

Towards Molecular Machines

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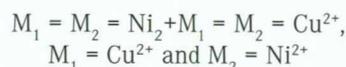
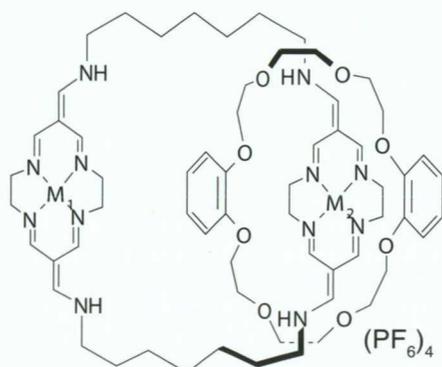
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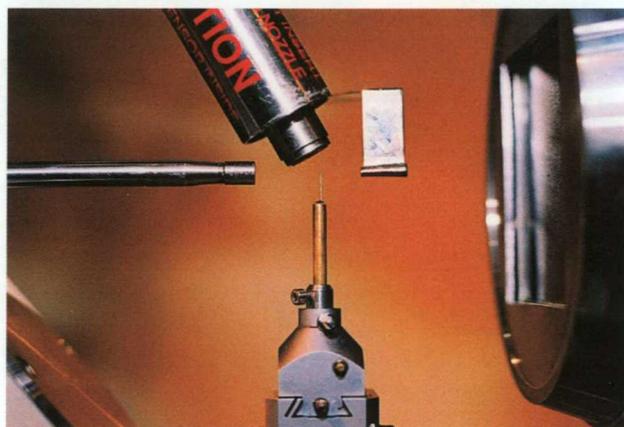
Nano-scale devices based on molecular machines could play a major role in the future of electronics, medicine and communications. Generating molecules with parts that can move like tiny "switches" is a step in the right direction

The term "molecular machines" refers to complex macromolecules (or biomacromolecules) that consume energy in order to perform certain specific actions. The problem of constructing such molecular machines was first discussed by Richard P. Feynman, Nobel Laureate in Physics, in his famous lecture entitled "There is Plenty of Room at the Bottom" delivered to a Meeting of the American Society of Physics in 1959: "What are the possibilities of constructing molecular-scale mechanical machines?... An internal combustion engine of molecular size is impossible. Other chemical reactions, liberating energy when cold, can be used instead.... Lubrication might

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[2]catenane ring components can not be separated, but one of them is able to rotate with respect to the other



Krzysztof Kalifiski

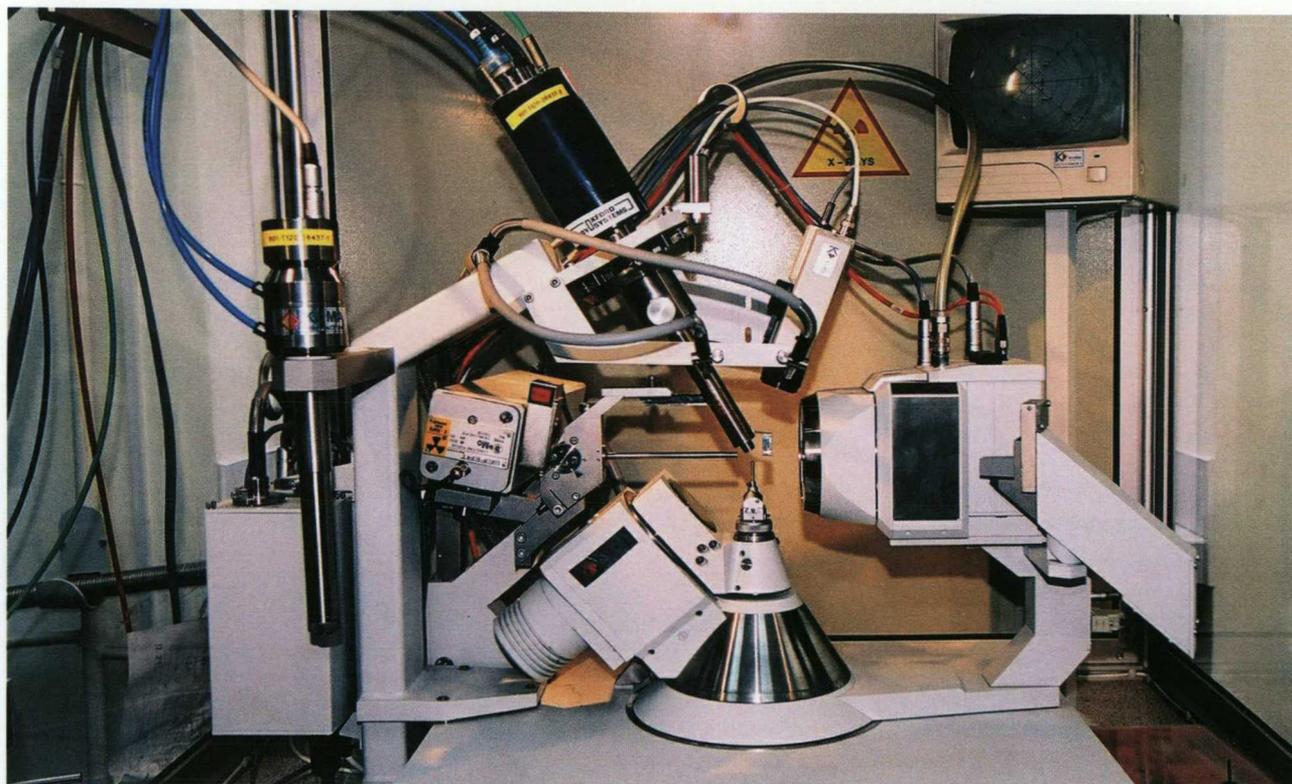
A tiny crystal on the top of the diffractometer needle is composed of several million molecules

