Molecular machines based on transition metal complexes : Rotaxanes and catenanes[†]

U. C. Agrawal[a]* and H. L. Nigam[b]

[a]C1 295A, Indira Nagar, Kanpur-208 026, Uttar Pradesh, India

[b]"Sneh Lok", B-332-B, Sector-A, Sitapur Road Yojana, Lucknow-226 020, Uttar Pradesh, India

Abstract : Human beings since ambiguity have been persistently designing mechanical devices which can perform certain functions useful to them. Recently along with this endeavour, emphasis has also been directed towards miniaturizing these devices leading to the possibility of constructing machines on nanoscale level, but for the past four decades it has been realized that miniaturization has reached its practical and fundamentals limit. Owing to the progress made to better understanding of the operation and mechanism of natural molecular machines of the biological world, it has however become possible to artificially design simple prototype of such device using molecular machines which provide atom-by-atom (bottom-up) approach towards the construction of microdevices.

These imitate biological systems which play essential roles in a wide variety of biological events particularly those related to the activities of cells and realize specific functions through their reponses of mechanical motions. Such studies have led to an enormous interest not only in basic research but also in the growth of nanosciences, in particular, towards designing molecular machines using "bottom-up" rather than 'top-down' approach. These are based on the synthesis of various molecular rotaxanes, catenanes, rotors, and other systems. In synthesizing the latter, various systems have been proposed based on redox reactions (electro-chemical; chemical) involving in particular the formations of dissociation of transition metal complexes. It will not be out of place to refer that a very large volume of work has also been carried out using organic and inorganic molecules.

In this paper attempts have been made to describe a few examples of Cu^I, Cu^{II}, Ru^{II}, Zn^{II} and other metal complexes using electrochemical, chemical and light-driven molecular motions. However the review will not be a complete one in any sense because of the very large and fast work going on in this area.

Keywords : Endowment lecture, catenanes, molecular machines, rotaxanes.

It is so kind of the Indian Chemical Society to consider me as a candidate worthy enouth to deliver Acharya Prafulla Chandra Ray Memorial Lecture before this august body. I thank the President, Secretary and members of the committee of the Society. My heart-felt thanks are also to the respected members and guests present here. Prior to starting the subject matter of my presentation, I will take a few minutes to pay my homage to Acharya Prafulla Chandra Ray [Khulna's (now in Bangladesh) boy]. He studied in Calcutta and Edinburgh, served as Professor in Presidency College and Calcutta University. Although, to say anything about him is like showing a candle to the sun but I will make an attempt.

When I received the information from the President for being selected to give this prestigious lecture, I was overjoyed and felt as if Acharya Ray has tapped my back in appreciation of my little contribution in chemistry (before my retirement). The emotions raised in me to the limit of "tears in happiness". I am not sure how effective my contribution was, so as to leave a little impact on the global chemist's minds, but an indirect association with Acharya's name in itself is a great satisfaction to me. Although he is not with us now, but his spirit is always with us to guide. I have an intense conviction that a Guru

like him seldom comes to this world. To me, he is like an incarnation of Ma-Saraswati and any word in his praise will look infinitesimal. Besides he being an ideal teacher, a great scientific researcher and inspirer for critical thinking, he was a great social reformer and had a keen desire to help the needy and that too in a period of our enslavement (1861-1944). Amazingly he was so fearless that at a time when a common man was scared of opening his mouth to give vent to his feelings in public, he always aspired emancipation of his motherland (India). He wanted India to be a potential leader on social, political and economical fronts too – his dream never fulfilled in his lifetime. I wish if he would have lived a few years more to see his dream to come true. More surprising was his intense love for literature – a keen lover of Shakespeare, Michael, Emerson and Carlyle write-ups. The filial intensity towards literature can be gauged by his often said statement. "I became a chemist only by accident". He has a multidmensional personality – Scientific, Social, Political, Literary Scholarly – with unsurpassable and not just tangential love of the fields.

Another uncommon track of his life, inspiring to me, is his life of austerity along with always placing principles and ideals much above his material interests. "His wealth lies in the smallness of his wants". Whatever penny he saved throughout his life, he donated it to the public in order to help to raise the human values e.g. scholarships, awards etc.

He believed (1) in the dissipation of knowledge among the most persons and that is why he started the Chemical Society of India and (2) the application of Science in Industry and that is why he started Bengal Chemicals and Pharmaceuticals Limited. All the above characteristics were quoed by Professor Thorpe in his statement published in 'Nature' :

"Her (India) elevation will not come in Sir Prafulla Chandra Ray's time. A small spaceman in feeble health and a confirmed dyspeptic he will be spending in her (India's) service, but the memories of these services will survive".

In essence I describe him "A *Sanatan Purush*" – ever lived – presently living and ever living, though not in body but in spirits – "A Rare Combination of all".

As a duty of mine, in his honour I must select a topic which should be multidimensional, as he was a combination of science and engineering leading towards industry

in the service of humanity. This is a topic towards which I can not do the real justice in a short time that I have at my disposal, though my attempt to expose the topic will not be intense but it will be just tangential.

Topic is "**Molecular machines – Role of transition metals (Cu and Ru)**" which I shall be presenting here.

The subject matter covered in this topic has such a vast sky-line that even a tangential touch of its initial development only will look limitless. It will not be possible for me to over-view it completely and effectively. I will therefore present a cursory-view of development of only a small portion of it. As I have told a few minutes before that the subject matter's beauty lies in its encompassing not only the salient features of Chemistry and Physics but those of engineering and medicine too. As a result, the designing of the molecular machines that form assemblies with signal triggered functions has become a challenging area of research for the past couple of decades. Novel synthetic-routes for complex molecules have to be desired for putting together the respective components in a way to retain their six external and one internal degrees of freedom which sets deliberately a certain part into motion with respect to the stationary parts. In this manner the latter motion defines the function of the assembly programmable into the molecular blue print in order to carry out the designed mechanical work. For achieving it one has to be well-versed with the various theories and structure-property relationships akin to the biological systems – Nature's invaluable gift to us as Molecular Machines.

