The peculiar properties of molecules in cages

John Emsley

SOMETIMES a compound can be trapped inside another molecule rather like a ball in a cage. Organic chemists in the US who have looked at such compounds have found that they are held in place unexpectedly tightly, and are unable to move about freely. They believe that these cage compounds could one day be made to behave like liquid crystals.

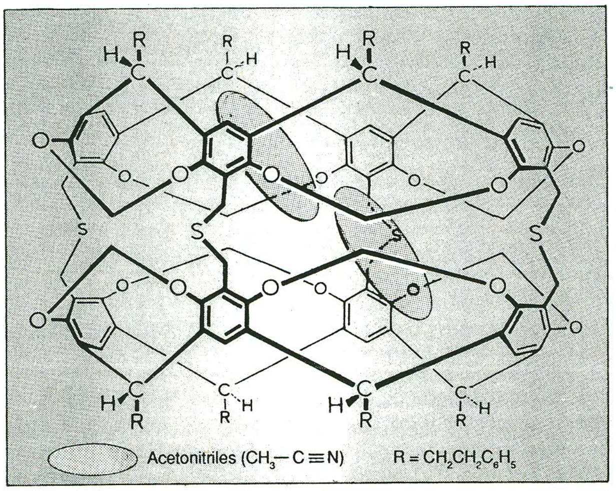
Donald Cram and his colleagues at the University of California, and Marco Vincenti of the Guido Donegani Institute at Novara, Italy, made seven new compounds in which one, or even two, "host" molecules, such as methanol (CH_3OH) or acetonitrile (CH_3CN), are trapped inside large "guest" molecules (*Journal of the Chemical Society: Chemical Communications*, p 1403).

Cram's group has been making cage molecules since 1985. Cages form in a reaction in which the two halves come together. In the process, a compound may be trapped. For example, when the two halves of a cage are joined in a solution such as acetonitrile or methanol, one or two of the solvent molecules may end up incarcerated.

Cram and his colleagues used the technique of nuclear magnetic resonance (NMR) spectroscopy to probe the inner secrets of the cages. The technique, which involves placing the cages in an intense magnetic field and subjecting them to radio waves, identifies the hydrogen atoms of the trapped molecules. The results reveal just how the prisoners are arranged. When two acetonitrile molecules are trapped, their CN parts are together at the host's equator, and their CH_3 groups in the temperate regions.

Cram's team found that acetonitrile molecules are not entirely stable in this arrangement. When the chemists heated the complex to 110 °C, one of the molecules escaped from the cage, probably through a hole at one of the poles. But the chemists found that they were unable to dislodge the remaining molecule, even by heating the cage at 215 °C for five days.

Cram believes he has an explanation. He believes that the first molecule is expelled only when it is struck by the other, rather like when two billiard balls collide. However, this mechanism no longer operates when the second molecule is left alone. It simply cannot accumulate enough energy to escape.



Caged compounds: one trapped molecule can gain enough energy to escape only if it cannons off the other

Cram and his colleagues find that when the trapped molecules are both methanols, even the billiard ball trick won't allow either to escape. Heating the cage at 110 °C for five days has no effect. Cram believes that methanol molecules stay together because a hydrogen bond connects their oxygen atoms. However, it is a peculiar hydrogen bond. When the chemists take an NMR spectrum, the signal that this hydrogen atom creates resonates in a different part of the spectrum from any other hydrogen bond.

Cram's group hopes to exploit the ability of host molecules to control their guests in order to make compounds that behave like liquid crystals. At the moment, the chemists are investigating host molecules in which the guest responds to visible light which is transmitted through the cage.

If the trapped molecules are polar—that is, there is a separation of positive and negative charge within the molecule—and an external electric field is applied, they will line up in the same direction temporarily. In this regular arrangement, they will diffract light in a regular pattern. When the electric field is removed, however, the molecules will relax into random positions and scatter light in all directions.

Inorganic chemists have also been encapsulating other chemicals, including chloride, bromide, iodide and carbonate ions. Achim Muller and his colleagues at the University of Bielefeld have discovered that vanadium and oxygen atoms will form "spherical cluster shells" which hold negatively charged atoms captive. Muller points out that this is remarkable because the shells themselves are negatively charged and should repel their captives.

Muller and his colleagues made a typical shell by treating a solution of caesium vanadate ($CsVO_3$) with hydrazinium hydroxide (N_2H_5OH) at 95 °C for an hour. To the dark brown solution they then added hydrobromic acid, and left the mixture for a further hour-and-a-half at the same temperature. On cooling, black crystals precipitated out with the formula $Cs_9(H_4V_{18}O_{42}Br).12H_2O$.

Muller's group analysed these using the techniques of infrared spectroscopy and X-ray diffraction. These revealed that the bromide ion was inside the ball. The chemists have discovered that the same cage will also trap a larger iodide ion. □

Scientists almost make water freeze at freezing point

IF ALCOHOL is added to pure water, it can raise the temperature at which it freezes to almost 0 °C, according to team of chemists in Israel. Surprisingly, pure water must sometimes be cooled to −40 °C before it turns to ice, and water in clouds must drop below −10 °C. Understanding how to freeze pure water at a higher temperature will help efforts to force clouds to rain and stop frost damage to crops.

Alcohols are used as antifreezes, to lower the temperature at which ice forms. But they can also increase the temperature at which ice forms. According to Meir Lahav of the Weizmann Institute of Science in Rehovot: "We can get to between −1 °C and 0 °C with some alcohols. The alcohol acts as a catalyst to induce freezing." (*Science*, 16 November, p 973).

Lahav and his colleagues added a single layer of alcohol to the surface of water drops and cooled them. They found that the alcohol encouraged ice to form earlier. The researchers used X-rays to analyse the process and concluded that the alcohol molecules form ice-like hexagons. The hexagons acted as a template, or seed, for the formation of ice crystals, and set off a chain reaction in the liquid.

In the past, efforts to force clouds to drop their water by "seeding" them with silver iodide failed. According to Lahav, silver iodide will induce freezing only at −8 °C, while many clouds carry water at temperatures closer to 0 °C. At these temperatures, he says, alcohols could catalyse the formation of ice. If it does prove practicable to seed clouds with alcohol, this might allow countries some control over their own rainfall.

Some bacteria are blamed for widespread frost damage to crops. The bacteria raise the temperature at which ice forms, creating frost on nights when there would otherwise be none. No one knows how the bacteria make frost, but Lahav suspects that a membrane on the surface of a bacterium may do the same job as a layer of alcohol.

Lahav and his colleagues have analysed ice formation with a technique known as grazing incidence X-ray diffraction. The technique is usually applied to three-dimensional crystals but Lahav has extended the idea to two-dimensional layers. The researchers directed X-rays at the alcohol layer so that they just skimmed the surface and were reflected. The rows of atoms generated a pattern of X-rays which revealed the structure of the layer.

Alcohol molecules consist of a chain of carbon atoms with a hydroxide (OH) tail. Lahav found that the hydroxide end of six alcohol molecules nestled in a hexagon the same shape as the hexagons in a layer of ice. This catalysed the process of ice formation.

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