FAMILY OF MULTIPLY BONDED BIMETALLIC COMPLEXES GROWS

Multiple bonds between transition-metal atoms have fascinated chemists for 50 years, ever since F. Albert Cotton’s group at MIT discovered a quadruple bond in a diruthenium complex. Synthesizing these multiply bonded complexes between like metals is now common. But such complexes involving two different metals remain rare.

A research team led by Connie C. Lu of the University of Minnesota, Twin Cities, has taken a systematic look at how multiple bonding varies across a series of heterobimetallic complexes in which chromium is paired with other first-row transition metals (J. Am. Chem. Soc. 2013, DOI: 10.1021/ja403503m). Chromium is an interesting target, Lu notes, because it is one of a few elements known to engage in more than a quadruple bond. In 2005, Philip P. Power’s group at the University of California, Davis, reported the first metal-metal quintuple bond in a dichromium complex. Lu’s team prepared Mn-Cr, Fe-Cr, Co-Cr, and Ni-Cr complexes that contain metal-metal bonds with bond orders ranging from one to five (two shown). The researchers’ electronic structure calculations show that each complex undergoes several one-electron transfer processes. Thus, the heterobimetallic compounds could be useful in multielectron catalysis without requiring expensive precious metals.—SR

SWITCH ON THE COLOR

Chemists have developed enough molecular switches to populate a molecular hardware store. Yet it’s rare for switching on the atomic scale to translate into an effect at the macroscopic level. Now, Xin Su, Ivan Aprahamian, and colleagues at Dartmouth College have developed a molecular switch that can change a liquid crystal’s color in response to pH (Angew. Chem. Int. Ed. 2013, DOI: 10.1002/anie.201305514). The switch is made from two cholesterol molecules connected by a hydrazine linker. In the presence of trifluoroacetic acid, the hydrazine turns like a rotor, changing the relative orientation of the cholesterol units. The orientation changes back in the presence of potassium carbonate base. By doping this switch into a liquid crystal called nematic phase 5, Aprahamian’s team rendered the material chiral and capable of developing a helical architecture that dictates color. They showed that adding acid changes the liquid crystal’s color from purple to green, which can be reversed by adding base. Aprahamian is now studying additional switches to produce other color changes, which could lead to detectors for the basic amines characteristic of spoiled foods. He also aims to reduce salt accumulation on the liquid crystal—a problem that currently gums up the works after just three cycles.—CD

WATER LUBRICATES MOLECULAR MACHINES

Lubrication is often key to getting a mechanical machine to work smoothly. For molecular machines that spin or ratchet through chemical reactions, lubrication takes on a new meaning. By experimenting with a molecular shuttle in acetonitrile and a wheel-and-axle device in pyridine, scientists have found that a small amount of water added to the solvents accelerates the amide-based machines’ movement, likely through hydrogen-bonding effects (Nat. Chem. 2013, DOI: 10.1038/nchem.1744). The team was led by Sander Woutersen and Matthijs R. Panman of the University of Amsterdam, in the Netherlands, and David A. Leigh of the University of Manchester, in England.

Other additives capable of hydrogen bonding, such as methyl alcohol, ethyl alcohol, and tert-butyl alcohol, did not have the same effect. The researchers hypothesize that water’s small size and ability to form hydrogen bonds in multiple directions allows it to form and quickly rearrange hydrogen-bond networks between the moving parts of the machines to stabilize CO and NH groups. In that way, water facilitates—or “lubricates”—machine movement.—JK

DESIGNER PROTEIN LOVES METAL

Scientists envision that someday computationally designed proteins could bind metals and catalyze chemical reactions unseen in nature for industrial and medical applications. A team has taken a step in that direction by generating a novel metal-binding protein that incorporates an unnatural amino acid with an exquisite taste for metals (J. Am. Chem. Soc. 2013, DOI: 10.1021/ja403503m). The researchers, led by David Baker of the University of Washington, Seattle, used an unnatural amino acid because no single amino acid typically found in proteins can bind metals unaided. They used (2,2′-bipyridin-5-yl)alanine, or Bpy-Ala, which alone has micromolar-level affinities for a variety of metals. The researchers instructed their computer program to place Bpy-Ala within a rigid part of a protein, such as an α-helix, to lock the unnatural amino acid in place. After expressing the computer-designed protein in bacteria, the team solved its crystal structure and found that it matches the design almost exactly. The team also found that the designed protein binds cobalt, zinc, iron, and nickel with affinities in the picomolar to micromolar range.—JNC