One-pot Synthesis and X-Ray Studies on Cyclic Oligobipyridines and one of their Dinuclear Ruthenium Complexes

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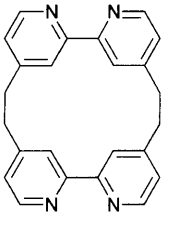
A one-pot synthesis of three new macrocycles containing two, three or four 2,2′-bipyridine units is described; the X-ray analysis of the bis-bipyridine ligand reveals a cyclophane type structure; the X-ray structure of one of the diastereoisomers of the dinuclear ruthenium complex is also described and shows two metal centres held in close proximity.

Design, synthesis and binding studies of multisite receptor molecules in which the interaction sites are outwardly oriented (exoreceptors) are of special interest since, by an iterative assembling process, these units may lead to large molecules with particular properties.[1] In this vein, we have reported the synthesis of exoreceptors based on calixarenes,[2a] amidines[2b] and bipyridines (bipy).[2c] A combination of Ru^{II} and bipy ligands gives rise to peculiar photochemical and electrochemical properties.[3] Homo- and hetero-binuclear complexes bearing oligopyridine ligands have also been prepared in order to study intramolecular long-range electron or energy transfer. In these complexes, the bridging ligands are of either the pyrazine, bipyrimidine or 2,3-bis(pyridyl)pyrazine types, allowing electronic communication through the π-network between the two metal centres,[4] or bipy units linked by polymethylene chains, thus leading to a more flexible architecture.[5] Furthermore, double and triple helices, ladders, arborols and multi-ring catenanes based on the binding of several metals by oligobipyridine ligands have also been obtained.[6]

Following our earlier investigations into the macrocyclic exoreceptor composed of two 2,2′-bipy units interconnected at the 4,4′-positions by two Ph$_2$Si(CH$_2$)$_2$ groups,[2c] we attempted to extend the size of the ligand and therefore we investigated the reaction of the dilithium salt of 4,4′-dimethyl-2,2′-bipyridine **1** with 1,2-dibromoethane. Interestingly, we noticed that this reaction, in addition to linear oligomers, affords the new macrocycles **2**–**4**. This type of oxidative coupling reaction has been previously used to prepare linear bis(bipy or phenanthroline) compounds.[7] The same strategy has also been used to improve the synthesis of the *meta*-dibenzyl [2.0.2.0]-*m*-cyclophane.[8] Whereas the yield could be increased to 30% for **2**, for the other two macrocycles **3** and **4** we have not been able so far to improve the rather poor yield of *ca.* 1%. The reaction mentioned above was further carried out with the 6,6′-dimethyl-2,2′-bipyridine and afforded the same type of linear and cyclic compounds. All oligomers were fully characterised by NMR and HRMS. The structures of both **2** and **3** were investigated in the solid state by X-ray analysis.



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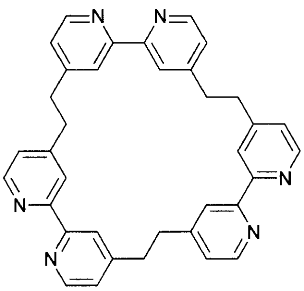

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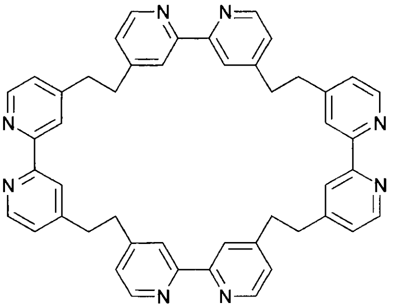

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Compound **2** might be regarded as the pyridine analogue of the above-mentioned cyclophane[8] or as a higher homologue of the pyridophanes studied by Staab *et al.*[9] In CDCl$_3$ solution, the cyclophane-type behaviour of **2** was suggested by ^{1}H NMR. Indeed, whereas the 6,6′ and 5,5′ protons in **2** were only slightly shifted with respect to **1** (δ −0.06 and 0.03, respectively), a substantial upfield shift of *ca.* 2 ppm (from δ 8.23 in **1** to 6.28 in **2**) for the 3,3′ protons was observed. According to Johnson and Bovey,[10] a shift of *ca.* 2 ppm may be expected for protons located above and on the hexagonal axis of the benzene ring at *ca.* 2.8 Å. This was further confirmed by the X-ray analysis of **2**[†] which indeed showed a cyclophane-type structure (Fig. 1).

In the solid state **2** appears as highly symmetrical and possesses three twofold axes. The conformation adopted by **2** is similar to that reported for the [2.0.2.0]-*m*-cyclophane.[8b] The macrocycle **2** forms an oblong cavity of length 8.5 Å and width 3.95 Å. The two pyridine subunits within the same bipyridine unit adopt a *trans* conformation with a twist angle of 32°. Moreover, whereas the pyridine rings remain planar, the bipyridine units are bent: both angles C^2–C$^{2'}$–C^5 and N–C^4–CH$_2$ are away from linearity by 7 and 8°, respectively (see Fig. 1). The 3,3′ protons are located *ca.* 3.1 Å above the pyridine ring of the opposite bipyridine, indicating that for **2** the preferential conformation in solution should be close to the one found in the solid state.

The homodinuclear Ru^{II} complex **5** was prepared as an orange solid in almost quantitative yield by reacting **2** with 2 equiv. of Ru(bipy)$_2$Cl$_2$[11] in a butanol–water solution. Precipitation of the PF$_6$ salt from an aqueous solution afforded the pure complex as a mixture of diastereoisomers.

