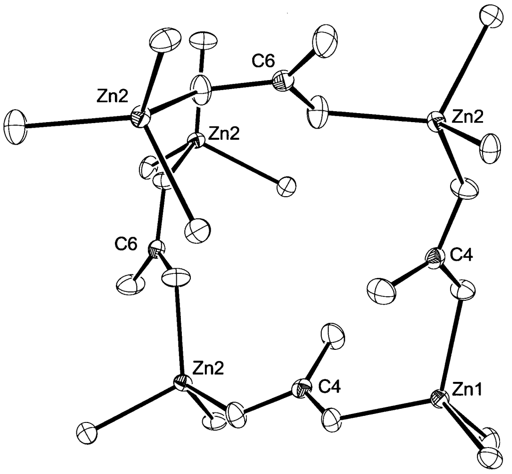

**Fig. 3** View approximately down [001] of one pitch of a $ZnO_4/CO_3$ helix in $[CN_3H_6]_2[Zn(CO_3)_2]$.

In $[CN_3H_6]_2[Zn(CO_3)_2]$, the spiral columns are crosslinked to each other in the *a* and *b* directions, thus forming an infinite open framework. The smallest identifiable loop is a 12-membered ring (*i.e.* an out-and-back progression through 12 polyhedral building blocks, consisting of six $ZnO_4$ and six $CO_3$ groups). These framework 12-membered rings delimit infinite, intersecting, channels propagating along [100] and [010]. There are no pores in the [001] direction.

**Table 1** Crystallographic parameters for $[CN_3H_6]_2[Zn(CO_3)_2]$

| | |
|---|---|
| Empirical formula | $C_6H_{12}N_6O_6Zn$ |
| $M_r$ | 305.56 |
| Crystal system | Tetragonal |
| Space group | $P4_12_12$ (no. 92) |
| $a$/Å | 9.0931(7) |
| $c$/Å | 38.333(3) |
| $V$/Å$^3$ | 3169.5(4) |
| $Z$ | 12 |
| $T$/K | 150(2) |
| $\lambda$/Å | 0.6923 |
| $\mu$/cm$^{-1}$ | 23.57 |
| $R(F)$ | 0.031 |
| $wR(F)$ | 0.032 |

**Table 2** Selected geometrical data (Å, °) for $[CN_3H_6]_2[Zn(CO_3)_2]$

| | | | |
|---|---|---|---|
| Zn1–O5 × 2 | 1.975(1) | Zn1–O6 × 2 | 1.948(1) |
| Zn2–O1 | 1.984(1) | Zn2–O2 | 1.954(1) |
| Zn2–O3 | 1.944(1) | Zn2–O4 | 1.9436(11) |
| C4–O4 | 1.2990(17) | C4–O6 | 1.2935(17) |
| C4–O8 | 1.2576(18) | C5–O1 | 1.3102(17) |
| C5–O5 | 1.3089(18) | C5–O9 | 1.2426(19) |
| C6–O2 | 1.3021(17) | C6–O3 | 1.2986(18) |
| C6–O7 | 1.2505(19) | | |
| Zn1–O1–C5 | 111.91(9) | Zn2–O2–C6 | 121.06(9) |
| Zn2–O3–C6 | 122.0(1) | Zn2–O4–C4 | 124.4(1) |
| Zn1–O5–C5 | 114.3(1) | Zn1–O6–C4 | 118.45(9) |

**Table 3** Hydrogen bond geometrical data (Å, °) for $[CN_3H_6]_2[Zn(CO_3)_2]$

| | | | |
|---|---|---|---|
| N1–H11 ··· O1 | 1.98 | 2.9229(19) | 175 |
| N1–H12 ··· O8 | 2.00 | 2.865(2) | 151 |
| N2–H21 ··· O8 | 2.18 | 2.997(2) | 143 |
| N2–H22 ··· O7 | 2.42 | 3.218(2) | 141 |
| N3–H31 ··· O5 | 2.01 | 2.9368(19) | 164 |
| N3–H32 ··· O7 | 2.03 | 2.934(2) | 158 |
| N4–H41 ··· O2 | 2.41 | 3.004(2) | 121 |
| N4–H41 ··· O7 | 2.03 | 2.857(2) | 144 |
| N4–H42 ··· O3 | 2.21 | 2.896(2) | 128 |
| N5–H51 ··· O4 | 2.33 | 3.070(2) | 134 |
| N5–H51 ··· O7 | 2.36 | 3.095(2) | 133 |
| N5–H52 ··· O9 | 2.11 | 3.021(2) | 161 |
| N5–H52 ··· O6 | 2.41 | 2.9525(19) | 116 |
| N6–H61 ··· O8 | 2.29 | 3.172(2) | 154 |
| N6–H62 ··· O4 | 2.34 | 3.139(2) | 142 |
| N7–H71 ··· O9 | 2.49 | 2.8810(18) | 105 |
| N7–H71 ··· O6 | 2.09 | 3.0273(19) | 169 |
| N7–H72 ··· O3 | 2.13 | 3.0650(19) | 169 |
| N8–H81 ··· O1 | 2.05 | 2.9921(18) | 171 |
| N8–H82 ··· O2 | 1.93 | 2.8587(19) | 164 |
| N9–H91 ··· O5 | 2.25 | 3.1410(19) | 157 |
| N9–H92 ··· O4 | 2.15 | 3.0802(19) | 165 |
| N9–H92 ··· O9 | 2.49 | 2.8828(19) | 105 |

