

Catenanes, Rotaxanes, and Interpenetrating Nets: A New Class of Molecules and Solids

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There are two types of molecules with parts which are mechanically linked and not chemically bonded. A catenane is two or more macrocycles threaded through one another, and a rotaxane is a long chain threaded through a macrocycle [1]. An analogous type of solid is an interpenetrating lattice. In most inorganic crystals, it is possible to travel from one point in a network of atoms to any other point via bonds. There are a few structures, however, that have two or more interpenetrating nets which, like the catenanes, are linked only mechanically [2].

Frisch and Wasserman [3] first proposed the synthesis of mechanically linked molecules. They used space-filling models to estimate the number of carbons needed in a macrocycle for it to allow another molecule to thread it. Wasserman created the first catenane [4] by a method called statistical threading, in which he self-reacted $\text{CH}_3\text{CH}_2\text{O}_2\text{C}(\text{CH}_2)_{32}\text{CO}_2\text{CH}_2\text{CH}_3$ in a solution of the cyclic $\text{C}_{34}\text{H}_{63}\text{D}_5$, and detected the 1% of the acyloin produced which had threaded through the ring.

There have been attempts at improving the yield of statistical threading. Harrison [5] attached a macrocycle to a column and, after 70 treatments with a solution containing reagents to create a long chain macrocycle with ends capped by bulky functional groups, obtained a 6% yield of the resulting rotaxane. Agam and Zilkha [6] attempted to produce a catenane by cyclizing the long chain of a rotaxane. The catenane was obtained from the pure rotaxane in 14% yield.

Stoddart and coworkers [7] have been using electron donor-acceptor interactions to encourage the threading of the macrocycles to make rotaxanes and catenanes. They have, for example, created a catenane with the macrocycles cyclobis(paraquat-*p*-phenylene) and bispara-phenylene-34-crown-10 with a 70% yield. The association of these two rings is mainly due to electron exchange between the phenyl groups of the crown and the cationic pyridinium groups of the paraquat ring.

Sauvage, Dietrich-Buchecker, and coworkers [8] have used transition metal templates to synthesize catenanes. Using Cu as the templating metal, they locked two diphenylphenanthrolines around each other, then used a long polyether to complete the macrocycles and removed the Cu with $(\text{CH}_3)_4\text{NCN}$ to produce the catenane (Figure 1) in 27% yield. Using similar techniques, they have produced a 3-catenane [9], which has 3 linked rings, and a molecular trefoil knot [10].

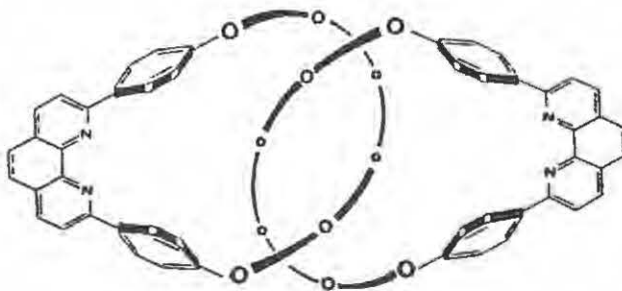


Figure 1.

A few inorganic crystalline compounds have layers which consist of two interpenetrating nets. Hittorf's phosphorus [11] has layers of perpendicular tubes, two tubes thick, in which every tube is only connected to every other perpendicular tube, but not the parallel tube next to itself. In $\text{AgC}(\text{CN})_3$ [12], the silver is three-coordinate, and the atoms are laid out in a puckered hexagonal pattern. Two of these nets are interwoven to produce one layer of the crystal.

Most three-dimensional interpenetrating frameworks are based the diamond net. The earliest known of these structures is cuprite, which was determined by Bragg [13]. Cuprite consists of two diamond nets interwoven (Figure 2).

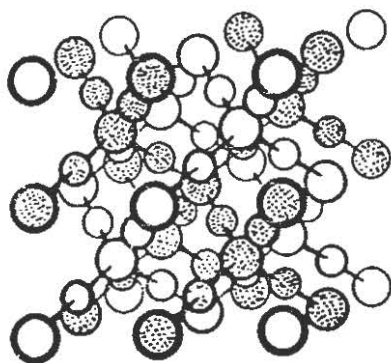


Figure 2.

Iwamoto and coworkers [14] proposed that cuprite has interpenetrating nets because the cavity in a single diamond net is too large. Using $\text{Cd}(\text{CN})_2$, which, like $\text{Zn}(\text{CN})_2$, crystallizes in the cuprite structure [15,16], they created a clathrate, $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$, which has a single diamond framework with a CCl_4 molecule in each cavity. These results imply that interpenetration occurs when the preferred crystal structure of the compound leaves large empty spaces in the crystal. This conclusion is supported by the structure of $[\text{N}(\text{CH}_3)_4][\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}(\text{CN})_4]$ [16], which has a single diamond net with the cation in the cavity, and by the structure of bis(adiponitrilo)copper(I) nitrate [17], which has a very large cavity, due to the length of the adiponitrilo ligand, that allows six interpenetrating nets.

There are very few examples of non-diamond interpenetrating lattices. Hoskins and coworkers [18] recently determined the structure of $\text{Zn}(4,4'\text{-bipy})_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$, which consists of two perpendicular interpenetrating stacks of nearly square grids.

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