Since octahedral metal complexes bearing three chelating ligands are chiral, for a binuclear octahedral complex one would expect a mixture of Δ,Δ; Λ,Λ and Δ,Λ; Λ,Δ isomers. In our

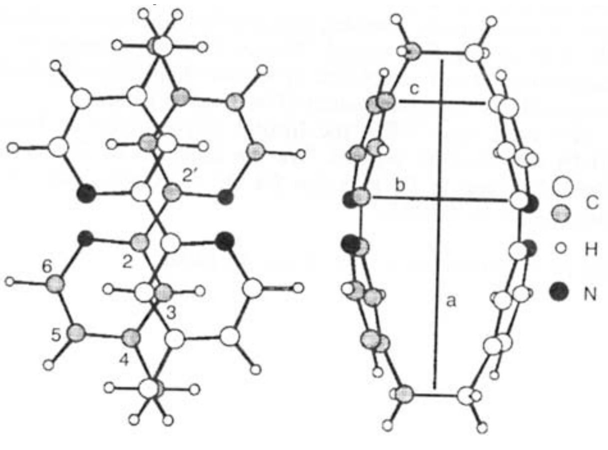
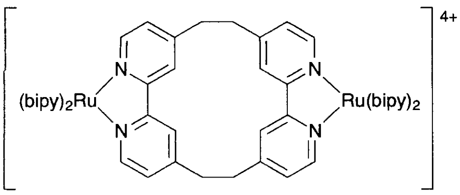


Fig. 1 Two orthogonal views of the crystal structure of **2**. For the sake of clarity the two CH$_2$-bipy-CH$_2$ fragments were differentiated. Selected distances: a = 8.5, b = 3.95, c = 2.95 Å.



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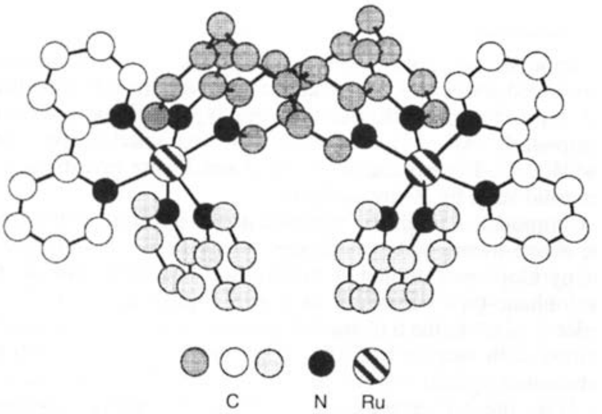

Fig. 2 Crystal structure of **5** (arbitrary isomer). For the sake of clarity hydrogen atoms are not presented and the three bipyridine units around each Ru atoms are differentiated. Selected distance: Ru–Ru 8.2 Å.

case, in solution using 2D NMR (^1H–^1H and ^1H–^{13}C) correlations, we were able to assign all the signals observed for the mixture of diastereoisomers. Moreover, fractional crystallisation of the Cl^- salt of the complex from an aqueous NaCl saturated solution afforded one of the diastereoisomers as a pure compound. After the exchange of Cl^- by PF_6^- anions, the latter complex was characterised by both ^1H and ^{13}C NMR. Furthermore, single crystals suitable for X-ray analysis‡ could be obtained by slow diffusion of diethyl ether into an acetone solution containing the complex (Fig. 2). It is worth noting that perhaps due to the presence of different diastereoisomers, despite the large number of studies dealing with the electrochemistry and photochemistry of homo- and hetero-dinuclear bipyridine complexes, only a few structural analyses have been reported for these complexes.[12]

The unit cell contains both the Δ,Δ and the Λ,Λ isomers. Both Ru^{II} are six-coordinated with an almost octahedral geometry. The Ru–N distances ranging from 2.052 to 2.064 Å, and the N–Ru–N angles for the three bipyridine ligands ranging from 78.7 to 79.8°, are similar to those observed for the well-known $Ru(bipy)_3(PF_6)_2$ complex.[13] Within the complex, the two Ru cations are 8.2 Å apart. The conformation of the macrocycle **2** in the complex is completely different from that observed in the free ligand. The cyclophane structure is no longer present and is replaced by a 'roof-shaped' conformation which allows the coordination of both metal cations.

We thank the CNRS, the Institut Universitaire de France (IUF) for financial support. We are indebted to Dr A. Van Dorsselaer and to Dr E. Leize for the characterisation of all compounds by HRMS.

Received, 10th March 1995; Com. 5/01506E

Footnotes

† *Crystal data* for **2** (colourless crystals, 20 °C): $C_{24}H_{20}N_4$, M = 364.5, orthorhombic, a = 19.632(6), b = 20.790(6), c = 9.429(3) Å, U = 3848.4 $Å^3$, space group *Fddd*, Z = 8, D_c = 1.258 g cm^{-3}, graphite-monochromated Cu-Kα radiation, 440 data with $I > 3\sigma(I)$, R = 0.038, Rw = 0.059. The structure was solved using MULTAN.

‡ *Crystal data* for **5** (orange crystals, −100 °C): $C_{64}H_{52}N_{12}Ru_2 \cdot 4PF_6 \cdot 2CH_3COCH_3 \cdot 2H_2O$, M = 1923.4, orthorhombic, a = 24.671(7), b = 14.287(4), c = 21.571(6) Å, U = 7603.2 $Å^3$, space group *Pbcn*, Z = 4, D_c = 1.680 g cm^{-3}, Cu-Kα, 2565 data with $I > 3\sigma(I)$, R = 0.042, Rw = 0.058. The structure was solved using heavy atom methods. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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