

these unusual compounds normally requires all the ligands to be sterically bulky to protect the under-coordinated metal centre.

Now, Patrick Holland and colleagues from the University of Rochester have created a tri-coordinate cobalt complex in which one of the ligands is a hydride ion — the smallest possible ligand. They reacted a previously known three-coordinate cobalt halide with KHBET_3 and formed some unusual compounds. Using one equivalent resulted in a dimeric complex bridged by two μ_2 -hydrides. The cobalt atoms are close enough together to contribute to the bonding.

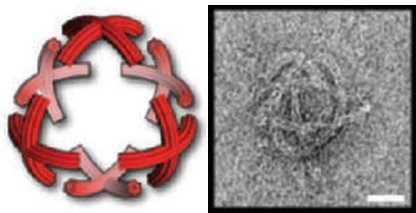
Two equivalents gave a more unusual structure, with two nearly parallel three-coordinate cobalt units. The two hydride ions each bridge a central K_2 unit, which itself interacts with the π systems of the bulkier ligands. In the absence of cobalt–cobalt bonding, these interactions stabilize the structure. Both complexes undergo reductive elimination of hydrogen in the presence of nitrogen, with the extra electrons going to form a $[\text{N}=\text{N}]^{2-}$ ligand that takes the place of the bridging hydrides. Beyond the intrinsic interest of these unusual complexes, this is also relevant to catalytic nitrogen reduction, in this case avoiding the use of harsh reducing agents.

DNA NANOTECHNOLOGY

Twist and curl

Science **325**, 725–730 (2009)

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The ability of DNA to self-assemble in a pre-programmed manner — relying on the hybridization of complementary strands — has been extremely useful for the construction of increasingly complex nanostructures. Now, William Shih and co-workers at the Dana-Farber Cancer Institute and Harvard Medical School in Boston have introduced precisely engineered curvatures to three-dimensional DNA assemblies.

The group recently extended the ‘DNA origami’ approach — in which a ‘scaffold’ strand is folded into the desired shape and held in place by hybridization with ‘staple’ strands — to three-dimensional structures (*Nature* **459**, 414–418; 2009). Parallel

DNA double helices, each consisting of repeating seven-base-pair sequences, were attached together to form three-dimensional honeycomb arrays. Now, by altering the length of these seven-base-pair units, Shih and colleagues have been able to form twisted and bent DNA assemblies.

The insertion or deletion of one base pair of a double helix constrained within the honeycomb framework causes a local under- or over-twist, respectively, which in turn leads to a curvature of the overall array. Judiciously choosing the locations of these sequence adjustments allows the formation of twists (of either handedness) and curves with a finely tuned angle. These tailored arrays have been assembled into a variety of complex nanostructures, including a spherical capsule and a spiral.

CONTROLLED RELEASE

A logical combination

J. Am. Chem. Soc. **131**, 11344–11346 (2009)

Molecular systems that release cargo have great potential for targeted drug delivery. Those that respond to a single external stimulus are well known but a system that requires two triggers for release — creating an AND molecular logic gate — would give improved control as it could respond to both external and biological triggers. Now, a collaboration between Fraser Stoddart at Northwestern University and Jeffrey Zink at the University of California, Los Angeles, has led to the development of a system that needs both light and a change in pH to release a guest molecule.

The system uses azobenzene-derived molecules — tethered to the inside of pores within mesoporous silica nanoparticles — to act as ‘nanoimpellers’ that drive any guest cargo out. Azobenzene can change between *cis* and *trans* forms on absorption of light, and a ‘wagging’ motion is induced when a wavelength is used that is absorbed by both.

The pore, however, is also blocked with a [2]pseudorotaxane tethered to the outer surface of the nanoparticle. This creates a nanovalve that opens on changes in pH, releasing the ring from the stalk of the pseudorotaxane by disrupting their mutual bonding. Both triggers are required for release and this was proven using a fluorescent bipyridine-derived guest molecule that was detected using luminescence spectroscopy.

The definitive versions of these Research Highlights first appeared on the *Nature Chemistry* website, along with other articles that will not appear in print. If citing these articles, please refer to the web version.

blogroll

Power to the people

Sceptical chemists head to the lab to try out a surprising reaction for themselves.

The collective eyebrows of the blogosphere were raised by a paper in *J. Am. Chem. Soc.* (doi: 10.1021/ja904224y), which, in the words of Paul Docherty of Totally Synthetic (<http://go.nature.com/c6c5ST>), “seemed to suggest that black was apparently now white”. And he wasn’t the only person to be surprised that NaH acts as an oxidant — Excimer at Carbon Based Curiosities (<http://go.nature.com/tUKHuf>) picked up on it, as did some commenters at In the Pipeline (<http://go.nature.com/jv9N9H>). However, when Docherty began to ‘live-blog’ his attempts to reproduce the work, people beyond the world of organic/synthetic blogs started to take note. More details appeared over the following day or two, with Docherty struggling to reproduce the results when he performed the reaction in an oxygen-free environment. Peter Murray-Rust (<http://go.nature.com/FEnMID>) thought the whole thing would make a good project for young chemists, and that “This should convince any sceptic that the blogosphere is an essential part of current science”. Even ‘real’ reporters from *Chemistry World* (<http://go.nature.com/dY7QYX>) and *C&EN* (**87**, 47; 2009) wrote about the events, with some useful perspectives from those involved, as well as interested bystanders. Chris Braddock, of Imperial College, provides a good summing up: “the mechanism they suggest is far less clear — it does seem that there is some oxidant associated with the NaH that is doing the business”.

Meanwhile, Katharine Sanderson blogged for Nature News (<http://go.nature.com/a7bKGq>) from the 42nd IUPAC Congress in Glasgow, reflecting the diverse range of chemistry on offer from methanol in space, carbon capture, lithium batteries to the small beginnings of a campaign to save the symbol Cp for the much-loved cyclopentadienyl ligand. It’s under threat from the newest element for which its discoverers are suggesting the name copernicium, but as the Polish spelling was Mikolaj Koppernigk, it was mooted that a more appropriate symbol would be Kp.