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Synthesis and structure of fluoride-containing GeO_2 analogues of zeolite double four-ring building units†

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Received (in Cambridge, UK) 29th July 2002, Accepted 27th August 2002
First published as an Advance Article on the web 5th September 2002

Double four-membered ring (D4R) anionic building units $[Ge_8O_{12}(OH)_8F]^-$ have been synthesised hydrothermally and their structures solved from powder X-ray diffraction.

Microporous solids, such as the aluminosilicate zeolites and aluminium/gallium phosphates are important materials, with applications in catalysis, ion exchange and gas separation, and are increasingly being studied as host species for nano-chemistry. The utility of microporous materials in many applications is intimately connected with their structural architecture and so the ability to control the structure of materials is an important goal in today's chemical research. The mechanism of synthesis of microporous materials has been the subject of much discussion, with excellent reviews coming from O'Hare,[1] Ozin[2] and Férey.[3,4] Férey has put forward the theory of microporous material formation based on ionic/molecular species, termed pre-nucleation building units (PNBUs).[4,5] These PNBUs are thought to be present in solution and condense, either directly or after undergoing small rearrangement/isomerisation reactions, to form the resultant solid. This view finds strong support in some elegant experiments performed by Férey and Taulelle where small PNBUs have been identified using *in situ* NMR.[5] This theory opens up possibilities in the rational design of microporous solids as control over the types of PNBU present in solution, coupled with control over how they condense to form 3D network solids, is a vitally important factor in the overall design of new structural architectures. A particularly attractive PNBU to target is one with a cuboidal structure known as the double four ring (D4R). We have, in previous work, prepared molecular D4R units in the solid state with various compositions including gallium phosphate.[6,7] The most important feature of this work is that it suggests that the D4R units are present in solution during the synthesis of these solids, since it is very likely that molecular solids are formed by crystallisation of the molecules out of solution. Other workers have prepared molecular D4R units based on silicate species.[8] However, a recent paper by O'Keefe and Yaghi postulated,[9] based on the differences between Ge–O–Ge and Si–O–Si bond angles, that certain germanium oxide framework structures containing D4R units would be stable, when identical silicate-based frameworks would be impossible to synthesise. This is because Ge–O–Ge angles have different magnitudes (~130°) to those Si–O–Si angles (~145°) and this effects how the cubes can be linked together into framework structures. A number of D4R-containing germanium oxide materials have since been prepared.[9,10,11] The germanium oxide D4R unit is therefore a particularly useful PNBU to target in an attempt to prepare new framework materials that are not possible in silicate-based zeolite chemistry. Our goal in this work was then to identify the synthesis conditions under which the germanium oxide D4R unit can be formed.

The double four ring analogues 'D4R-GeO_2' of composition $[Ge_8O_{12}(OH)_8F]^-$ (Fig. 1) can be synthesised from GeO_2 and HF with the help of an organic cation, *N*,*N*-diethyl-*cis*-dimethylpiperidinium (DECDMP). A typical synthesis is as follows: 1.32 grams of GeO_2 is dissolved in 35.28 grams of a solution containing 1.8×10^{-4} mols of DECDMP per gram. After removing 33.91 grams of water by evaporation under vacuum, 0.26 grams of HF (48%) were added to the mixture and stirred by hand. The overall molar composition is $GeO_2 : 0.5DECDMP^+OH^- : 0.5HF : 1.5H_2O$. The final mixture was poured into Teflon-lined autoclaves and allowed to react under static conditions and at 130 °C for 8 days. The solids were washed with mixtures of H_2O/methanol (approx. 1 : 1) in a sonication bath, and acetone and dried at room temperature.

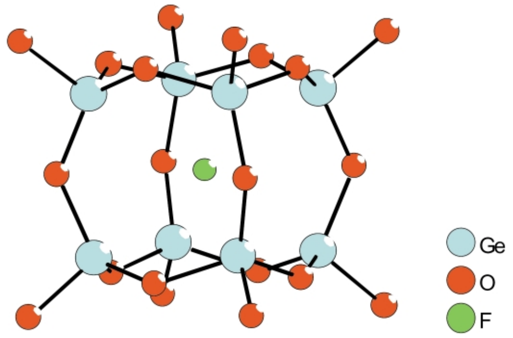

Fig. 1 The D4R unit from [DECDMP,F]–GeO_2–D4R.