We define a Macromolecular Machine as one that is densely packed complex assembly having many components acting together in a synchronized way to transfer motion, force, or energy from one part of it to another. It is designed to accomplice a particular task or/and to acquire process or/and to store information. Depending on the nature of function or purpose to use, the machine can be very large or very small. From the early fifties there is continuing effort to miniaturize all the large macro-constructs by shrinking them to the micro-level by the so called "Top-down" approach. But the physical limits arising out primarily due to quantum effects or Brownian motion in solution put a limit to this approach. A good example of it is that of integrated circuits. In this desperate situation, Feynmann's lecture at the American Physical Society in 1959 was a great help. He argued that there is plenty of room at the bottom and the principles

of physics do not speak against the possibility of manoeuvering things 'Atom-by-Atom' and so one can start from atoms to construct bigger systems using 'Bottom-up' approach (Fig. 1).
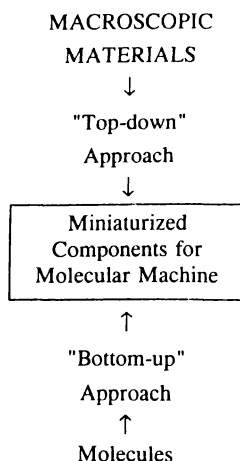
MACROSCOPIC

MATERIALS

↓

"Top-down"

Approach

↓

| Miniaturized |
| Components for |
| Molecular Machine |

↑

"Bottom-up"

Approach

↑

Molecules

Fig. 1. "Top-down" and "Bottom-up" approaches to molecular machines.

Although this 'Bottom-up' approach where one starts with individual atoms and builds from there, began to take shape in 1970; but the chemists were not happy with the unmanageable atoms, having no shape and no tendency to exist in free state. They initiated these projects with molecules which have a certain shape, and are stable. Furthermore, most of the chemical processes deal with molecules. So the preference went in favour of molecules as an alternative to Feynmann's atoms for self-assembling in order to make larger structures by "Bottom-up" approach. In this process further support came from nature which too starts from molecules to build complex biomolecules acting as molecular machines in the material basis of life. In these systems inside non-isotropic cells most of the cellular functions like translocation of organelles from one part of it to another, maintenance of voltage across the membranes, etc. all involve directional movements and transport of chemical species. Processes such as replications, transcriptions are encoded in the linear biopolymers which are read and copied. To overcome the randomizing effects due to Brownian motion in solution, and to carry out the directional processes inside the cells, the latter molecules (biopolymers etc.) behave like molecular machines empowered by external chemical energies which get converted into molecular work. However these bio-processes are extremely complicated and one cannot think of mimicking them in the present

state of development. But one can at least "Tame" their basic principles and adopt them while constructing crude molecular machines using "Bottom-up" approach. This is, in fact what the present day chemists are following while constructing artificial molecular machines.

During the past 10-15 years, a large number of multi-component dynamic systems both in solution and in solid state have been devised and put to use in very initial stage of molecular machines. In all these systems, motions of various components have been controlled by some external stimulii without fail. We refer these systems as molecular machines. The motions in them are accomplished either electronically or by nuclear rearrangement. These motions are characterized by the (1) kinds of energy-input, (2) types of motion (linear, gliding, rotational, oscillatory, etc., (3) types of monitoring the operation, (4) types of processes (cyclic, etc.) carried out by them, (5) types of performed functions (It should be noted here that despite their external stimulus, the machine is also always accompanied by the partial conversion of free energy of reaction into heat). Another distinguishing feature of macro-systems from micro-systems is that in the former case, the equations of motion are governed by inertial terms (mass-related) and one applies only one directional force for moving the component. In micro-systems, inertial and directional forces do not play any important role at all. On the contrary, viscous forces depending on the surface area dominate in solution. Analogous to macro-system one can not give one "push off" to a component for its directional movement, but the latter's motion are determined by the net forces acting on it at that particular instant irrespective of their being externally applied, viscous, random thermal fluctuations (Brownian) forces.

From the preceding discussion one implies that in the artificial molecular machines, mechanical work can be obtained through the controlled motion of some chosen component/s occurring within the molecule. These motions can be controlled either by external stimulii or by the arrangement of the components in the molecule (Template effect), by redox properties of some part of the system, non-interacting forces (like pH changes, π-π interactions, etc.) within various system or/and by varying the geometries of the components, etc. Consequently one must have within the molecule one stationary part and one mobile part which will move relative to the stationary part either linearly, circularly or oscillatory,

etc. In most machines studied so far, the mobile and the stationary parts are held together initially by non-covalent interactions and in transition metal complexes by covalent forces. This is followed by triggering the motion in the system by destroying the initial interactions or by changing the oxidation state of the metal ion. It can be achieved electrochemically, chemically or photochemically. One can annul this changeover by opposite redox, photochemical inputs, thus promoting a reverse mechanical movement leading back to its original state (cyclic process).

In all the artificial machines, both the organic and the inorganic molecules (supramolecules) have been used. In transition metal complex - containing micro-constructs, threaded or interlocking rings are ideally suited. This is

because a large amplitude motion like translocation of the metals in a linear fashion or in rotatory fashion can be envisaged without breaking or damaging the chemical structure of the system. Some of frame works which obey this principle, are shown in Fig. 2. Along with this there names are also written.

As illustrated in the Fig. 2, rotaxanes are dumbell shaped molecules (axis = linear molecules) threaded in a macro-cyclic ring (rings are usually crown ethers of different sizes). On both ends of the axis of rotaxanes, there are bulky groups called stoppers. Rotaxanes without stoppers are known as pseudo-rotaxanes. Since there are two components (axis + ring), these rotaxanes are referred as [2]-rotaxanes. If $(n - 1)$ such axes are linked together with one ring going along all the length of axis, it is
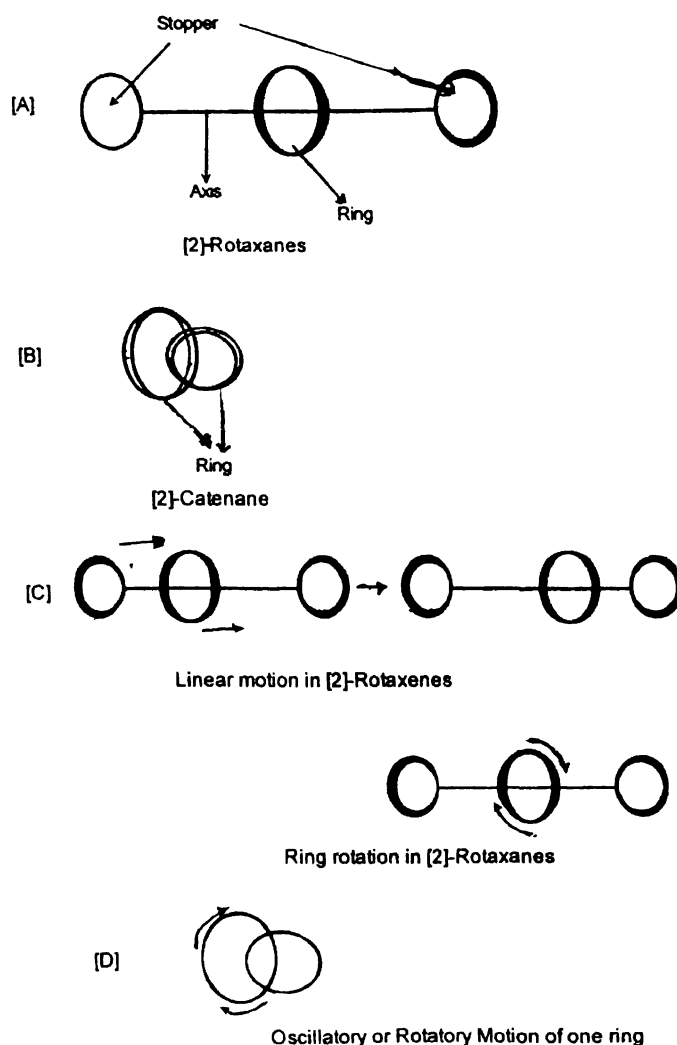

