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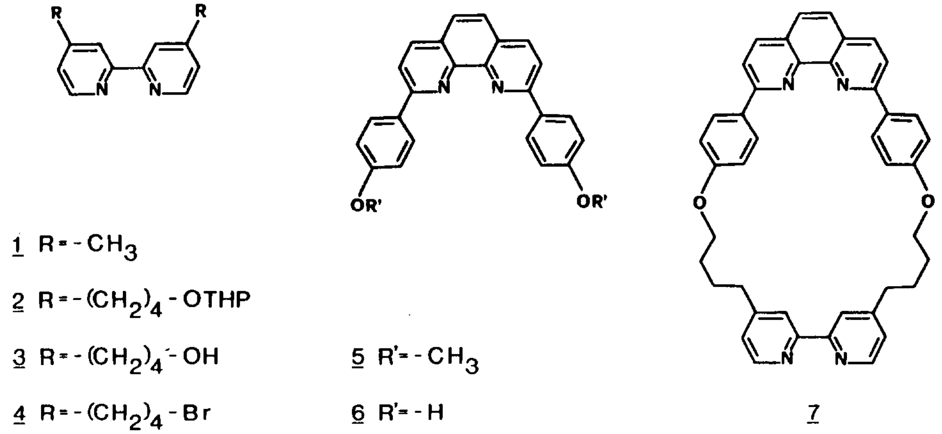
A MACROCYCLIC LIGAND INCORPORATING BOTH A 2,2'-BIPYRIDYL AND A 2,9-DIPHENYL 1,10-PHENANTHROLINE FRAGMENT: RECIPROCAL CONTROL OF ONE SITE BY COMPLEXATION OF THE OTHER SITE TO A TRANSITION METAL.

Jean-Claude CHAMBRON and Jean-Pierre SAUVAGE

Laboratoire de Chimie Organo-Minérale, U.A. au CNRS N°422, Institut de Chimie,
1, rue Blaise Pascal, 67008 Strasbourg Cédex, France

Abstract. A coordinating system containing two different complexing sites has been synthesised. Binding of ruthenium(II) to the octahedral-preferred part allows complexation of copper(I) at the tetrahedral site.

Molecular systems containing several complexing functions are of considerable interest. Such multiligands may display allosteric properties, a given site of the molecule being able to affect complexation of another coordinating fragment[1,2]. In addition, photo- and electro-active centres gathered within the same molecule at strictly controlled distances allow electron transfer studies, relevant to biological redox processes[3] including photosynthesis[4]. In relation to previous work on the redox behaviour of $Cu(dpp)_2^+$ (dpp= 2,9-diphenyl 1,10-phenanthroline)[5,6] we have synthesised a molecule containing both a copper(I) complex and a derivative of $Ru(bipy)_3^{2+}$ (bipy=2,2'-bipyridine). In order to control the spacial arrangement of the two transition metal complexes, macrocyclic systems seem to be well adapted. The ligand synthesised 7 is represented in Figure 1, as well as its acyclic precursors[7].



