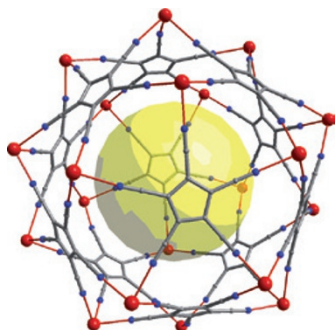


METAL-ORGANIC FRAMEWORKS

Fullerene fashion

Angew. Chem. Int. Ed. **50**, 8279–8282 (2011)



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A myriad of discrete and extended molecular assemblies have been prepared by coordinating metal ions to organic ligands, yet only a few have relied on planar components with a five-fold symmetry. Pentagonal or star-shaped building blocks cannot tile a planar surface without tilting or curving, and the few metal–organic structures assembled with such ligands have thus been discrete spherical cages exhibiting fullerene-like morphology. Now,

John Bacsá and colleagues from Cambridge University and the University of Liverpool have described a three-dimensional metal–organic framework based on the fullerene units.

An anionic five-membered aromatic ring decorated by five cyanide moieties $\{C_5(CN)_5\}^-$ was chosen as the ligand. On crystallizing this ligand with sodium ions by slow vapour diffusion of ether in a nitromethane solution, the researchers observed the assembly — directed by the solvent molecules — of a highly solvated, highly metastable, three-dimensional metal–organic framework. Characterization by X-ray diffraction revealed that each ligand binds five sodium centres through nearly linear $C\equiv N-Na$ bonds. These in turn organize into a coordination network comprising sodium–ligand pentagonal and hexagonal faces, making up units that resemble fullerene moieties. The resulting MOF exhibits both discrete cavities and linear non-intersecting channels that run through the empty faces.

Removal of the solvent molecules under mild conditions does not cause the MOF to collapse but leads to a different morphology. The unsolvated framework adopts a more densely packed layered arrangement, favoured

by π -stacking between the ligands, in which the $C\equiv N-Na$ bonds are no longer linear. *AP*

CO OXIDATION

Stand and deliver

Science **333**, 736–739 (2011)

The key to improving the activity of heterogeneous catalysts is understanding exactly what is going on at a molecular level; once you know how a catalytic system works you can look to make rational and hopefully beneficial changes. Gaining such understanding, however, can be an extremely difficult task, even for a seemingly straightforward process such as a bimolecular reaction on a surface. For example, one must consider the multiple possible adsorption sites, surface diffusion and the various possible intermediates.

The oxidation of carbon monoxide on titania-supported gold nanoparticles is one such bimolecular process that researchers are striving to comprehend. It was previously assumed that the reaction occurred on gold sites at the perimeter, and that the titania surface was only involved in stabilizing oxygen

MAIN-GROUP CLUSTERS

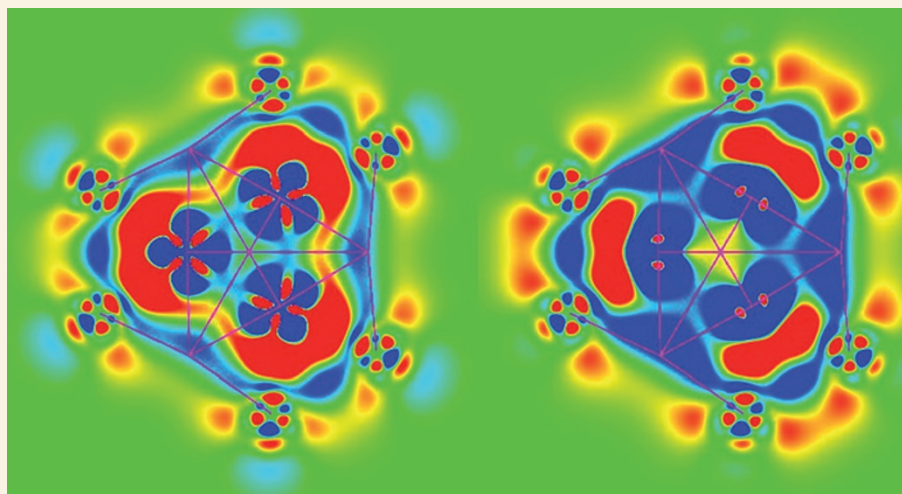
A question of bonding

J. Am. Chem. Soc. **133**, 14168–14171 (2011)

Clusters or cages of main-group elements that incorporate transition metal atoms have recently interested chemists because of their unusual shape and bonding, as well as their similarity to Zintl-type phases. These generally fall into two groups: cages with an encapsulated transition metal dimer or alloy-like clusters.

Now, Stefanie Dehnen from the Philipps University of Marburg and colleagues have made an endohedral cluster anion where three atoms of palladium are held by a 14-atom tin–bismuth cage: $[Pd_3Sn_8Bi_6]^{4-}$. The triangularly arranged palladium atoms are close enough to each other to suggest bonding interactions. The tin–bismuth cage is similar in structure to some previous examples, but these enclosed either no atoms or just one. To account for the -4 charge of the cluster, Dehnen and colleagues considered two bonding models. In one, the Pd_3 centre is neutral and the tin–bismuth cage has two extra valence electrons: $[Pd_3]^0[Sn_8Bi_6]^{4-}$. In the other model, the Pd_3 centre is a dianion: $[Pd_3]^{2-}[Sn_8Bi_6]^{2-}$.

To test the two models, Dehnen and colleagues calculated the difference



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between the electron densities of the anion as a whole and the sum of the constituent parts of each of the two models (pictured; blue shows the model gives a relative excess of electron density and red shows a relative lack). For the model with the neutral palladium centre (left), there were places with too much or too little electron density

on the surface of the cages, whereas the dianion model (right) shows only a lack. As might be expected, modelling the Pd_3 centre as a dianion seems to give too much electron density to this area. Although neither model is perfect, Dehnen and colleagues suggest that the $[Pd_3]^0$ gives the better fit. *NW*