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MS18 O3

Predicting and Engineering Inclusion Frameworks
Aurora J. Cruz Cabeza,^a Graeme M. Day,^a W. D. Samuel Motherwell^b and William Jones^a; ^aThe Pfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK; ^bCambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.
E-mail: ajc220@cam.ac.uk

Keywords: organic inclusion compounds, crystal structure prediction, computer modelling solids

Inclusion compounds have attracted the interest of materials chemists for the last fifty years or so, with one of the main reasons being their numerous potential applications. However, since they were first discovered in 1810 (eg. choleic acid discovered by H. Davy), inclusion compounds have been obtained mainly by serendipity. Amongst these compounds we also find organic inclusion solvates: crystal structures in which the main component is an organic molecule forming a well-defined hydrogen bonded network that serves as a host to the solvent molecule. In many instances, inclusion solvates tend to be isostructural: while the host structure is always maintained, a great variety of solvent molecules can serve as guest. This is the case of sulfathiazole, a drug well known for its numerous solvates. Prediction of this type of behavior for molecules of pharmaceutical interests would be of great importance, since in many cases solvates tend to be avoided, whenever possible, in drug formulation. In this context we describe, for the first time, a way of anticipating possible and likely inclusion frameworks *ab initio*, using only a knowledge of the molecular connectivity of the host. We suggest that crystal structure prediction calculations, combined with voids analysis in putative crystal structures of high energy and low density, as a way of identifying possible inclusion frameworks. We present preliminary results for some well known inclusion systems and drug molecules with inclusion properties.

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Twinning in Clathrates-II Reiner Ramlau, Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany.
E-mail: ramlau@cpfs.mpg.de

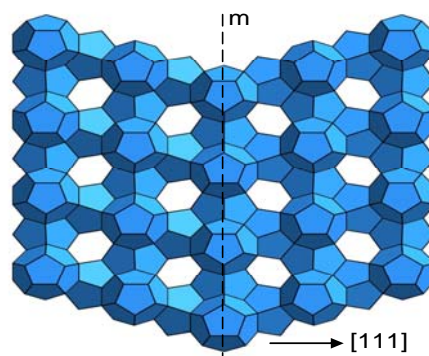
Keywords: clathrates, twinning, germanium

A new crystalline modification of elemental germanium, the guest-free germanium clathrate-II $\square_{24}\text{Ge}_{136}$, has been successfully prepared recently [1] through oxidation of Ge_9^{4-} Zintl anions in ionic liquids under ambient conditions. The new modification—shortly called clathrate-II germanium—(space group $Fd\bar{3}m$) is an open, covalently bonded 3D network of tetrahedrally coordinated Ge atoms forming pentagon-dodecahedral Ge_{20} and hexakaidecahedral Ge_{28} cages. Each unit cell contains 16 pentagon dodecahedra [5^{12}] and 8 hexakaidecahedra [$5^{12}6^4$]. (In a completely filled clathrate-II the 24 polyhedral cages would provide space for 24 guest positions.) Investigations by electron diffraction and

high-resolution transmission electron microscopy (HRTEM) revealed the strong tendency to both polysynthetic and cyclic twinning. Twinning has already been reported for the partly filled binary clathrate-II $\text{Na}_x\text{Si}_{136}$ ($x < 11$) [2].

The present study shows that an intrinsic structural feature, the approximate mirror symmetry of an extended structural entity, compels repeated twinning and may seriously compromise single-crystal growth. The mentioned entity is not only own to the elemental clathrate-II germanium but also to the host framework of all binary type-II clathrates. It is supposed that multiple twinning occurs also in clathrate-II hydrates [3] and dodecasil-3C [4], although this is seemingly not reported yet.

The twin law is comprehensively formulated as reflection twinning with a $\{111\}$ -type plane as the twin plane, intersecting the corners 0,0,0 of the cubic unit cell. The twin interface is identical with the twin plane. It is completely coherent and smooth. An atomic model of the interface is established (Figure). In this model the dodecahedra which are constituting the layer at the twin interface adopt perfect $\{111\}$ mirror symmetry and are, hence, slightly distorted with respect to those inside the twin components. (Which on their part are slightly distorted regular dodecahedra.) Model-based image simulation is in very good agreement with experimental HRTEM images of the twin interface.



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Self-assembly of functionalized calixarenes.

Kinga Suwinska^a, Oleksandr Shkurenko^a, Florent Perret^b, Anthony W. Coleman^b

^aInstitute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland. ^bInstitut de Biologie et Chimie des Protéines, Université Lyon 1 CNRS UMR 5086, Lyon, France. E-mail: kinga@ichf.edu.pl

Keywords: calixarenes, self-assembly, X-ray structure

The calix[n]arenes are aromatic macromolecules that can engender a wide range of derivatives thanks to their easy and selective chemical modifications. An extremely wide range of solid-state studies have been undertaken on these

derivatives, showing high structural diversity. For para-sulfonatocalix[4]-arene for example, both classical organic clay bilayer systems, classic bilayers, zig-zag bilayers, stepped bilayers, capsules and tubes, spheres or other geometrical solids have been observed. Concerning calix[n]arenes functionalised on the lower rim, such as calix[4]arene di-hydroxyphosphonic acid, there is an apparent constant in self-organisation, the same interpenetrating motif. Such dimeric motifs are also

present in the structures of di-propylether calix[4]arene or di-cyanomethoxy calix[4]arene. Other calix[n]arene derivatives, carrying one or more pendant acidic arms on the lower rim, give rise to architectures such as inclusion polymers or nanotubes.

In the present paper self-assembly of calixarenes functionalized on the lower rim, especially amfifilic calicarenes will be discussed.