[DECDMP,F]-GeO_2-D4R crystallises with an *I*-centred tetragonal unit cell and its structure was solved using the crystal structure of gallium phosphate D4R[6,7] units as an approximate starting model.§ Rietveld refinement of this model proceeded successfully (Fig. 2). Carbon-13 MAS NMR indicates that the DECDMP cation is intact within the structure.

The final model shows isolated $[Ge_8O_{12}(OH)_8F]^-$ with fluoride encapsulated at the centre of the D4R unit. This situation is similar to that seen in a number of D4R-containing zeolites such as AST[12] and ISV[13] where the fluoride ion is

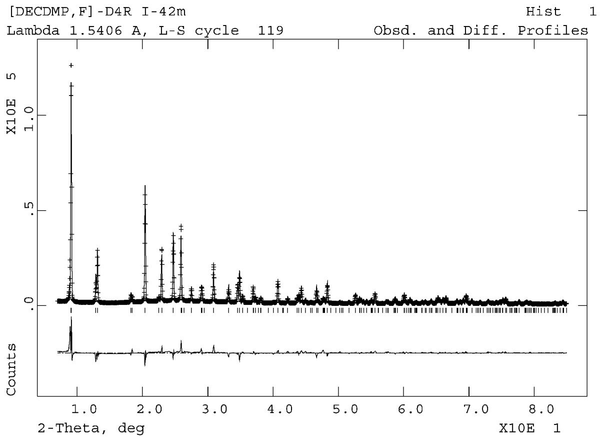

Fig. 2 Observed, calculated and difference plots for Rietveld refinement of [DECDMP,F]-GeO_2-D4R.

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† Electronic supplementary information (ESI) available: X-ray diffraction data. See http://www.rsc.org/suppdata/cc/b2/b207374a/

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DOI: 10.1039/b207374a

effectively packed tightly inside the smaller silicon D4R unit. However, simple molecular modelling using semi-empirical calculations contained in the program HyperChem[14] indicates that, because of the larger size of germanium compared to silicon, the fluoride ion is more likely to be displaced away from the exact centre of the cube. The modelling yielded two possibilities of almost equal energy, one with the fluoride displaced towards one face of the D4R unit and one with the fluoride displaced towards the vertex of the unit. The fluoride position found in the XRD experiment is an average of these two positions in all their possible orientations. Disordered situations of this type are very difficult to resolve even with high quality single crystal diffraction data,[15] and so with the powder data in this study it is difficult to be precise about the actual position of the fluoride ion inside the D4R unit. However, the crystallography is clear that the fluoride is inside the D4R unit. This is further supported by the ^{19}F NMR of [DECDMP,F]-GeO_2-D4R (Fig. 3), which shows a single resonance at -14.8 ppm, similar to those seen by us in samples of fluoride containing GeO_2 materials with the BEC (-9.0 ppm) and ASV (-12.6 and -15.4 ppm) structures, both of which contain D4R units and in our hands, hosting F anions. This in itself is interesting in that in the original syntheses of ASV and BEC, there was no fluoride reported at the centre of the D4R cages.[10,11] Characteristic ^{19}F chemical shifts for these materials range from -9 to -16 ppm, compared to about -40 ppm for D4R-SiO_2 and -70 ppm for $GaPO_4$-D4R units in previously reported cases within zeolites.

The overall structure of [DECDMP,F]-GeO_2-D4R shows an arrangement of $[Ge_8O_{12}(OH)_8F]^-$ anions (Fig. 4) where negative charge is balanced by the corresponding organic cation. The inorganic cluster is composed of 8 GeO_4 tetrahedra at the corners of a D4R 'cube', linked together by sharing oxygen atoms. The 'external' O atom of every GeO_4 unit is assumed saturated by H atoms, giving Ge–OH moieties readily available for further condensation. Within every cube resides a fluoride anion, responsible for the charge that the inorganic cluster bears.

The units are linked together *via* strong inter-ionic H-bonds (O(3) – O(4) = 2.42 Å in [DECDMP,F]-D4R, with the organic cations acting as space-fillers.

