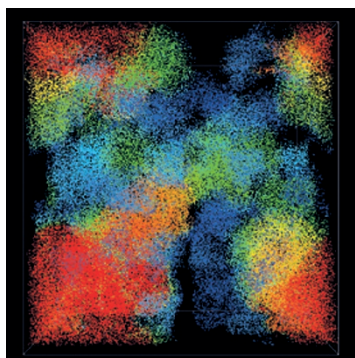


AMORPHOUS SOLIDS

Cage calculations

J. Am. Chem. Soc. <http://doi.org/p7q> (2013)



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Porous solids offer rich 'host-guest' chemistry that is being increasingly exploited, in particular for molecular recognition and gas-separation uses. These applications rely on understanding structure-property relationships to enable tuning of the materials' properties. Crystalline solids are well suited to these investigations, but amorphous ones consisting of organic cages packed in

a disordered manner also show promising high porosity. This is because, in addition to the cages having hollow cavities, they have accessible space between them. The porous domains of such amorphous molecular solids, however, are much less straightforward to characterize and tailor than those of their crystalline counterparts.

Andrew Cooper at the University of Liverpool and co-workers have now used molecular dynamics simulations to study the porosity of amorphous molecular solids, and their ability to support gas diffusion. Amorphous materials are difficult to model, partly because they are metastable; however, the researchers devised a four-step procedure to generate amorphous structure models for a given organic cage. In this procedure an ensemble of 40 cages is considered in an initial configuration, and subsequently stabilized into a low-density structure. The volume of that structure is in turn compressed until no further reduction is observed and the resulting structure is geometry-optimized. Six initial ensembles give six models that are averaged to take into account the non-homogeneity of the structure.

Cooper and colleagues investigated two isostructural cages — with either ethane or cyclohexane vertices — experimentally and computationally. The materials were synthesized by 'freeze-drying', which involves rapid precipitation of the cages from a solution and subsequent removal of the frozen solvent. Gas-sorption measurements showed different selectivities for hydrogen and nitrogen. The models were used to determine the materials' pore size distribution and connectivity — the extent to which a guest can diffuse through the void — and their gas-diffusion behaviour. The computational results were in good agreement with the experiments and point to a 'gas hopping' mechanism through the pores. *AP*

PHOTOCYCLOADDITIONS

Asymmetric at last

Science **342**, 840–843 (2013)

Cycloadditions are popular reactions in the context of complex molecule synthesis because they involve the formation of several bonds in a single step and can often be performed stereoselectively. Despite having some of the same attributes,

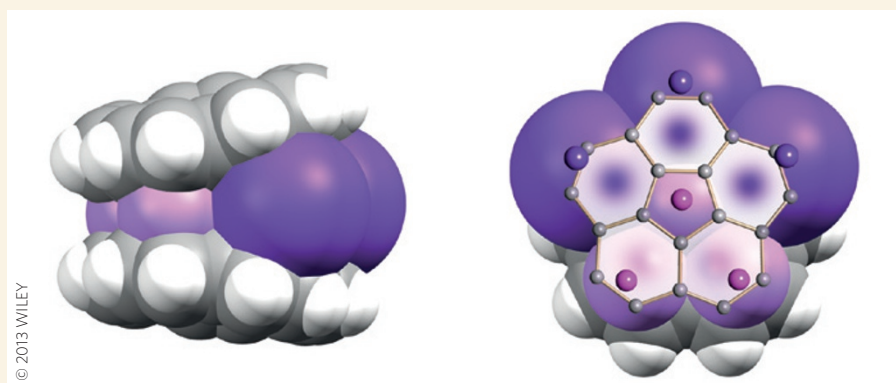
SANDWICH COMPLEXES

Metals in the middle

Angew. Chem. Int. Ed. <http://doi.org/f2nqcs> (2013)

One of the most iconic structures in chemistry is undoubtedly ferrocene, a compound with an iron atom neatly sandwiched between the faces of two cyclopentadienyl rings. By increasing the surface area of the organic ligands, sandwich structures with more than one metal-atom filling can also be made. For example, two corannulene molecules — a bowl-shaped hydrocarbon with five six-membered rings fused around a central pentagonal hub — can form a sandwich complex with five lithium ions bound between their convex surfaces. In this structure, each ion interacts with a six-membered ring from each ligand.

Now, a team of researchers in the US led by Marina Petrukhina at the University of Albany have prepared and studied mixed-metal corannulene sandwich complexes and shown that it is possible to squeeze six metal ions between the two organic ligands. When corannulene was reduced with a mixture of lithium and potassium, a LiK_5 complex was formed in which the five potassium ions sit between the eclipsed six-membered rings of the two organic ligands and the lone lithium ion occupies the site



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between the two five-membered hubs. In this structure, the larger potassium ions push the corannulene ligands further apart, creating space for a lithium ion to bind between them, unlike in the parent Li_5 complex where there is not enough room for a sixth metal to bind at this position. After careful re-examination of the mixed-metal reduction reaction, another sandwich complex — filled with three lithium and three potassium ions — was also isolated and characterized by X-ray crystallography (pictured).

The Li_3K_3 assembly retains the lithium ion in the hub site, and also has two lithium ions in adjacent coordination sites between the six-membered rings of the corannulene bowls. Computational studies suggest that the Li_3K_3 complex could be an intermediate in the conversion of the Li_5 system to the LiK_5 structure, with the two non-hub lithium ions acting as the hinge for a clamshell-type opening of the structure that makes the central hub binding site accessible. *SC*