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Cover Profile

Proton in a Confined Space: Structural Studies of $H^+\subset$Crypt-111 Iodide and Some Halogen-Bonded Derivatives


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Invited for the cover of this issue is the group of Giuseppe Resnati at the Politecnico di Milano. The image depicts proton cryptation by crypt-111, the smallest cryptand and an effective proton sponge. Read the full text of the article at 10.1002/chem.201701699.

What is the most significant result of this study?

The paper describes the single-crystal X-ray structure, the solid-state ^{15}N NMR spectra, and some modeling of $H^+\subset$crypt-111 iodide and four halogen-bonded adducts. The obtained results confirm the tendency of crypt-111 to induce unique characteristics in processes occurring within its cavity. X-ray data indicate that the encapsulated proton is covalently bonded to a single nitrogen atom and the proton is further involved in a network of intramolecular hydrogen bonds. ^{15}N solid-state NMR points to the magnetic equivalency of the two N atoms of crypt-111. Theoretical modeling confirms structural information from X-ray analyses and indicates that hopping of the caged proton between the two N atoms of the cage can occur in the halogen-bonded co-crystals. In contrast, this hopping does not take place in the pure $H^+\subset$crypt-111 iodide.

Who designed the cover?

Elena Amadio is a Master student in R. Gobetto's laboratory and has unique artistic attitudes. When seeing a Japanese watercolor picture of birds flying around a tree, she realized that a bird in a cage would be an eye-catching representation of a proton encapsulated in crypt-111. Claudia Resnati was recently awarded her Master degree in Architecture and Urban Planning at Politecnico di Milano and developed Elena Amadio's idea into different drafts. Some of them were more rigorous, others more fancy, and all of them were very intriguing. A poll during a Friday happy hour determined the version to be proposed for the cover.

What other topics are you working on at the moment?

Our interests are in self-assembly processes driven by halogen atoms. X-ray analyses, NMR techniques, and computer modeling are our preferred investigation tools. Our focus is on showing that halogen atoms close to electron-withdrawing residues can work as electrophilic sites and that they attractively interact with a variety of nucleophiles. We have introduced the term "halogen bond," now recommended by IUPAC, to designate these interactions and we are exploring their relevance in relation to material properties. More recently, we have extended our attention to self-assembly processes where the electrophilic site is an element of Groups 16, 15, or 14 of the periodic table, and we are showing that the respective interactions, namely chalcogen bonds, pnictogen bonds, and tetrel bonds, are informative tools in many fields where molecular recognition plays a role.