In this paper we have reported, for the first time, the synthesis of GeO_2 analogues of the well known D4R units. This new material now stands as a very promising starting point for altering the conditions of synthesis to see if the D4R units can be transformed, either in the solid state or *via* a solution mediated process, to produce novel germanium oxide zeolite frameworks. Further work in this area is continuing.

The authors thank the EPSRC for funding and David Apperley for access to the EPSRC NMR service. REM thanks the Royal Society for provision of a research fellowship and LAV thanks the Ministerio de Ciencia y Tecnología.

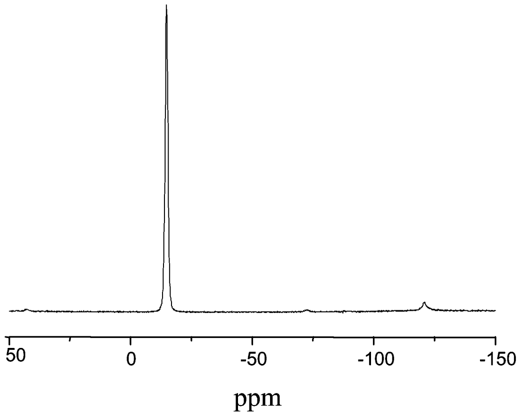

Fig. 3 ^{19}F MAS NMR of [DECDMP,F]-GeO_2-D4R. The resonance at ~ -122 is an impurity.

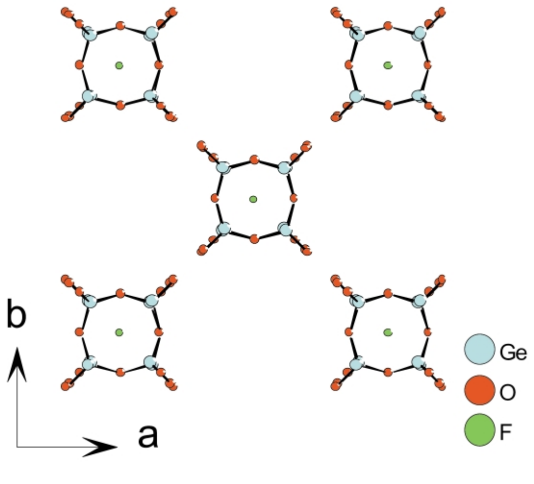

Fig. 4 The structure of [DECDMP,F]-GeO_2-D4R viewed parallel to the fourfold symmetry axis. The disordered template is not shown for clarity.

Notes and references

§ Crystal Data for [DECDMP,F]-D4R, $[Ge_8O_{12}(OH)_8F](C_{11}NH_{24})$, crystal system tetragonal, space group I-42m (No. 121), unit cell (298 K) a = 13.7488(4) Å, c = 7.7446(3) Å, V = 1464.0(1) Å^3, Z = 2, 176 reflections (5–85° 2θ), CuKα_1 radiation, No. of variables = 30, No. of restraints = 18, R_{wp} = 15.4%, R_p = 11.4%. Powder X-ray diffraction data were collected on a Stoe STADI/P transmission diffractometer, using Ge-monochromated CuK$_{\alpha1}$ radiation. The sample was mounted in a capillary. Data were collected using a small position-sensitive detector covering about 6° in 2θ, with data points at 0.02° intervals. Rietveld analysis was carried out with the program GSAS using the '$GaPO_4$' analogue as a starting model for the D4R unit, in space group I-42m. This space group permits two crystallographically distinct Ge sites in the $[Ge_8O_{12}(OH)_8F]$-D4R, but necessitates considerable disorder of the DECDMP cation. The simplest model for this disorder places the piperidine ring around a site of 222 point symmetry at (0,1/2,1/2). Soft contraints were placed on all bond distances and angles. The DECDMP was kept fixed in the disordered high symmetry position, producing a significant improvement in the profile fit (with DECDMP, R_{wp} = 15.4%, without DECDMP, R_{wp} = 26.2%). Further details of the final Rietveld refinement are given in the supplementary material.

^{19}F MAS NMR spectra were acquired on a Varian UNITY 300 spectrometer at a resonance frequency of 282.2 MHz. Sample spinning frequencies and recycle delays of 15.4 kHz and 5 s respectively were used. A direct-polarisation experiment with a 90° pulse was used and the spectra were obtained with ^{1}H decoupling as well as the reference. Chemical shifts are reported with respect to $CFCl_3$, used as external standard.

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