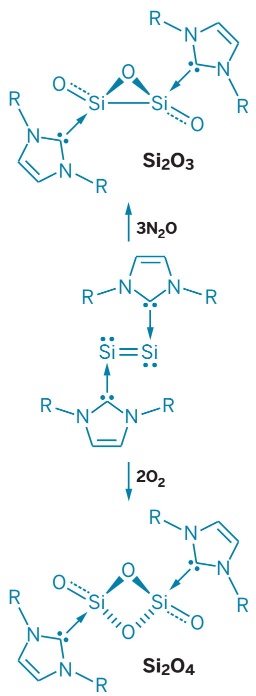


ELUSIVE SILICON OXIDES UNVEILED

MAIN-GROUP ELEMENTS: Chemists prepare the first examples of simple monomeric silicon oxides

USING A NEW APPROACH to marry silicon and oxygen, inorganic chemists have created the first monomeric silicon oxides: complexes of Si_2O_3 and Si_2O_4. This fundamental discovery, which might one day factor into how silicon-based electronics are made, is another feather in the caps of Gregory H. Robinson, Yuzhong Wang, Henry F. Schaefer III, and their colleagues at the University of Georgia.

Although carbon and silicon sit together in group 14 of the periodic table, they display disparate behavior when it comes to forming oxides. Carbon monoxide and carbon dioxide—monomeric carbon oxides—are ubiquitous under normal room conditions. But simple silicon oxides don't exist. Silicon oxide is a monomeric compound only at high temperature. And although silicon dioxide is one of the most abundant materials on Earth—as silica, quartz, and sand—it's a covalent network of silicon atoms bound to neighboring oxygen atoms, rather than discrete molecules.

Robinson's group previously synthesized an unprecedented silicon(0) compound containing a silicon-silicon double bond, with the silicon atoms stabilized by bulky N-heterocyclic carbene (NHC) ligands. Building on that development, the Georgia team made the Si_2O_3 and Si_2O_4 complexes (shown) by oxidizing the disilicon complex with N_2O or with O_2 (*Nat. Chem.* 2015, DOI: 10.1038/nchem.2234).

The researchers were motivated to try the reactions after using the NHC-stabilization approach a year ago to prepare diphosphorus tetroxide, P_2O_4, a long-sought phosphorus analog of N_2O_4, by adding O_2 across a diphosphorus bond (C&EN, Jan. 6, 2014, page 21). Altogether, their achievements help resolve some of the final missing pieces of main-group oxide chemistry.

"Isolating the first monomeric silicon oxides is a spectacular breakthrough, both because of its fundamental importance and scientific beauty," says Yitzhak Apeloig, a silicon chemistry expert at Technion—Israel Institute of Technology. "Obtaining Si_2O_3 and Si_2O_4 at ambient conditions opens up the opportunity to study in detail the chemistry of silicon oxides, which may help to understand the oxidation and doping of silicon surfaces, an important process in the microelectronics industry."—STEVE RITTER

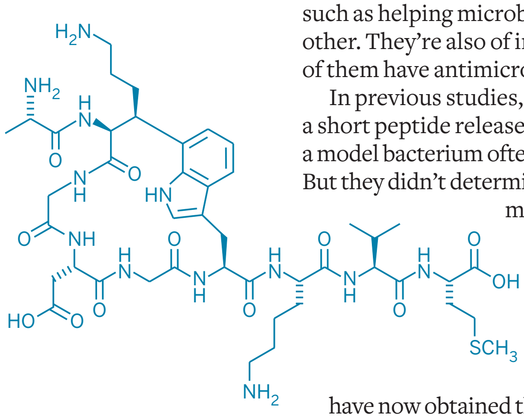
FAMILY OF CYCLIC PEPTIDES IDENTIFIED

CHEMICAL BIOLOGY: Novel cross-link places streptide in new family

PRINCETON UNIVERSITY researchers have uncovered a new family of naturally occurring cyclic peptides (*Nat. Chem.* 2015, DOI: 10.1038/nchem.2237).

Cyclic peptides play many roles in bacterial biology, such as helping microbes communicate with one another. They're also of interest to science because some of them have antimicrobial activity.

In previous studies, French researchers discovered a short peptide released by *Streptococcus thermophilus*, a model bacterium often used in yogurt production. But they didn't determine a structure or biosynthesis mechanism for the peptide, which is thought to be part of the bacterium's communication system.



Streptide

Mohammad R. Seyedsayamdost, Kelsey R. Schramma, and Leah B. Bushin of Princeton have now obtained the structure via mass spectrometry and nuclear magnetic resonance. And they determined that the peptide, which they call streptide after its bacterium, contains a never-before-seen cross-link between the side chains of its tryptophan and one of its lysine residues. This novel cross-link makes streptide the first in a new family of peptides.

The researchers determined that streptide begins as a 30-member amino acid chain. A radical SAM (S-adenosylmethionine-cleaving) enzyme cyclizes the chain, forming the new cross-link. Afterward, the peptide is trimmed to a 9-mer.

"The radical SAM enzyme that makes the cross-link is very interesting," says Wilfred A. van der Donk, a chemistry professor at the University of Illinois, Urbana-Champaign, who studies macrocyclic peptides. "New cyclization strategies can represent powerful new methodology in the toolbox for making cyclic peptides, provided the enzyme has tolerance for different peptide sequences."

"Adding this chemotype to the bestiary of known, naturally occurring macrocyclic peptides is highly valuable," says Adrian Whitty, a chemistry professor at Boston University who studies synthetic macrocycles. Such new classes of naturally occurring macrocycles can help researchers design molecules with good pharmacological properties, he says.

There's still a lot of new chemistry to be discovered in the molecules produced by bacteria, Seyedsayamdost says, both with regard to the structure of the molecules and the enzymatic mechanisms by which they're made.—CELIA ARNAUD