The three values correspond to the H ··· O and N ··· O separations, and the N–H ··· O bond angle, respectively, with $d$(N–H) fixed at 0.95 Å in each case.

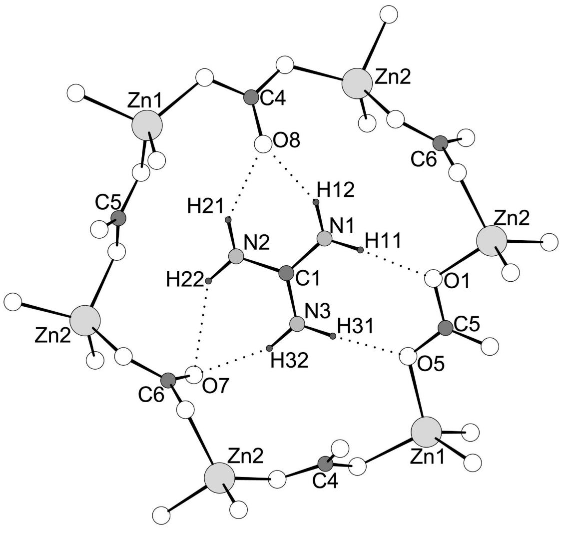

**Fig. 4** Detail of $[CN_3H_6]_2[Zn(CO_3)_2]$ showing the hydrogen bonding interactions (dotted lines) between the C1-centered guanidinium template molecule and a 12-membered ring window in the ZnCO framework.

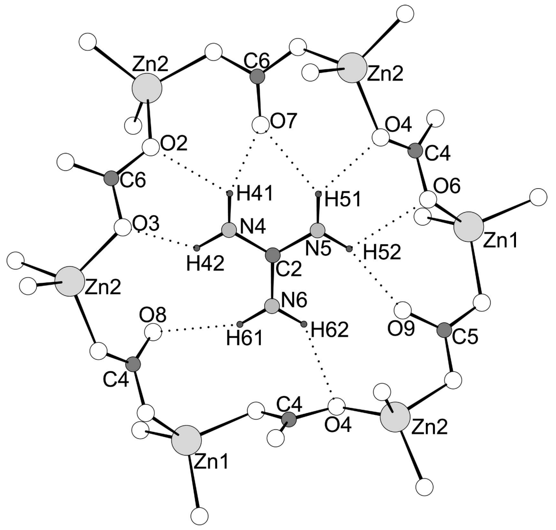

**Fig. 5** Detail of $[CN_3H_6]_2[Zn(CO_3)_2]$ showing the hydrogen bonding interactions (dotted lines) between the C2-centered guanidinium template molecule and a 12-membered ring window in the ZnCO framework.

The C–N distances for the propeller-shaped $[CN_3H_6]^+$ guanidinium cations are typical.[4,11] A strong and clear templating effect occurs in this phase with every guanidinium cation occupying a 12-membered ring window (atom-to-atom maximum dimensions of ≈7.8 × 7.8 Å), and interacting with the anionic zincocarbonate framework by way of N–H ··· O hydrogen bonds (Table 3). These include simple N–H ··· O links and some bifurcated N–H ··· (O,O) hydrogen bonds. All nine framework O atoms act as acceptors. There is a considerable variation in H ··· O bond lengths (based on geometrically placed hydrogen atoms), from 1.94 to 2.49 Å (maximum length considered to be significant = 2.50 Å). Interestingly, the hydrogen bonding pattern of the guanidinium species in their respective 12-membered ring windows is subtly different for each of the three molecules (Figs. 4, 5 and 6). In particular, the C1-centered $[CN_3H_6]^+$ species participates in six simple N–H ··· O bonds, the C2 species in three simple hydrogen bonds and three bifurcated hydrogen bonds and the C3 species in four simple and two bifurcated bonds.

The $^{13}$C NMR spectrum of $[CN_3H_6]_2[Zn(CO_3)_2]$ (Fig. 7) showed two groups of signals of roughly equal intensity at $\delta$ 167.14, 166.85, and 166.32 (triplet) and 158 (broad singlet), corresponding to resonances from the carbonate and guanidinium C atoms, respectively. This is in accordance with the crystal structure results (three carbonate and three guanidinium carbon atom sites).