1 R=-CH_3

2 R=-$(CH_2)_4$-OTHP

3 R=-$(CH_2)_4$-OH

4 R=-$(CH_2)_4$-Br

5 R'=-CH_3

6 R'=-H

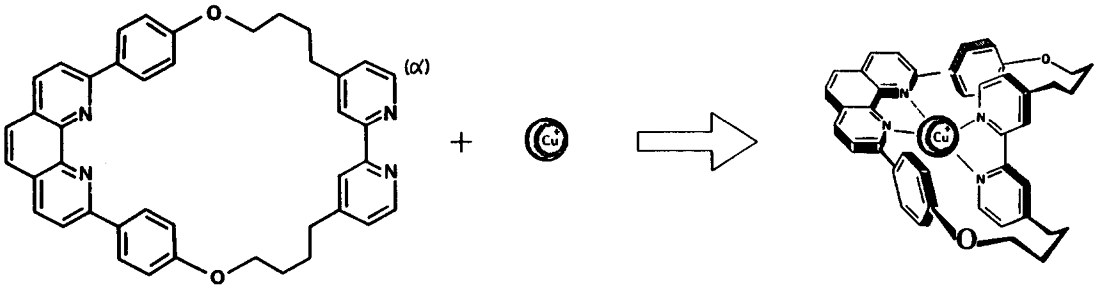
7

FIGURE 1

4,4'-dimethyl 2,2'-bipyridine, 1[8], is reacted with lithium diisopropyl amide in THF at 0°C, under argon (1 hr). $Br(CH_2)_3OTHP$[9] (THP=tetrahydropyranyl) in THF is then added. The mixture is stirred between 0°C and room temperature overnight. After work-up a 42% yield of 2 is obtained (white solid, F=68-72°C). Deprotection of 2 is performed by acidic treatment (para-toluene sulfonic acid; refluxing ethanol), yielding quantitatively the diol 3 (white crystals, F=98-99°C). Treatment of 3 by an excess HBr (48% in H_2O) in the presence of a catalytic amount of H_2SO_4 yields the dibromo derivative 4 as a waxy solid (77%). Cyclisation of 4 with 6[10] in the presence of a three times excess Cs_2CO_3, under high dilution conditions (DMF; 65°C; argon) leads to 7 in 39% yield (F=238-240°C). 7 is a thirty membered ring. It contains an inward coordinating site (dpp) and an external bipy subunit whose complexing properties are interdependent, as discussed below.

Complexation of copper(I) by 7.

With the aim of elaborating dimetallic species consisting of Cu^I bound to the dpp fragment, the bipy chelate complexing another selected transition metal, we reacted $Cu(CH_3CN)_4^+ . BF_4^-$ with 7 in CH_3CN-CH_2Cl_2 (50/50). Surprisingly, we always obtained the folded conformation, as shown in Figure 2.



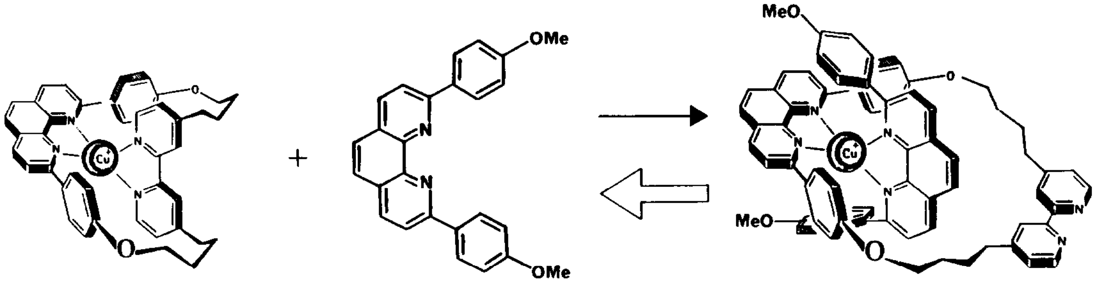
7.Cu+

FIGURE 2

Solutions of $7.Cu^+$ are deep red (λ_{max}=417 nm; ε =3300; CH_2Cl_2) and slightly air sensitive. Cyclic voltammetry measurements in DMF show a reversible oxidation wave (E°=-0.128 V vs ferricenium$^+$/ferrocene) and a very negative reversible wave (-2.050 V vs. ferricenium$^+$/ ferrocene) analogous to that of $(5)_2.Cu^+/(5)_2.Cu$ [11]. The shrivelled shape of the cycle in $7.\ Cu^+$ and the coordination of the bipy fragment to Cu^I have been demonstrated by ^1H NMR spectroscopy. In particular, the bipy H_α protons are shifted upfield (Δ =-0.97 ppm) by complexation of 7 to copper(I).

Attempts to outstrech the ring.

In order to build up copper(I) catenates[11] containing peripheral coordinating sites, we tried to unfold the system by threading 5 or 6 into the ring while disengaging the bipy fragment from the copper(I) coordination sphere. The equilibrium studied is schematised in Figure 3.



