

Metallo-Based Cyclophanes and [2]Catenanes

TOWARDS MOLECULAR-SCALE FUNCTIONAL ASSEMBLIES

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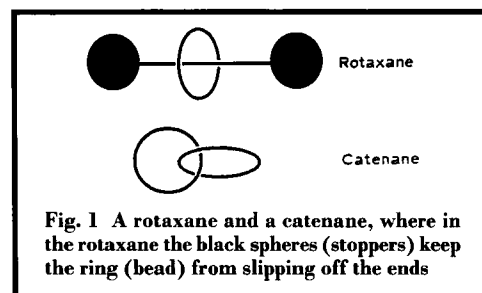
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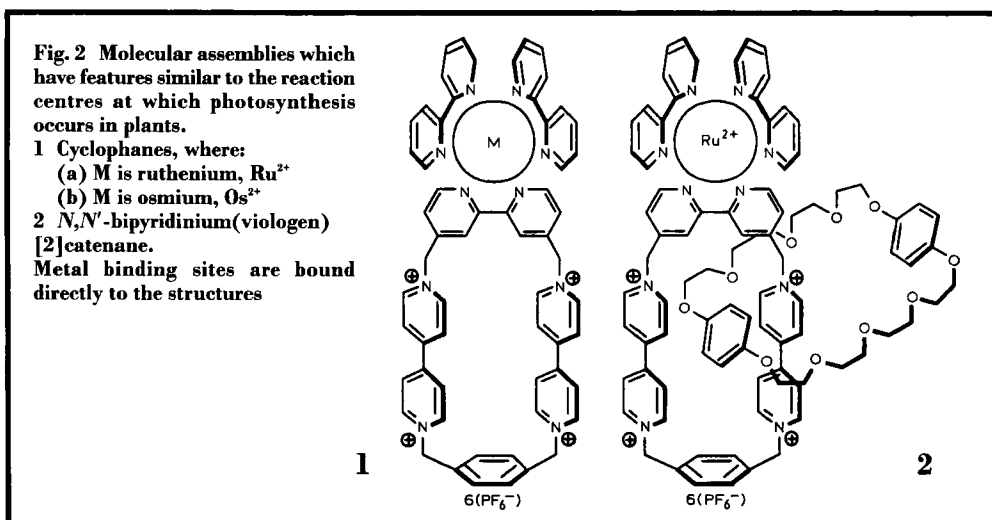
The creation of systems that are capable of performing molecular-scale operations is currently under extensive investigation, particularly in the emerging field of nanotechnology. Towards this end, we have been actively involved in the construction and study of the properties of metallo-based assemblies based on electron-deficient cyclophanes and donor-acceptor [2]catenanes. Metallic moieties, such as $[Ru(bipy)_2(L)]^{6+}$ and $[Os(bipy)_2(L)]^{6+}$, where $bipy = 2,2'$ -bipyridyl and $L =$ tetracationic cyclophane ligand, form an integral part of the molecular structures of these assemblies and in these specific cases create photoactive complexes. The photoinduced electron transfer reactions which occur within these molecules have been extensively studied, especially in relation to the corresponding processes found in natural photosynthetic reaction centres. Here, we present a short review on relevant aspects of this work as well as the potential use of metal-based cyclophanes as binders for aromatics.

The ultimate aim of research in supramolecular chemistry is to control the intermolecular bond so that large-scale molecular aggregates can be constructed (1). Although supramolecular chemistry is still at an early stage of development, chemists are now able to build complex molecular assemblies, where the shape, size and functionality can, to a limited degree, be controlled. Functionality, for instance, could be the simple recognition of a specific molecule, with the resultant interaction being communicated to a remote part of the structure, such as in chemical sensors (2). Topologically intriguing rotaxane and catenane molecules stand out as prime examples of cases where external triggering, for example, by photons, ions or

redox changes, can be used to drive large-scale conformational changes, see Figure 1 (3).

For an operational molecular-scale system, the required reaction-functionality is to control the bead positioning in the rotaxane (4), or the ring





gliding motion in the catenane. As well as utilising the mechanical properties of rotaxane/catenane assemblies these structures also contribute to the investigation of electron transfer processes in structurally well-defined models (5).