Fig. 2. Various frameworks used in molecular machines. Their names and motions.

named as [n]-rotaxanes. On the axis of [2]-rotaxanes, there are two recognition sites (where interaction takes place with one recognition site), present on the ring. If these two recognition sites on the axis are identical, such rotaxanes are known as (degenerate rotaxanes). In case these are different, then non-equivalent rotaxanes. Similarly one has [2]-catenanes, where two rings are interlocked. In case there are n-rings which are interlocked, then the system is referred as [n]-catenanes. In catenanes, one of the two ring, contains two recognition sites (usually stationary) – while the mobile ring has one recognition site (Fig. 2).

Both rotaxanes and catenanes are appealing systems for the construction of molecular machines in which interactions like (1) electronic donor/acceptor, (2) hydrogen bonding, (3) hydrophobic/hydrophilic character, (4) π-π stacking non-covalent or coulombic force, (5) metal/ ligand interaction, etc. keep the components together. These interactions are also responsible for the efficiency of their template directed synthesis in order to cause controllable mechanical movements. The non-covalent interactions are modulated by some external stimulii like electro-chemical, chemical or spectral forces. In both rotaxanes and catenanes, the conformational changes are induced by switching off/on of one of the two recognition sites. It shoud be noted that in both systems threading of axis and threading of ring inside another ring is a necessary requirement of the system for their synthesis. Many complexes of organic cyclic hosts e.g. donor/acceptor complexes, transition metal complexes, crown ether complexes, etc. have been used for rotaxanes and catenanes. Below we will survey very briefly the molecular machines based on transition metal complexes.

It will be impossible to cover all the rotaxanes and catenanes described so far in the literature in such a short period of available time because of the large volume of work already done. We will take up only those rotaxanes and catenanes that are based on copper and ruthenium complexes as illustrative examples of molecular machines.

(1) Copper complexes based rotaxanes and catenanes in motion (induced electrochemically)

(A$_1$) Copper complexes based rotaxanes in gliding motion :

Among the first row transition metals, copper(I) and copper(II) ions exhibit markedly different stereochemistries which provide a force sufficient for setting our system in motion. Roughly copper(I) prefers to have a tetrahedral geometry with CN = 4, while copper(II) ion, square pyramidal or trigonal bipyramidal with CN = 5, or octahedral with CN = 6. Thus if one switches alternately from Cu^I to Cu^{II}, one induces changes in the complexes favourable to the corresponding oxidation state of copper. In rotaxanes, the ring component, usually a crown ether, contains a bipyridyl unit (bidentate ligand) is allowed to translate along the rotaxanes's axis threaded through the ring. The axis component (usually a long linear molecule) has two different complexing sites linked in the linear molecule. Out of these one is usually a bidentate (e.g. bipyridyl or phenanthroline) while the other, a tridentate (e.g. terpyridyl). This whole composite system (viz. rotaxane) functions in such a way that a coordination No. 4 using two bidentate ligand (one each on ring and axis) with a tetrahedral geometry around Cu^I is obtained when some Cu^I salt interacts with this rotaxane. This complex formation also keeps the axis and the ring together at one place (Fig. 3a$_1$). On (electrochemically) oxidation of Cu^I to Cu^{II} a movement is induced and CN = 5 with trigonal bipyramidal geometry is obtained around Cu^{II} using one bipyradyl unit on ring + one terpyradyl unit on axis (Fig. 3a$_2$). In this manner, a change in oxidation state of copper from +1 to +2 induces a movement of the ring along the axis of rotaxane. This movement can be electrochemically monitored (usually by CV) (Δr of the process $\approx$ 30 Å). This switching on the rotaxanes axis can be carried out alternately from Cu^I to Cu^{II} oxidation for forward movement and Cu^{II} to Cu^I reduction for back movement.

We would like to emphasize here that in the conversion process of Cu^I to Cu^{II} and back from Cu^{II} to Cu^I via whether there is first fully demetallation in the Cu^I complex followed by oxidation to Cu^{II} and simultaneously complexation is not very clear. Most probably the chances are that various intra-molecular reactions involving several elementary association/dissociation reactions take place in this process.

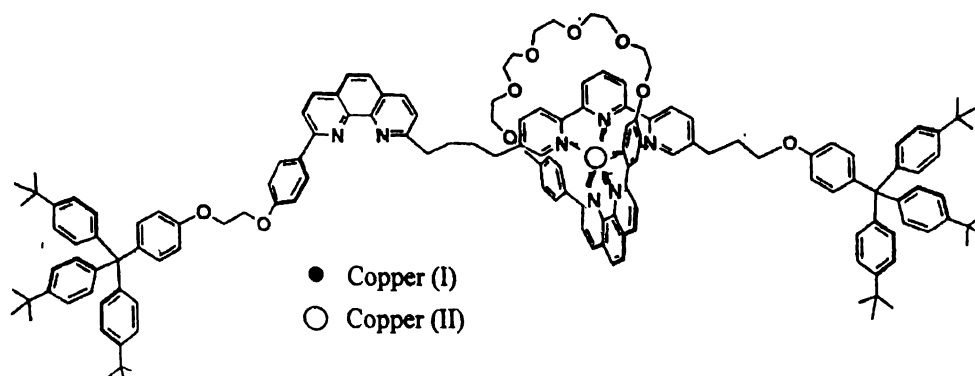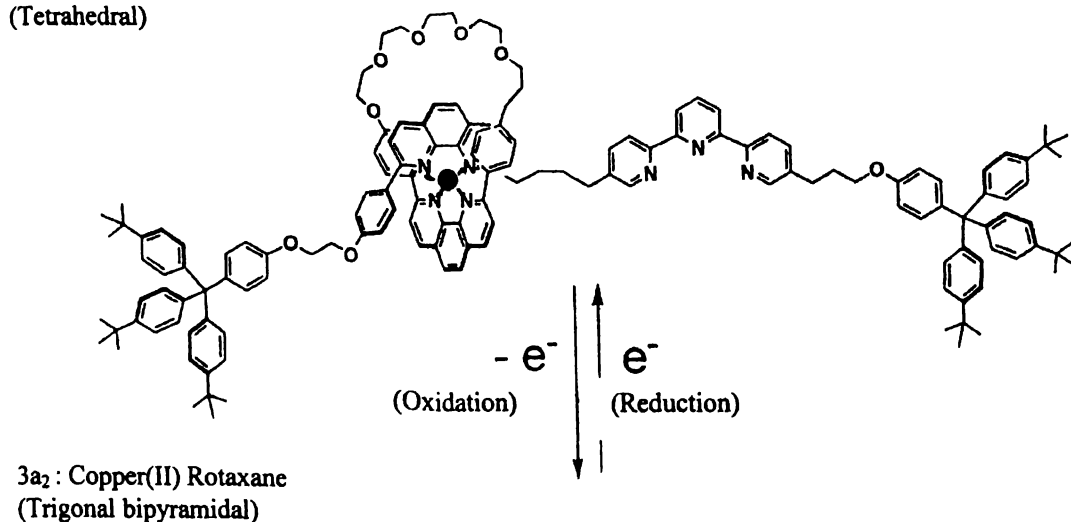*(A$_2$) Copper complexes based – rotaxanes in pirouetting motion of ring on the rotaxane axis :*