## Discussion

$[CN_3H_6]_2[Zn(CO_3)_2]$ is the first organically templated open-framework phase containing the triangular carbonate ion as a constituent part. Thus, the compositional variety[1] of open-framework, organically templated solids is extended still further. The only other open-framework carbonate reported so far, $Na_2Zn_3(CO_3)_4{\cdot}3H_2O$,[12] contains 8-membered ring channels

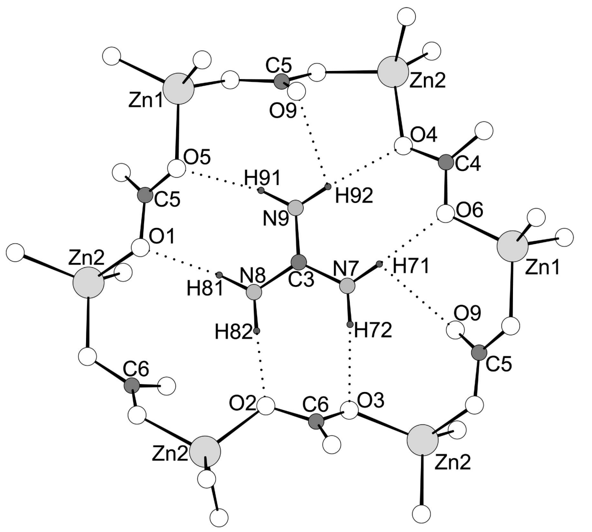

**Fig. 6** Detail of $[CN_3H_6]_2[Zn(CO_3)_2]$ showing the hydrogen bonding interactions (dotted lines) between the C3-centered guanidinium template molecule and a 12-membered ring window in the ZnCO framework.

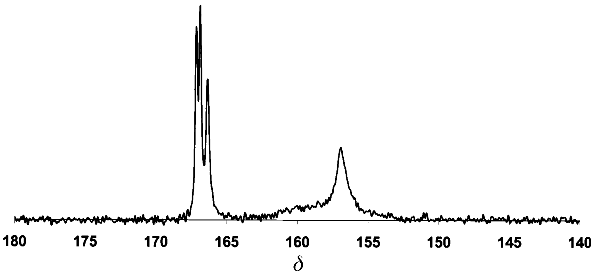

**Fig. 7** $^{13}C$ MAS NMR spectrum of $[CN_3H_6]_2[Zn(CO_3)_2]$.

and has a totally different, cubic, structure to that of the present compound.

Surprisingly, $[CN_3H_6]_2[Zn(CO_3)_2]$ shows a close similarity to various other open-framework phases templated by the guanidinium cation. Both the zinc phosphate $[CN_3H_6]_2[Zn(HPO_4)_2]$[11] and the zinc *phosphite* $[CN_3H_6]_2[Zn(HPO_3)_2]$[13] are built up from equivalent 12-membered ring-based frameworks of $ZnO_4$ tetrahedra + $HPO_4$/$HPO_3$ tetrahedra/pseudo pyramids to the $ZnO_4$ tetrahedra + $CO_3$ triangles seen here. Precise crystallographic details, including space groups, differ, but all three networks are topologically equivalent in their nodal connectivity.[14] In fact, all three networks are "metastructures"[14] of the α-cristobalite ($SiO_2$) framework type, *i.e.* Zn corresponds to Si and $HPO_4$/$HPO_3$/$CO_3$ corresponds to O in the $SiO_2$ phase. The approximate degree of magnification[14] to relate the separations of silicon species in $SiO_2$ and the zinc nodes in the $[CN_3H_6]_2[Zn(HPO_4)_2]$ family is 1.8. Thus, phosphate, phosphite, and carbonate are acting in very similar ways in these frameworks. In each case two links to Zn are made; for phosphate there are terminal P–O and P–OH bonds, for phosphite terminal P–O and P–H and for carbonate terminal C–O. Such structural similarity between phosphate, phosphite and carbonate is not seen in condensed inorganic phases.

$[CN_3H_6]_2[Zn(HPO_4)_2]$ is notable for its extremely low framework density[15] (FD; number of nodal framework atoms per 1000 Å$^3$) of 9.10. The comparable FD value for $[CN_3H_6]_2[Zn(CO_3)_2]$ is somewhat larger, at 11.36. However, the carbonate pore volume (percentage of the unit cell volume *not* occupied by the framework component of the material) of 58% is somewhat larger than the 55% for the phosphate.

## Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. We thank the DARTS Scheme administered by the EPSRC for providing synchrotron beam time access at Daresbury.

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