not be necessary; bearings could run dry; they would not run hot because heat escapes from such a small device very rapidly...". This vision is indeed slowly becoming a reality: today a search on Google for "molecular machines" (or its derivatives "protein machines" and "molecular motors") turns up over 60,000 hits.

Like for macroscopic machines, the energy to make molecular machines work can be supplied as light, electrical energy, or chemical energy. Due to the tiny scale involved, mechanical movement in a molecular machine is usually monitored by spectroscopic techniques (particularly NMR, absorption and emission spectra) and electrochemical methods. Nano-scale devices based on molecular machines could play a major role in the future of electronics, medicine and communications. For example, electronic technology has nowadays managed to reduce the room-size computers of the early 1950s to a few silicon chips. And even far smaller devices are now being made, slinging herds of atoms at a crystal surface to build up wires and components one tenth the width of a fine hair. Nonetheless, computers based on the interactions of individual molecules with one another still hold the potential to be orders of magnitude smaller, faster, and more efficient than those based on semiconductor technology. Successful examples of molecular systems capable of rectification, wiring, memory storage and switching have already been demonstrated.

In the last decade it has proven possible to design and construct molecular-scale systems, based on pseudorotaxane, rotaxane and catenane structures, where the component parts display changes in their relative positions as a consequence of an external stimulus - e.g. the ap-

Reinventing the wheel



Krzysztof Kallinski

The Kuma KM4CCD diffractometer, the instrument which enables us to study the structure of crystals and molecules

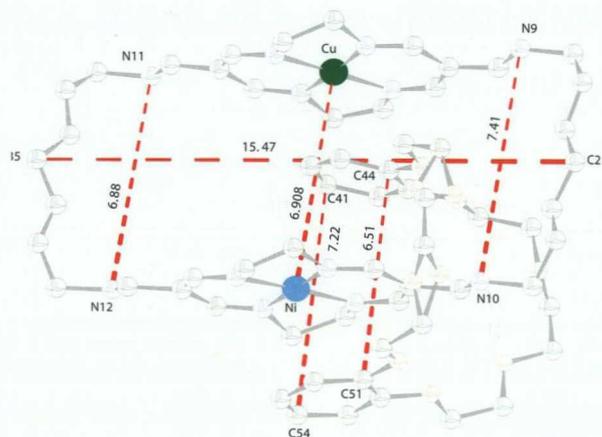
plied potential. Note that we are discussing motion that occurs within the bounds of a single molecule!

“Moving parts” of nano-scale machines

One species that is interesting from the standpoint of molecular-level machines is the double-ringed structure called [2] catenane, as it can be possible to make one of its ring components rotate with respect to the other. At the Institute of Organic Chemistry of the Polish Academy of Sciences in Warszawa, we have synthesized the first dinuclear bismacrocylic transition metal complexes exhibiting potential-driven intramolecular motion of the interlocked crown ether unit. These molecules exhibit motion reminiscent of the moving parts in macroscopic machines. Since both of the coordinated ions are identical, the translocation of the crown ether moiety from one site to the other results in the same catenane arrangement. However, intertwining of the dibenzo-24-crown-8 with a heterodinuclear bismacrocylic complex leads to two possible arrangements, where the π -electron-rich benzene rings are located in the vicinity of either the copper or the nickel-complexing macrocycle, depending on the oxidation state of the coordinated ions.