3a₁: Copper(I) Rotaxane
(Tetrahedral)

3a₂ : Copper(II) Rotaxane
(Trigonal bipyramidal)

- e⁻   e⁻
(Oxidation) (Reduction)

● Copper (I)
○ Copper (II)

Fig. 3. Copper(I) rotaxane (4-coordinate) and copper(II) (5-coordinate).

Besides the above gliding motion of the ring on the rotaxane axis another type of motion viz. pirouetting of the ring around the axis of the rotaxane can also be achieved electrochemically because of the driving force based on different geometrical preferences for Cu^I and Cu^{II} (Fig. 4). In this system, the ring component of rotaxane has two coordinating sites - one bidentate (e.g. phenan. or bipy.) and another, a tridentate (terpyridyl) and the axis contains one coordination site - a bidentate (bipy or phenan). One can synthesize Cu^I complex (a)
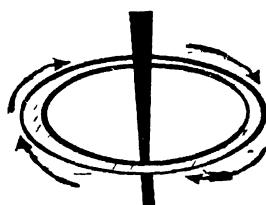
and Cu^{II} complex (b). Electrochemical oxidation of Cu^I complex (a) undergoes a complete rearrangement upon oxidation of copper in going from tetrahedral geometry of CN = 4 to penta-coordination mode of Cu^{II} complex with CN = 5.

The rates of rearrangement process is very important in this type of motion. The kinetic studies have shown that arrangement of divalent copper complexes are much slower than that of monovalent copper. It has also been found for certain that pirouetting movement of the ring around the axis is much faster than the gliding movement of the ring along the axis. It can be monitored either electrochemically or by spectral methods. As mentioned in the previous paragraph, rate of pirouetting motion is very important. It has been observed that subtle structural changes in the ligand structures have a significant influence on the rate of movement, particularly in Cu^I/ Cu^{II} based machines and this rate increases with the time

Fig. 4. Pirouetting motion.

4-Coordinate Cu^{II} rotaxanes

5-Coordinate Cu^{II} rotaxanes

● Copper (I)

○ Copper (II)

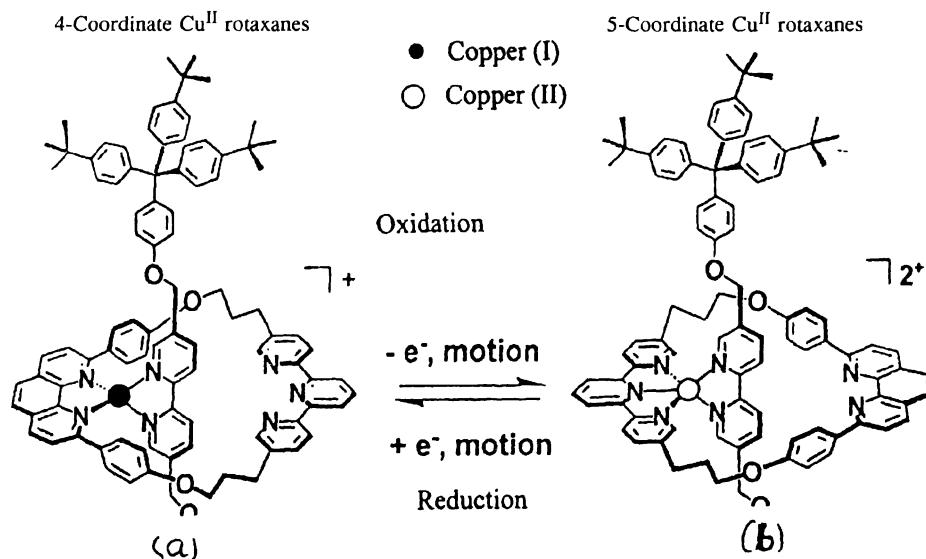Oxidation

- e⁻, motion

+ e⁻, motion

Reduction

(a)

(b)

Fig. 5. Electrochemically induced pirouetting of the ring in rotaxane (copper center).

for which metal center is accessible to the ligand. Thus the rate when sterically hindered ligand is used for complexation will give a fastered rate relative to one with an unhindered ligand. This has been shown when in place of 1,10-phenanthroline, some substituted 1,10-phenanthroline are used. Or in place of less bulky 2,2′-bipyridyl, more bulky 2,2-bipyridyl has been used.

(A₃) Cu^{II} and Zn^{II} based rotaxanes showing stretching/contracting action - molecular muscles :

A multicomponent system capable of showing stretching and contracting motions induced by external chemical system is developed. It is based on a symmetrical double threaded pseudo rotaxane system in which two

axes of two pseudo rotaxanes can glide along one another in the two rings (inside the ring of one pseudo rotaxane, the axis of the second rotaxane glide and inside the ring of second pseudo rotaxane, the axis of the first pseudo rotaxane glide). The two systems are held together by the rotaxane nature and by the complex of Cu^{II} or Zn^{II} with the coordinating ligands on the axis and in the ring (see Fig. 6).