The two projects described below are some of our attempts to make use of the unique structural features of cationic *N,N'*-bipyridinium (viologen) catenane and the counterpart cyclophane assemblies. In these examples, the most important design feature is the incorporation of metal binding sites directly into the molecular structures.

Artificial Models of Photosynthetic Reaction Centres

Without doubt the unique machinery that Nature has constructed to capture light and convert it into energy is a model of ingenuity and efficiency, the workplace for the energy conversion being termed the photosynthetic reaction centre (RC). The RC for purple bacteria, which are typical light-harvesting membrane protein complexes, consists of a "special pair" of bacteriochlorophyll, positioned close to two identical electronic relays (the co-factors) made up of bacteriochlorophyll and bacteriopheophytin, the latter having nearby quinone groups that act as the final destination of the electrons

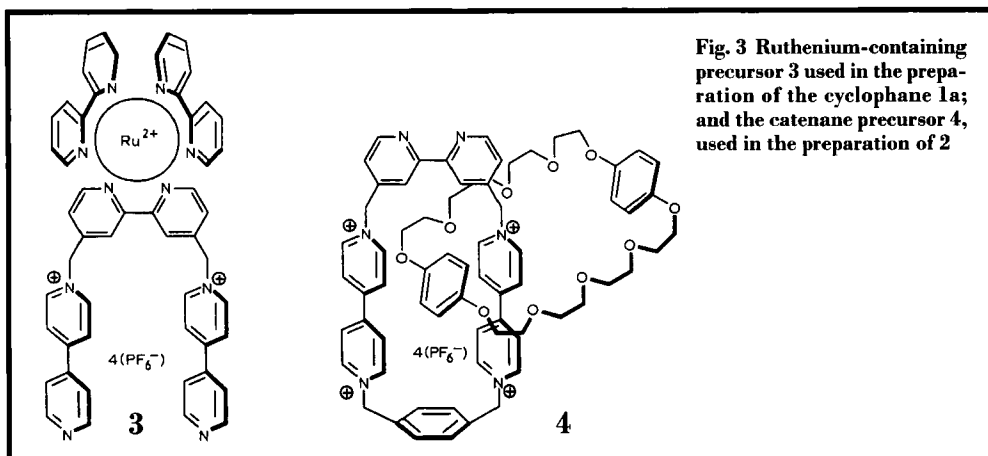
in the electron transfer process. Perhaps one of the most intriguing aspects of photosynthesis is the observed unidirectional electron transfer which occurs despite the almost two-fold symmetry in the RC co-factors (6).

The unidirectionality of the electron transfer is a fascinating phenomenon since discrimination by electrons between the two sets of co-factors is due to differences in the local dielectric environment. In an attempt to mimic RC asymmetry we have begun a programme in which redox differences are introduced into complexes by relatively simple means (7).

Some molecular assemblies which have features of the photosynthetic RC are illustrated in Figure 2. Here, the bipyridyl chelates of ruthenium(II) and osmium(II) function as ideal photosensitisers in the assemblies, with the viologen-based cyclophanes acting as electron-accepting moieties. Due to predetermined design criteria, the redox chemistries of the assemblies are quite different, either because of:

- (i) the introduction or removal of donor-acceptor interactions (that is 2 and 1a), respectively,
- (ii) the exchange of the bound metal ion (that is ruthenium by osmium in 1b).

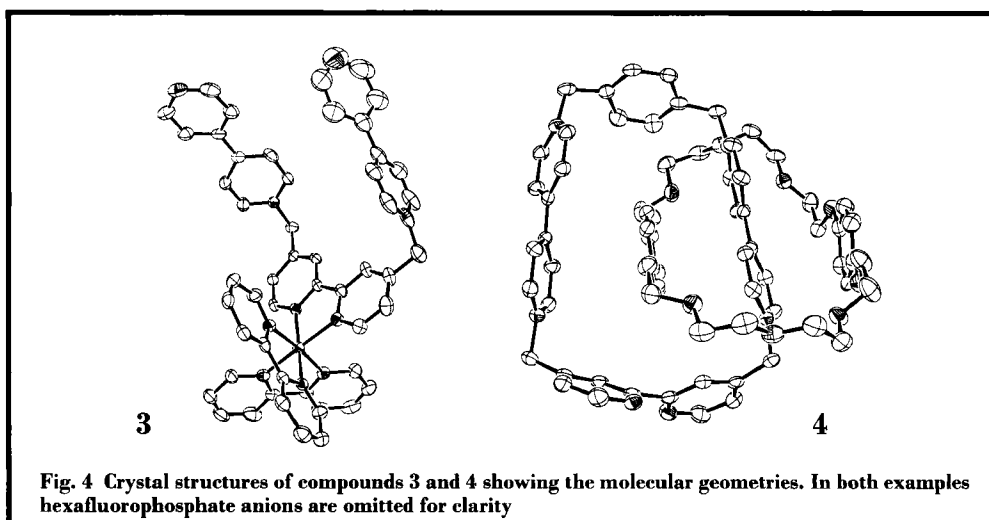
In particular, wrapping the electron-donating crown ether around one of the electron-accepting units in 2 results in a significant difference