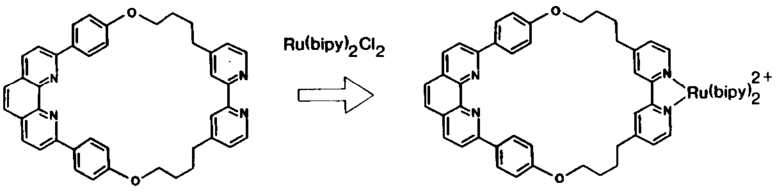
(7,5).Cu$^+$

FIGURE 3

Although copper(I) is expected to selectively bind dpp fragments (tetrahedral geometry) with respect to bipy (octahedral complexes), the equilibrium represented in Figure 3 is greatly shifted to the left, as shown by ^{1}H NMR spectroscopy. This observation is disappointing from the synthetic viewpoint, preventing interlocking of rings by further cyclisation, but it shows how strong entropic effects might be: the folded geometry is preferred in spite of a strained conformation and a supposedly weak interaction between bipy and Cu^I. The outstretched and threaded form (7,5).Cu$^+$ seems to be ideally adapted to Cu^I coordination but it requires an intermolecular coordination reaction simultaneously to the decomplexation of an intramolecularly bound ligand (bipy). Under stoichiometric conditions (7/Cu(CH$_3$CN)$_4$$^+$/5:1/1/1) only a small fraction of unfolded complex (7,5).Cu$^+$ is observed (~ 10%).

Protection of the octahedral bipy site: preparation of 7.Ru(bipy)$_2$$^{2+}$.

As shown in Figure 4, 7.Ru(bipy)$_2$$^{2+}$ was obtained quantitatively as its tetrafluoborate salt (orange solid: λ_{max} = 458 nm; ε = 13 100 in DMSO) from 7 and Ru(bipy)$_2$Cl$_2$, under experimental conditions close to those previously used for making other Ru(bipy)$_2$L^{2+} complexes[12] (L= diimine chelate).



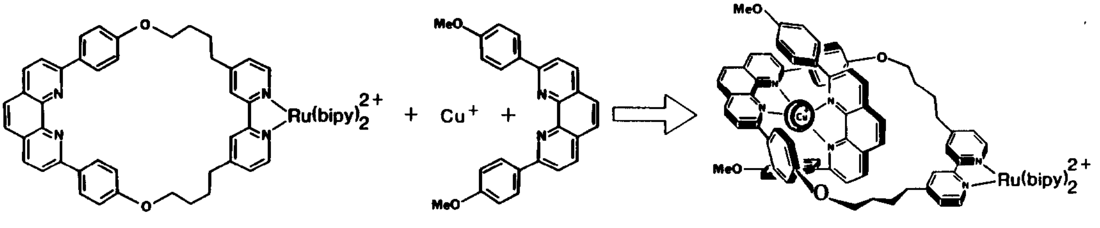
7.Ru(bipy)$_2^{2+}$

FIGURE 4

Ruthenium(II) complexation occurs selectively at the bipy site of 7. The interest of 7.Ru(bipy)$_2$$^{2+}$ is two fold: (i) Ru (bipy)$_2$$^{2+}$ acts as a protecting group, allowing coordination chemistry at the dpp site of 7 without interfering of the bipy fragment and (ii) the molecule now contains a photo- and electro-active subunit analogous to Ru(bipy)$_3$$^{2+}$ [13].

Formation of the hetero-dimetallic complex $[(\underline{7},\underline{5}).Cu^{I},Ru^{II}(bipy)_2]^{3+}$.

With $\underline{7}.Ru(bipy)_2^{2+}$ as ligand, folding of the macrocycle is prevented: indeed, stepwise addition of $Cu(CH_3CN)_4^+$ and $\underline{5}$ (stoichiometric proportions) leads to quantitative formation of $[(\underline{7},\underline{5}).Cu^{I},Ru^{II}(bipy)_2]^{3+}$, as shown in Figure 5.



$[(\underline{7},\underline{5}).Cu^{I},Ru^{II}(bipy)_2]^{3+}$

FIGURE 5

The above equilibrium is easily studied by ^1H NMR spectroscopy, due to the characteristic pattern of copper(I) complexes containing two entwined dpp fragments[14]. In addition, owing to the intense ring current effect of the phenanthroline nucleus of $\underline{5}$, the signals corresponding to the methylene groups of the $-(CH_2)_4-$ links are clearly distinguishable after threading of $\underline{5}$ within the open ring of $\underline{7}$.

Electrochemical and photophysical studies of the dinuclear complex $[(\underline{7},\underline{5}).Cu^{I},Ru^{II}(bipy)_2]^{3+}$ and related compounds are now under way.

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