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Spotlights on Recent *JACS* Publications

REDOX-INACTIVE METAL IONS PLAY PIVOTAL ROLES

Oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions are important chemical processes in the study of metalloenzymes and their chemical models. High-valent metal-oxo species have been identified as key intermediates in oxidation reactions, and redox-inactive metal ions have an important part to play in the reactivities of the metal-oxo complexes in Photosystem II (PS II), the light-harvesting assembly that allows plants to make energy from sunshine.

Working with a mononuclear non-heme manganese−oxygen compound, Wonwoo Nam and co-workers examine the binding of redox-inactive scandium(III) ions (DOI: 10.1021/ja312113p). The result shows the first example of a redox-inactive metal ion that has a contrasting effect on the reactivity of Mn-oxo complex in OAT and HAT reactions. The researchers find that while OAT reactivity increases, most likely due to an electron transfer pathway, HAT reactivity decreases. They attribute this difference to the steric hindrance of the Sc^{3+} ion bound to the Mn-oxo compound.

These results show that redox-inactive metals can have a critical effect on high-valent metal−oxo species in oxidation reactions. Moreover, this research gives key glimpses into the reactions of PS II, one of which is the oxidation of water to produce O_2, a reaction that generates $4H^+$ and $4e^-$ that are converted to H_2 as a byproduct, an important fuel in alternative energy production. **Leigh Krietsch Boerner, Ph.D.**

STREAMLINING THE SYNTHESIS OF PROMISING NATURAL PRODUCTS

Sarah E. Reisman and colleagues streamline the synthesis of an intriguing set of alkaloids—an important class of natural products—with a common structural motif, aryl-substituted pyrroloindolines (DOI: 10.1021/ja4023557).

Morphine, cocaine, caffeine, and nicotine are well-known examples of alkaloids with potent physiological effects. Scientists continue to discover pharmacologically promising alkaloids made by a wide range of organisms. The ocean is a rich source of these compounds, and in recent years many new alkaloids have been isolated from marine bacteria and sponges. The challenge is synthesizing them to fuel study and potential drug development.

Here, the team has developed a copper-catalyzed reaction to arylate tryptophan derivatives in a stereoselective manner. The researchers then use this method to execute an efficient five-step synthesis of naseseazines A and B, alkaloids isolated from bacteria in marine sediments. The simplified method will facilitate the synthesis and study of similar compounds, potentially driving the development of new pharmaceutical agents. **Deirdre Lockwood**

SEEING SILICATE MATERIALS IN 2D

X-ray crystallography has made solving three-dimensional atomic structures practically routine, but it does not work as effectively on solid materials that are not crystals. Yet some interesting and useful silicate materials have structures in only two dimensions, and the development and uses of these sheet-like materials have been hindered because scientists have not had a good way to study them in molecular detail. Now, Bradley Chmelka, Darren Brouwer, Sylvian Cadars, and colleagues have developed a general approach for solving the structures of ordered, but not crystalline, silicate materials by combining solid-state nuclear magnetic resonance (NMR) spectroscopy with *ab initio* calculations and X-ray diffraction (XRD) (DOI: 10.1021/ja311649m).

The researchers test their method on silicate layers, enriched with NMR-active ^{29}Si, which were synthesized with a surfactant. Such layered frameworks can often be converted into porous solids, such as zeolites of pillared clays, that are important in numerous industrial applications, including water purification, oil refining, and fine chemical production. The researchers prepare the material as a powder and obtain its XRD pattern, which provides some basic information about the geometry of the material's repeating structure. But to go deeper, they perform ^{29}Si NMR measurements to assess the connectivities and arrangements of silicon atoms in the material. Finally, to tie it all together, the researchers use density functional theory calculations to build models of possible structures, which they refine using NMR data to arrive at the material's structure. **Erika Gebel, Ph.D.**

THE RUSH IS OVER, BUT MINING CONTINUES

Yet to be identified "genetic machinery" could be put to work in the creation of new pharmaceuticals by pioneering a largely unexplored area of plant biology: specialized metabolites. A process referred to as "mining the genome" may allow researchers to unravel the unique chemistry that genes of unknown function perform to generate novel metabolites.

In a recent paper, Seiichi Matsuda and co-workers describe a process in which they mine, or dig through, a genome to streamline the functional analysis of gene clusters (DOI: 10.1021/ja401535g). The authors use triterpenes as sample metabolic substrates in yeast strains expressing enzymes of unknown function. After incubation, the crude *in vivo* oxidation products are analyzed using HSQC. This high-resolution 2D NMR experiment simultaneously acquires data for proton and carbon nuclei. The compounds are subsequently purified and fully identified by GC-MS and NMR.

Previous efforts in this area were limited by a lack of general methods for studying a range of genes and metabolites, or by the significant phytochemical background present when directly analyzing plant material. With this new technique the authors efficiently determine the location and configuration of the triterpene oxidation. Although they note it is uncertain if this analysis method could predict the step order and length of an entire metabolic process, it is certainly a positive starting point toward more general and efficient genome mining. **Rebecca Guenard, Ph.D.**

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