in the redox potential (of around 130 mV) between the more “open” ($E = -0.32$ V) and “wrapped-up” ($E = -0.45$ V) viologens. This small, but significant, difference in redox potential between the two chemically identical electron acceptors is enough to calculate that quenching of the ruthenium chromophore occurs via preferential electron transfer to the more exposed viologen (**8**). Although the analogy to the natural photosynthetic reaction centre is rather basic, altering the local environment synthetically could pave the way to controlling the pathways that the electron transfer takes.

It is worth noting that the synthesis of the met-

allo-assemblies which are shown in Figure 2 is not trivial and relies on the building of molecular units, such as those illustrated in Figure 3. In this case, the two key intermediates, **3** and **4**, are required in the preparation of ruthenium-containing cyclophane **1a** and the [2]catenane **2**, respectively. The structures of **3** and **4** have been verified by single-crystal X-ray crystallographic studies, see Figure 4. The conformation of **3** reveals that the two bipyridinium units are prearranged in a manner that facilitates cyclisation to form the metallo-cyclophane **1a**. It is noteworthy that in the structure of **4** the two nitrogens of the 2,2'-bipyridyl unit are almost



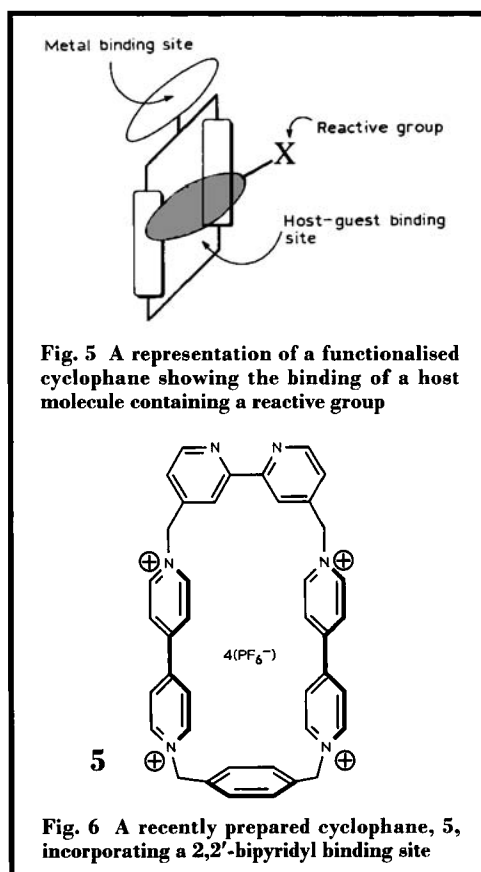
transoid (diagonally opposite each other) and not predisposed for chelation. In view of the metal ion binding properties of the ligand, it is reasoned that structural alterations occur which help flip the bipy unit to the required *cisoid* conformation, where the nitrogens approach the closest together.