In each pseudo rotaxane, the axis contains two coordinating ligands (one bidentate and the second tridentate (terpyridyl)) while each ring contains one bidentate ligand. Thus when Cu$^+$salt is added to the solution, it forms a tetrahedral complex (CN = 4) and adopts an
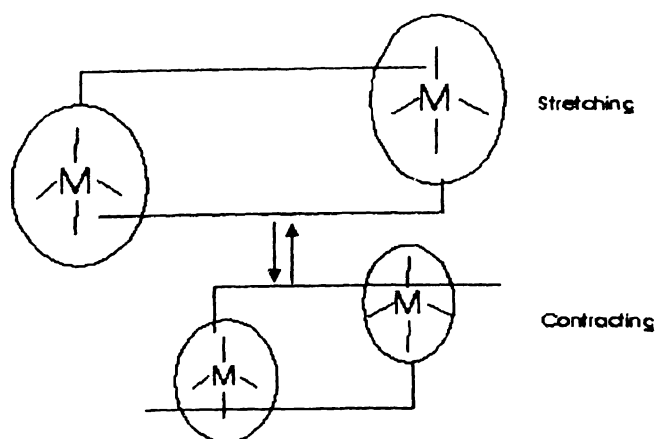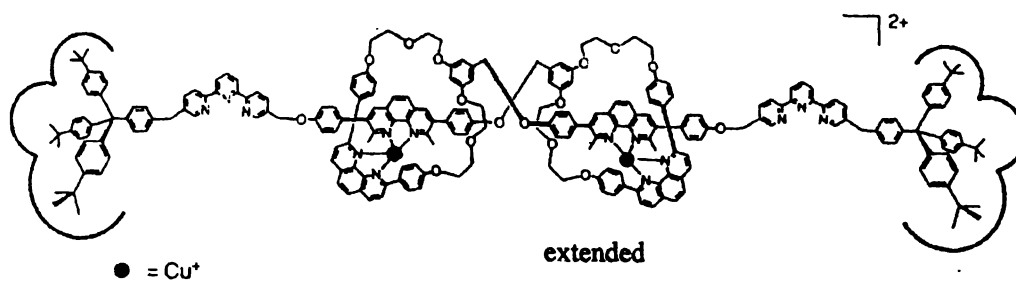
Stretching

Contracting

Fig. 6. Gliding of axes in rotaxane dimer.

(a) Extended rotaxane-copper(I) complex

● = Cu⁺

extended

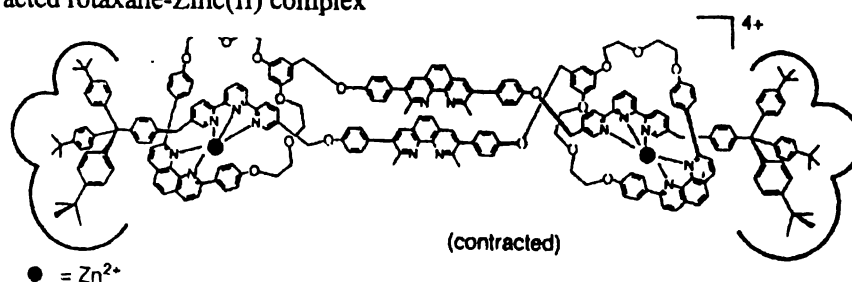(b) Contracted rotaxane-Zinc(II) complex

● = Zn²⁺

(contracted)

Fig. 7. Two states of pseudo ratoxanes – stretching and contracting muscle like motion.

"extended" form system whereby two phenanthroline units, one on the axis of one pseudo rotaxane, and second in the ring of second rotaxane both coordinate with Cu^+ and forms a tetrahedral complex of Cu^I. When Cu^+ is removed and Zn^{2+} is added to this system, the 1,10-phen unit in the ring of one pseudo rotaxane and the terpyridyl unit in the axis of second pseudo rotaxane coordinate to Zn^{2+} to form 5-coordinated complex so that the entire molecule turns to adopt a "contracted" form (Fig. 7). On repeating this sequential complexation/decomplexation cycle, the molecule undergoes respectively elongation/contraction reversibly. The system thus can be regarded as artificial molecular muscle mimicking Myosin muscle.

(A₄) Translocation of metal centers in rotaxanes :

If a movable metal system has two oxidation states $M^{n+}/M^{(n+1)+}$ of nearly the same stability (like Fe^{2+}/Fe^{3+}) and $M^{(n+1)+}/M^{n+}$ change is reversible, it is then possible to design a ditopic ligand in which one compartment (A) displays a selected affinity towards oxidized metal center. $M^{(n+1)+}$ whereas the other compartment (B) shows a greater affinity for the reduced state M^{n+} (Fig. 8). Therefore the metal center can be glided between (A) and (B) in a repeatable manner $M^{(n+1)+}/M^{n+}$ redox cycle. An example which fits well with this scheme is given by Cu^{2+}/Cu^+ system with the ligand shown in

Fig. 9. This system which operates through the Cu^{2+}/Cu^+ couple contain a compartment (A) consisting of four secondary amine groups suitable for Cu^{2+} system and a 2,2'-bipyridyl compartment (B) suitable for Cu^+. This system is flexible to fulfill the stereochemical requirement of each oxidation state of copper.

The translocation process is fast and reversible and can be monitored usually spectrophotometrically. An MeCN soluble containing ligand and Cu^{2+} is blue violet indicating Cu^{2+} being coordinated to the tetraimine compartment. On addition of ascorbic acid (Red. Agent), the
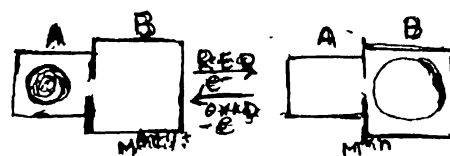
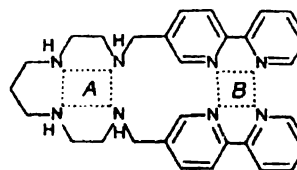

Fig. 8. Redox driven translocation of a metal ion.
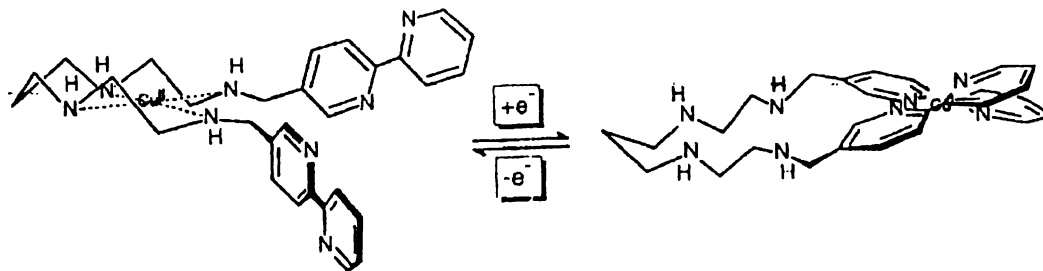

Fig. 9. Ligand/Rotaxane.