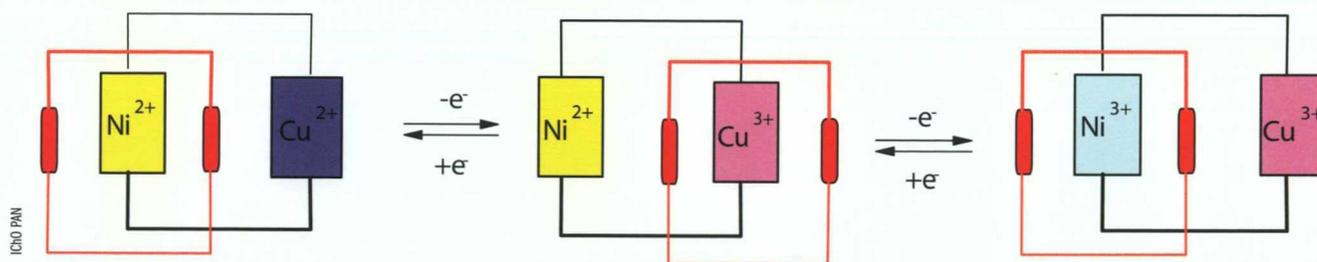
These new compounds raise new questions about property-structure relationships, and enable us to envision

new classes of materials. Their properties are likely to be novel and useful, reflecting the effects of the great flexibility that results from tunable weak and strong interactions. Strength and deformability suggest applications in such fields as art, information storage and security, and in the design of switches and other parts for molecular machines. One of the greatest advantages of our compounds is the fact that their properties can easily be fine-



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The structure of CuNi-catenane (distances in Å; 1 Å=10⁻¹⁰m)



Relocations of the macrocyclic crown ether ring (red) triggered by the application of an appropriate potential

-tuned by changing the metal ions, the lengths of the linkers, or by varying the substituents.

X-ray structure of CuNi-catenane cation

The crown ether and the grand bis-azamacrocyclic ring in CuNi-catenane form a sandwich-like structure in such a way that one of the crown ether aromatic rings is located between the two metal-coordinated macrocyclic rings. The second aromatic ring is located almost parallel to the previous one, outside the two linked macrocycles. Thus, one aromatic ring of the crown ether is interlocked between the two macrocycles, and one of the macrocyclic rings is positioned between the two aromatic rings of the crown ether.

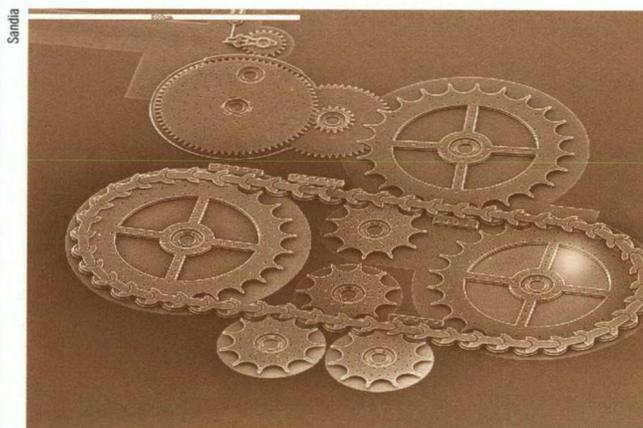
Intramolecular movement

Electrochemical studies have revealed a very interesting feature of the heteronuclear CuNi-catenane system: a splitting of Ni oxidation signals as a function of time and temperature. Such behavior may be understood by assuming the formation of two different populations of Ni^{II} centers. Each of them has a different local microenvironment around Ni^{II}, although this happens within the same molecule. The donor properties of the first group of the Ni^{II} centers is affected by the proximity of the electron-rich crown ether, while the other group is not. At lower frequencies, upon oxidation of Cu^{II} to Cu^{III}, the crown ether unit has enough time to relocate from its initial position close to the Ni^{II} center towards the more positively charged Cu^{III} center. As a result of this relocation, the Ni^{II} to Ni^{III} oxidation process appears at more positive potential since it is free from the influence of the π -electron rich crown ether. However, when the timescale is decreased or the temperature lowered, the movement of the crown ether unit is too slow, and in a fraction of the molecules the Ni^{II} cations remain weakly interacting with the crown ether, giving rise to the splitting of peaks. The most remarkable feature of this new catenane is that each electrochemical step triggers a rearrangement of the compound.

These electrochemically switched relocations reflect a shuttle-like behavior triggered by the application of an appropriate potential. We want to stress the importance of a good understanding of weak interactions in the design of such supramolecular entities. This ability of our catenanes to undergo a switchable and easily tunable mechanical movements, as illustrated in this article, seems to represent an interesting step towards creating molecular machinery. ■

Further reading:

- Molecular Switches*. (2001). Weinheim: B. L. Feringa, Wiley-VCH GmbH
 Raehm L, Sauvage J, P. (2001). Molecular Machines and Motors. *Struct. and Bonding* 99, 55.
 Korybut-Daszkiewicz B., Więckowska A, Bilewicz R., Domagała S., Woźniak K., (2001). Novel [2] Catenane Structures Introducing Communication Between Transition Metal Centers via $\pi\cdots\pi$ Interactions, *J. Am. Chem. Soc.* 123, 9356.
 B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak (2004). An Electrochemically-Controlled Molecular Shuttle, *Angew. Chem. Int. Ed.* 43, 1668; *Angew. Chem.*, 116, 1700.



The distance between chain link centers in this microchain created by Sandia is 50 microns - less than the width of the human hair. Still, molecular machines could be orders of magnitude smaller and more efficient