Functional Cyclophanes

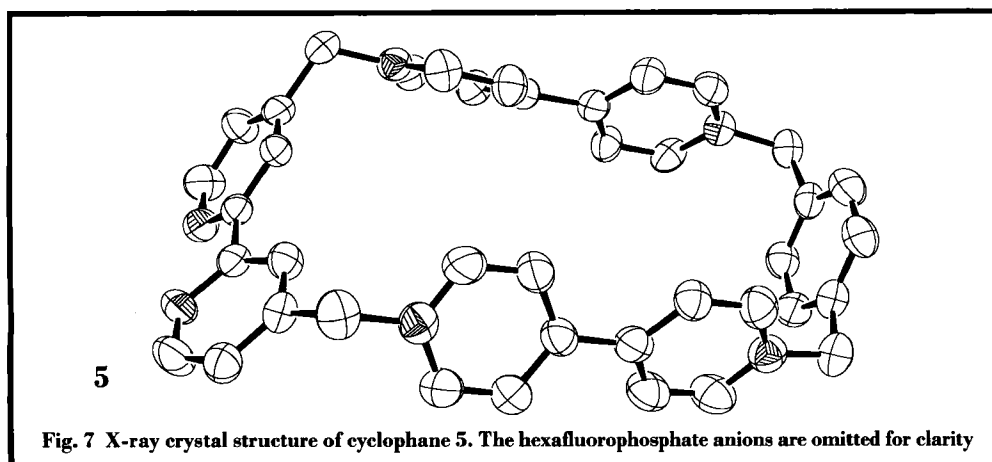
Host-guest interactions offer the possibility of selectively and reversibly binding a substrate and reaction centre adjacent to each other, in order to enhance and catalyse reactions, for example oxidation/reduction, see Figure 5. The binding site in Figure 5 has not been specified, but in principle it could be a chelator or macrocyclic ligand, which would enable a redox-active metal ion to be positioned close to the reactive site on the bound substrate.

As a first step towards creating functional systems, the cyclophane **5** in Figure 6 has been prepared. This incorporates the necessary design criteria so that it can act not only as a metal ion binder but also can encapsulate electron rich aromatics in its central cavity.

X-ray crystallography has also been invaluable here in the unequivocal verification of molecular structure (9). The structure of cyclophane **5** is shown in Figure 7 and clearly shows a slight twisting of the *N,N'*-bipyridinium groups and more importantly the *cisoid* conformation of the bipy unit. It should also be



remembered that in the counterpart [2]catenane structure the bipy unit was *transoid*, suggesting that interlocking of the two rings



induces steric strain into the molecule.

Although still at the early development stage, the binding of *p*-dimethoxybenzene, *p*-phenylenediamine and other functionalised aromatics inside the central cavity of **5** has been verified by using UV-visible and ¹H NMR spectroscopies. The obtained binding constants are modest (around 0.5 to 100 M⁻¹) but nevertheless encouraging for future work using metal ion redox reactions to transform substrate functionality.

Future Work Using Terdentate Chelators

In view of the success in the construction of systems incorporating bipy binders, attention has now been turned to the well known terdentate chelator 2,2':6',2''-terpyridine (terpy). Ligand **6** represents the first step towards this goal from the functionalisation of the terpy backbone with tolyl groups at the highly unusual 3,3'' locations (10). The chelator readily forms a 2:1 complex with a first row transition metal such as iron(II), with the ligand co-ordinating around the meridian, as expected. The crystal structure of the cation [Fe(6)₂]²⁺ is illustrated in Figure 8.

By functionalisation of the methyl groups we expect to be able to "build from the back" of the chelator in a similar fashion to the bipy cyclophanes and catenanes. In particular, because of the increase in size in moving to the terpy chelator it is expected that larger cavities can be constructed with the potential for binding larger substrates.

Conclusions

The chemistry of catenanes and counterpart cyclophanes which incorporate metal binding groups such as bipy and terpy is still very much at the development stage. Our studies have demonstrated the potential application of these systems as artificial models for photosynthesis, with extensions towards redox-active and photoactive catalysts. In particular, we are now exploring ways to induce greater redox asymmetry into assemblies by altering both the type of electron acceptor and size of the crown ether donor. By attaching high oxidation state ruthenium-oxo species to the cyclophane bipyridyl group the production of oxidation catalysts is also being explored. Of course, our ultimate aim will be to produce working systems that will have a real commercial benefit, though at this stage this is still a long way off.