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Fig. 10. System of rotaxane.

colour changes brick-red suggesting [Cu$^+$(bipy)$_2$] ion in reduced state. It indicates the translocation of Cu$^+$ in the bipyridyl compartment. On adding H$_2$O$_2$ (oxidizing agent) the colour changes to blue violet indicating Cu^{2+} coordinated to tetraimine center (A) (Fig. 10).

(B) Catenanes based on Cu^I/Cu^{II} complexes :

(B$_1$) : The first Cu^I/Cu^{II} based-catenane was synthesized by Stoddart. It is a copper complexed [2]-catenane displaying two very distinct coordination modes with two different geometries. As discussed in rotaxanes, Cu^I prefers a tetrahedral geometry while Cu^{II}, a bipyramidal with CN=5 and an octahedral with CN = 6. In [2]-catenane, one of two interlocked (mobile) rings consists of one bidentate ligand [2,9-diphenyl-1,10-phenanthroline (dpp)] linked to organic background while the second ring (stationary) contains two coordination sites; (I) dpp – a bidentate chelate and a tridentate ligand terpyridine (typy). Depending upon the mutual rearrangements of these two rings and the oxidation state of copper ion, the metal can be coordinated tetrahedrally in the case of Cu^I ion or trigonal bipyramidally in the case of Cu^{II} ion. The tetrahedral coordination takes place as a result of coordinating copper(I) ion with two dpp ligands (one on each ring) and trigonal pyramid coordination, by linking with one dpp ligand of one ring and one terpyridine ligand of the second ring. The inter conversion of these two modes of coordination by the oxidation or reduction of Cu^I and Cu^{II} respectively corresponds to rotation of one ring of catenane with respect to another. This interconversion is affected electrochemically and monitored either spectroscopically or electrochemically (CV). This interconversion is reversible i.e. Cu^I → Cu^{II}, and Cu^{II} → Cu^I. The decomplexation Cu^{II} → Cu^I is slower than that of complexation Cu^I → Cu^{II}. The basic principle of the process

and its example are shown in Fig. 11.

(B$_2$) Copper complexed [2]-catenane involving three geometries :

Three stage – catenanes are particularly important because these give unidirectional rotational motion [two stage [2]-catenane give generally an oscillatory motion]. In these catenanes, the molecules displays three distinct geometries (each stage corresponds to three different coordination number 4, 5 and 6). The principle of these catenanes are shown in Fig. 12. Analogous to other catenanes, it also relies on the important differences in the stereochemical requirements for the coordination of Cu^I and Cu^{II}, for the Cu^{II} case, the stability order of the coordination No. is 4 >5 >6. On the other hand for Cu^{II}, this stability order is just the opposite i.e. CN6 > CN5 > CN4. Each ring of such catenanes contain two coordination sites : one bidentate and one tridentate. The path of these motions is generally monitered electrochemically. Starting from the tetra coordinates (2 dpp ligands one on each ring with Cu^I metal) viz. [Cu(N)$_4$]$^+$ the metal ion is oxidized to Cu^{II}, a thermodynamically unstable species [Cu(N)$_5$]$^{2+}$ (one dpp + one terpy ligand) is formed by reorganizing ligands by gliding of the mobile ring within the stationary ring and finally to the hexacoordinate stage [Cu(N)$_6$]$^{2+}$ is expected by coordination of Cu^{II} with two tridentate ligands (one ligand on each ring). The whole process is reversed by reducing [Cu(N)$_6$]$^{2+}$ to the monovalent stage, viz. [Cu(N)$_4$]$^+$. The whole process is monitored spectroscopically because the colour of each species is different. In some cases, the oxidation process was carried out chemically, viz. by using (NO)$^+$(BF$_4$)$^-$ and reduction is done electrochemically.

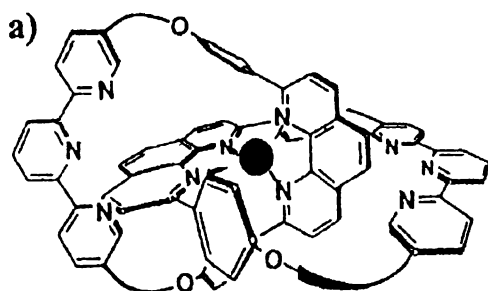*(B$_3$) Translocation of crown ether ring inside another ring containing two hetero metal center ring* :

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(A) Tetrahedral Cu^I and Cu^II complexed catenane
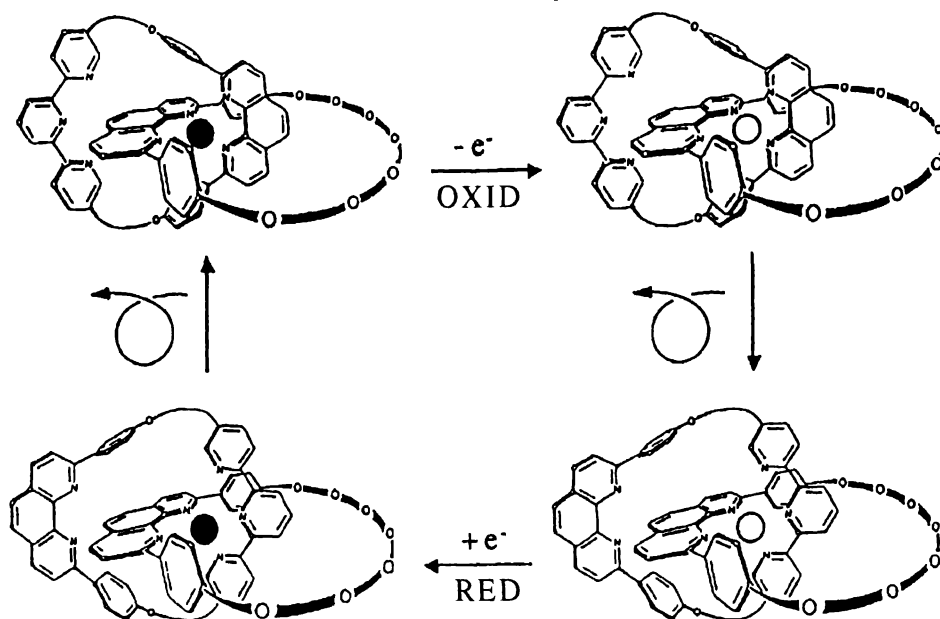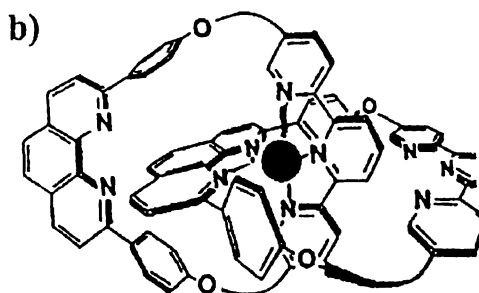

(B) Pentacoordinated Cu^II and Cu^I complexed catenane

Fig. 11. Square scheme for catenane.

