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Spotlights on Recent *JACS* Publications

PUSHING THE LIMITS OF LANTHANIDE CHEMISTRY

William J. Evans and colleagues have isolated crystalline molecular complexes of four members of the lanthanide(II) series previously thought to be too unstable for complex formation (DOI: 10.1021/ja403753j). Their work suggests that all lanthanides can form molecular complexes in the +2 oxidation state, revising the canonical view of the reactivity of these elements.

For many years, chemists thought that only 6 of the 15 members of the lanthanide(II) series could be isolated in molecular complexes and that the others were too unstable in common solvents because of the redox potential of their presumed electron configuration. Recently, however, researchers have obtained crystalline molecular complexes of several of the remaining nine, making chemists curious about whether the others in the series could also be coaxed into complexes.

Now Evans and colleagues fill in the remaining gaps in the series by isolating crystalline molecular complexes of terbium(II), praseodymium(II), gadolinium(II), and lutetium(II). By characterizing the complexes using UV−vis and electron paramagnetic resonance spectroscopy and density functional theory calculations, they show that the electron configuration of these ions is most likely different than has been previously assumed. Although the authors could not assay promethium because of its radioactivity, they predict that it could behave similarly. **Deirdre Lockwood, Ph.D.**

HOW ACYL CARRIER PROTEINS CARRY OUT THEIR JOBS

Acyl carrier proteins (ACPs) are components of intricate multienzyme factories inside the cell that make important biomolecules, such as fatty acids and polyketides. To help understand how they carry out their jobs as tethers upon which the biomolecules are manufactured, Michael Burkart and co-workers devise a method to trap ACPs in the midst of their actions (DOI: 10.1021/ja4042059).

The authors exploit a unique property of ACPs that requires them to be attached to a chemical tether called a pantetheine in order to function properly. They create analogs of pantetheine embedded with an inhibitor of an enzyme with which the ACPs interact, called a dehydratase. When the dehydratase and the ACP come together, the inhibitor acts like a tiny piece of glue, locking the proteins together in the precise structural configurations in which they function.

This approach provides a snapshot of the active structures of ACPs, and offers clues about the mechanisms of their actions. By tweaking the structures of the inhibitor-embedded pantetheines, this strategy can be applied toward the structural and functional characterization of other ACP interactions as well. **Eva J. Gordon, Ph.D.**

COMPUTER PREDICTS 3D CAGE STRUCTURES

Predicting how molecules will assemble into supramolecular structures is an important first step to designing new structures and materials. But the process is not as straightforward as it may sound. Small changes in the structure of precursor molecules can have dramatic, nonintuitive effects on the resulting structures, and experimental conditions, such as concentration, solvent, and the order the reagents are added, can also influence the outcome.

For the first time, researchers present a computational procedure that can predict the structure of supramolecular cage compounds made from organic precursor compounds (DOI: 10.1021/ja404253j). The computational method, created by Andrew Cooper and co-workers, calculates the lowest-energy conformers based on knowledge of the precursors alone. The researchers find the method's predictions are in near-perfect agreement with experimental crystal structures of the imine cage molecules.

Although it will be extremely challenging to generalize this strategy to other systems that are more sensitive to solvent effects, this work is an important first step toward the goal of enabling researchers to computationally design new organic crystalline porous structures prior to attempting their syntheses. **Christine Herman, Ph.D.**

IT'S RAINING XENON: NANO DROPLETS BOOST NMR SENSITIVITY

Hydrogen is abundant in humans, particularly in the water that permeates the body. Each hydrogen atom's environment affects its behavior in a magnetic field, allowing doctors to generate detailed structural images of the body with magnetic resonance imaging (MRI). Even with all that water, hydrogen MRI is not very sensitive and can miss important features, such as tumors. Alexander Pines and colleagues Todd Stevens and Matthew Ramirez have developed a nuclear magnetic resonance (NMR) method that probes xenon instead of hydrogen, offering exceptional sensitivity and a potential path to new imaging techniques (DOI: 10.1021/ja402885q).

Hyperpolarized xenon, which has an enhanced NMR signal, can be bubbled into solution for detection. To create contrast in the xenon signal, the researchers' generate a "nanoemulsion" that xenon can easily penetrate. The nanoemulsion consists of a fluorocarbon and a stabilizing surfactant that form tiny droplets in water of between 160 and 310 nm in diameter. The xenon signal from outside the droplets is shifted from and is more intense than the droplet signal, but the two populations continuously exchange, allowing the researchers to detect droplet concentrations as low as 100 fM in just 5 s. Evidence suggests that nanoemulsions accumulate in tumors, which may allow doctors to someday use xenon NMR to diagnose cancer. **Erika Gebel, Ph.D.**

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