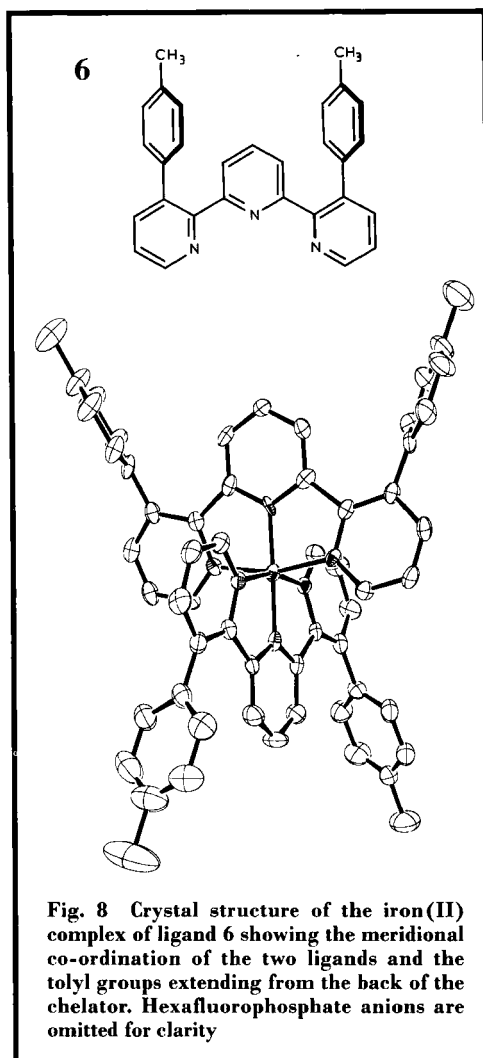


Fig. 8 Crystal structure of the iron(II) complex of ligand **6** showing the meridional co-ordination of the two ligands and the tolyl groups extending from the back of the chelator. Hexafluorophosphate anions are omitted for clarity

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Platinum 1998

Johnson Matthey's latest annual market survey of the platinum group metals, "Platinum 1998", was launched in London on Monday, May 18th. The review covers the supply and demand for the platinum group metals during 1997, with a particular emphasis on platinum and palladium.

Supplies of platinum during 1997 were similar to 1996 at 4.97 million oz. The economic problems in Asia, a declining gold price and other factors led to a high price volatility, with an average for the year of \$395.91/oz, virtually unchanged from 1996.

Demand for platinum grew by 5 per cent in 1997 to reach 5.2 million oz. This was mainly due to an increase in demand for platinum jewellery in China and the U.S.A.

The use of platinum in autocatalysts fell by 40,000 oz to 1.84 million oz in 1997 as European car manufacturers continued to adopt palladium-based technology. This was however offset by an increased demand for diesel cars. Since the start of 1997, virtually all diesel cars sold in the EU have been fitted with platinum-only catalysts. In North America, consumption was also slightly lower due to the switch to palladium-based catalysts on some models of cars.

The demand for platinum in the industrial sector rose by 80,000 oz to 1.28 million oz in 1997. This came from the wider use of platinum in hard disks for personal computers which is expected to continue to rise due to the superior data storage properties imparted by platinum. The glass industry also consumed more platinum in 1997 because of continuing investment in new plant for the production of high

quality glass for cathode ray tubes and liquid crystal displays.

"Platinum 1998" contains a special feature on fuel cell cars, reporting on developments towards commercialisation which occurred during 1997. In April, Daimler-Benz announced a joint venture with Ballard Power Systems and plans to launch a commercial fuel cell car by 2004. Other major car companies have similar plans. This has been encouraged by the rising concern about global warming, with governments focusing on fuel cell technology as a way to reduce carbon dioxide emissions. As fuel cell catalysts contain a much higher loading of platinum than current platinum-based autocatalysts, this is expected to have a positive impact on platinum demand in the next decade.

The demand for palladium soared by 1.31 million oz during 1997 to reach 7.46 million oz. European car makers continued to adopt palladium-based catalysts on their gasoline models and U.S. companies are increasing the palladium loadings on their cars to meet Low Emissions Vehicle legislation. Consumption by the electronics sector also increased further during the year as the demand for palladium-containing multi-layer ceramic capacitors (MLCC), used in products such as mobile phones and computers, expanded rapidly.

Readers of *Platinum Metals Review* who would like to receive a free copy of "Platinum 1998" can do so by writing to Alison Cowley, Johnson Matthey PLC, 40-42 Hatton Garden, London EC1N 8EE; Fax: +44-(0)171-269-8389.