Tetrahedral 4-coordinated Cu^I or Cu^II   5-Coordinated Cu^I or Cu^II
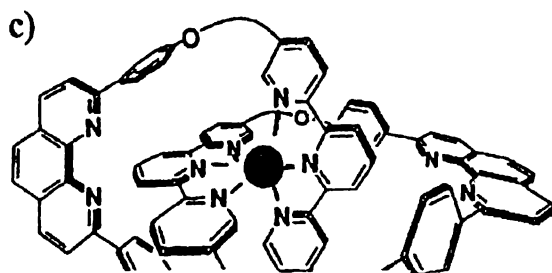

Octahedral 6-coordinated Cu^I or Cu^II

Fig. 12. Three forms of the copper-complexed catenane, each species being either a monovalent or a divalent complex.

Another type of heterodinuclear catenanes have been synthesized that show translocation of the crown ether ring in either direction i.e. back and forward between two different metal centers (Ni or Cu in +2 state) located
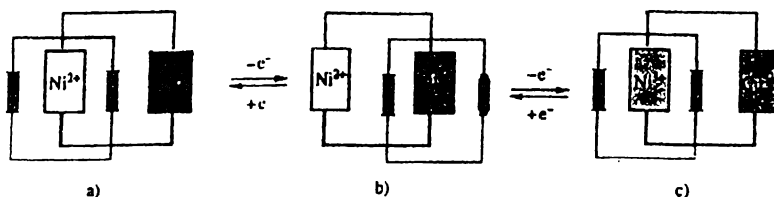
Fig. 13(a). Schematic representation of electrochemically controlled intramolecular motion.
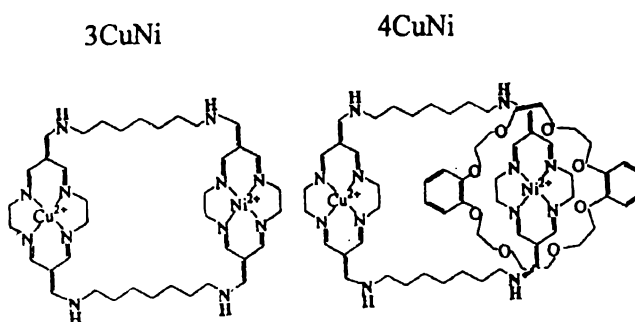
3CuNi   4CuNi

Fig. 13(b). Heteronuclear [2]-catenane.

on another ring by some external stimulation – an applied potential. By applying an appropriate potential, either copper or nickel (or both) are reversibly oxidized to their higher oxidation state (i.e. +3). The latter state favours an interaction of these metal system with the electron rich aromatic unit present in the crown ether unit. This will result in the movement of the crown ether ring towards its preferred oxidized metal center (Fig. 13). The "frozen" interconversion within the molecule can be better observed at lower temperature. The intramolecular motion can potentially be applied in molecular devices.

(2) Light-driven molecular machines based on the dissociative excited states

Ruthenium (II) complex based rotaxanes and catenanes :

(i) General principle : Most of the systems discussed in the preceding paragraph containing transition metal complexes are driven using redox process (electrochemically). An alternative approach is based on photochemistry. The excited state is now considered as a photo-reagent whose functions will be to act as reagent in the reaction rather than just exchanging energy or an electron. Consequently a real photochemical reaction will take place and one of the ligands from the complex will be expelled, if the light excitation generates a dissocia-

tive excited state. Complexes of the $(Ru(diimine)_3)^{2+}$ family are particularly well adapted for this approach. The only requirement for these types of photo reactions is that they must contain sterically hindering chelates because of which octahedrally symmetrical field gets distorted so much as to decrease the ligand field stabilization energy sufficiently large. As a consequence of this decrease in CFSE, the dissociative ligand field state (^{3}d-d state) gets sufficiently and efficiently populated as a result of M $\rightarrow$ L charge transfer. Thereby the distorting ligand gets expelled (Fig. 14). In order to regenerate the

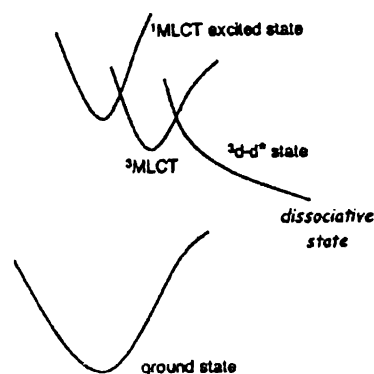**Fig. 14.** The ligand field state ^{3}d-d* can be populated from the ^{3}MLCT state, provided the energy difference between these two states is not too large. Formation of this dissociative state leads to dissociation of a ligand.

system's original state, another thermal impulse will have to be given to complete the whole cycle. We give below an example of pseudo rotaxane and one of [2]-catenane which are based on such photochemical reaction.

(a) Pseudo rotaxane : In this rotaxane, the axis component contains a ruthenium(II) bis-phen complex (phen : 1,10-phenanthroline) and the ring is a microcycle of 35 membered crown ether in which a chelate (2,2'- bipyridine) is incorporated (Fig. 15). The axis is threaded inside the ring. It has been reported in the literature that one can introduce [Ru(diimine)$_2$]$^{2+}$ in the axial component by the appropriate substitution of diphenanthroline by imine. Thus [Ru(diimine)$_2$]$^{2+}$ containing axial fragment becomes this pseudo rotaxane axis and the bulky groups are linked at the end of the axis forming it as a rotaxane. Thus by suitable reaction [Ru(diimine)$_2$L$_2$]$^{2+}$ distorted octahedral complex forms as an axis. It when threaded in the ring reacts with 2,2'-bipyridyl of the crown ether, and then forms a rotaxane [Ru(diimine)$_2$(bipy)]$^{2+}$.

Visible light irradiation of a solution of this rotaxane in acetonitrile ($\lambda > 400$ nm) leads to dethreading reaction. The photochemical reaction can easily be monitored spectroscopically. In order to regenerate the original complex, the mixture after irradiation is heated. Similar reactions were carried with and without stoppers at the end of the axis. In every case, threading (on heating) and dethreading (photochemically) reactions were observed.

