The rarely understood ammonium carbonate monohydrate

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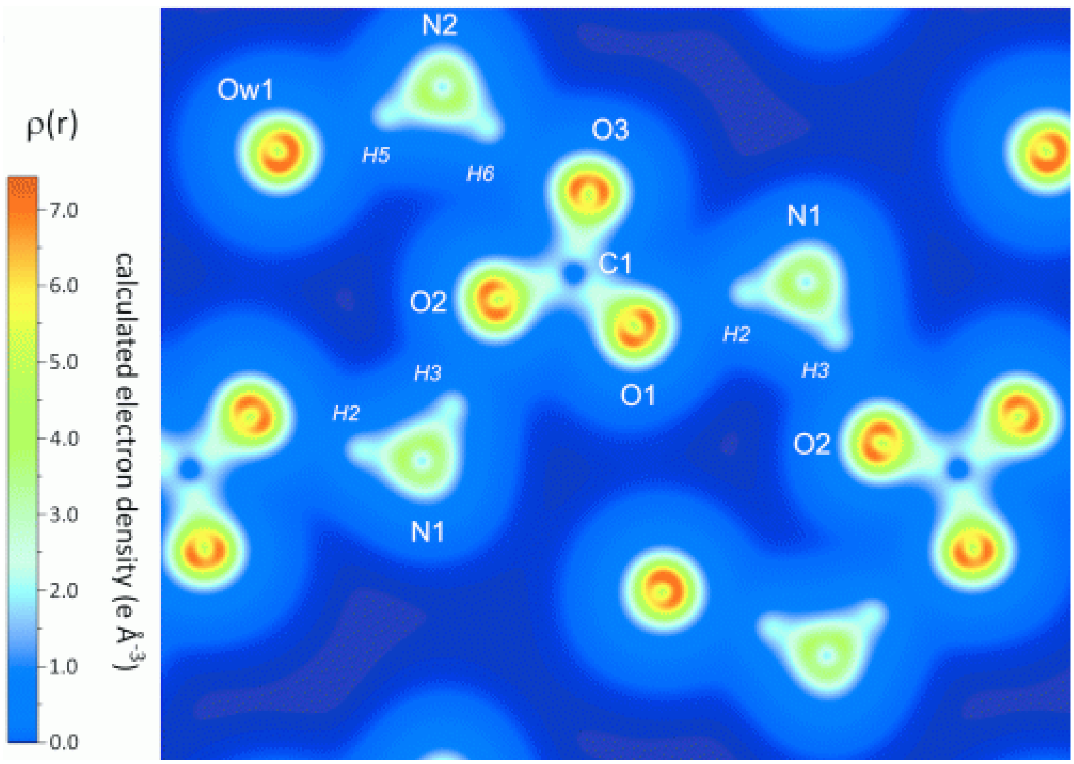

Electron density map of ammonium carbonate monohydrate. Credit: Fortes et al.

New structural studies of the superficially simple ammonium carbonate monohydrate could shed light on industrial processes, biochemistry and even the interstellar building blocks of life.

Researchers in Spain and the UK have used Laue single-crystal diffraction methods with pulsed neutron radiation at 10 and 100 Kelvin to obtain a crystal structure of ammonium carbonate monohydrate and have corroborated their findings with X-ray powder diffraction data obtained at 245 to 273 K, Raman spectra (80-263 K) and density functional theory calculations of the electronic structure and phonon spectrum.

Seemingly simple molecules are of fundamental interest as their apparent lack of complexity and limited number of atoms should make them more amenable to structural studies and reduce the size of the data stream that needs to be processed in computations of their properties. One such compound ammonium carbonate monohydrate, (NH4)2CO3.H2O, was first described by Sir Humphrey Davy in 1800 but despite its purported simplicity it remains something of an enigma, its shifting phases, thermal expansion and hydrogen bonds, giving even the most determined theoretical chemist problems in explaining the properties of the compound.

Dominic Fortes of the University of London and colleagues at University College London, the Instituto de Ciencia de Materiales de Madrid, Spain, the ISIS Facility at the Rutherford Appleton Laboratory in Didcot, UK and the University of Bristol, UK explain how this compound is, at its simplest a ternary system involving a carbon dioxide, an ammonia and a water unit. A trio important in industrial chemistry as well as in many biological reactions.

As the crystalline material, the compound exists in various forms although since its discovery there have been conflicting reports through the years regarding the correct composition of the solid. Even as recently as 1992, the tendency of phase mixtures to crystallize ambiguously is common and some researchers have questioned the veracity of the formula given for a commercially available product. A sample from one supplier tested by the researchers proved to be something entirely different - ammonium carbamate.

However, Fortes and colleagues suggest in a paper [Fortes et al. (2014). B70, 963-972; doi: 10.1107/S205252061402126X] that they have new definitive evidence of the nature of ammonium carbonate monohydrate. The team used Laue single-X-ray powder diffraction data measured from 245 to 273 K, Raman spectra measured from 80 to 263 K and an athermal zero-pressure calculation of the electronic structure and phonon spectrum carried out using density functional theory (DFT).

"We find no evidence of a phase transition between 10 and 273 K," the team reports, "above 273 K, however, the title compound transforms first to ammonium sesquicarbonate monohydrate and subsequently to ammonium bicarbonate."

The chemical cousins of the rather innocuous ammonium carbonate monohydrate, including the toxic ammonium oxalate and the explosive ammonium chlorate and ammonium nitrate have been much better studied despite their obvious drawbacks as useful laboratory reagents when compared to the rather innocuous ammonium carbonate monohydrate. It is curious, the team suggests, that there has been so little interest in the compound's structure and properties. This is also true given that carbon dioxide, ammonia and water are apparently so common in interstellar, cometary and planetary ices and may have a role to play in explaining cosmic chemistry and perhaps even the building blocks of life on Earth and putatively elsewhere in the universe.

"The next step is to measure other physical properties of the carbonate and related compounds," Fortes told us. "In due course, we'll do high-pressure experiments on ammonium carbonate to determine its compressibility and to look for high-pressure polymorphs."

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