Ruthenium(II) complexed [2]-catenane :

Two [2]-catenanes have been synthesized. One catenane contains crown ether of 42 membered ring containing bipyridyl ligand and the second ring of the same catenane 50 membered ring in which two phenanthroline units were incorporated. The second [2]-catenane contains the same bipyridyl – incorporating 42 membered crown ether as one ring, but the second ring as a 63 membered ring. Because of the larger size of the ring in the latter [2]-catenane, it is more adapted to molecular motion com-
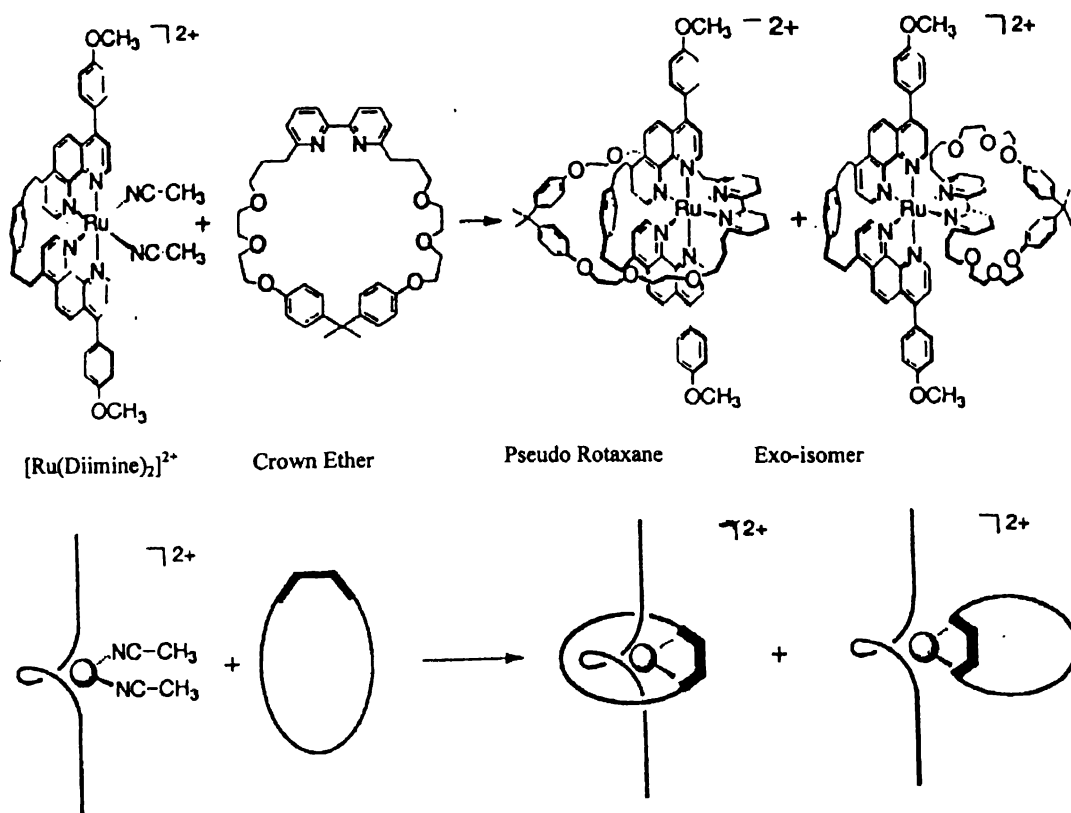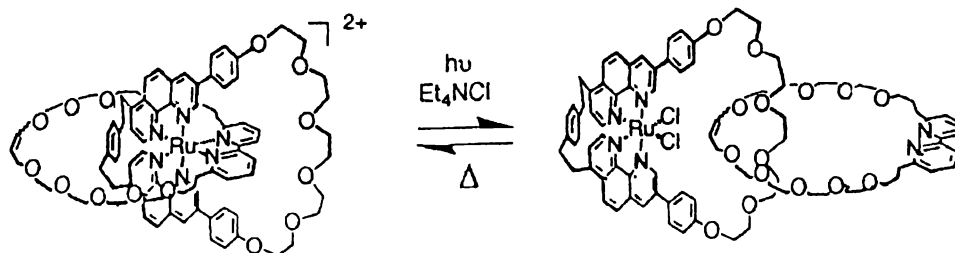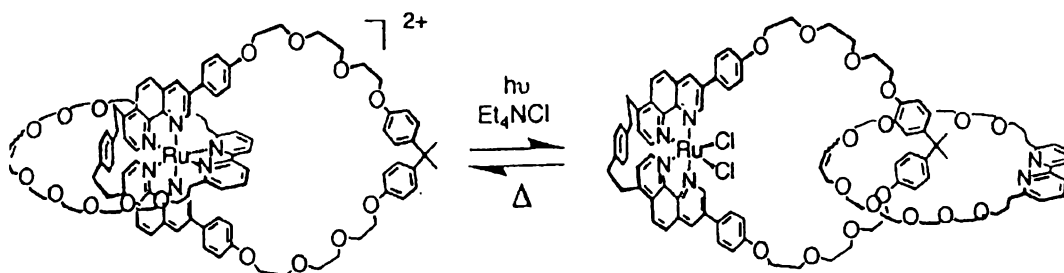

[Ru(Diimine)$_2$]$^{2+}$ Crown Ether   Pseudo Rotaxane   Exo-isomer

Fig. 15. Synthesis of pseudo rotaxane and its exo-isomer.

(A) [2]-Catenanae with 50 membered ring

(B) [2]-Catenanae with 63 membered ring

Fig. 16. Catenanes 19^{2+} or 22^{2+} undergo a complete rearrangement by visible light irradiation.

pared to that of former [2]-catenane in which both constituting rings would move with respect to one another. The light induced motion with $\lambda = 458$ nm and the thermal back reaction have been observed in both cases. In both system the reactions were quantitative as indicated by UV and Visible spectroscopy. The back reaction or recoordination was carried out by heating their light exposed solutions. One week point of the reactions is the production of photoproducts with large number of shapes with could not be controlled. These reactions have been shown in Fig. 16.

Conclusions :

Besides synthetic challenges of these machines, it is to be stressed that the present machines are extremely primitive compared to those present in Nature (Biomolecules). Presently one cannot think of synthesizing molecules mimicking Biomolecules. Until now artificial systems have almost exclusively been investigated as a collection of molecules in solutions or on films.

With respect to their practical applications several possibilities can be explored. We presently can not pre-

dict for the future technical applications though some ambitious futuristic practical application can be considered like micro robots capable of performing various functions like transport of molecules, sort out different kinds of molecules, store energy, giving a drug to its position of action, gate-valve, brakes, storage of information etc. Finally Feynmann's conclusion will seem more appropriate who said in the same address before the American Physical Society in 1959 "what would be the utility of such machines ? Who knows ? I can not see exactly what would happen, but I can hardly doubt that when we have some control of the rearrangement of things on a molecular scale, we will get an enormously greater range of possible properties that substances can have and of different things we can do". We further collaborate the truthfulness of his comment even today because the seeds that were sown in the past will definitely bring fruits to us. Let us see our glass half-full, rather than half-empty.

For more detail on this topic, one may refer to the following reviews and references therein.

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