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INTERLOCKED MACROCYCLIC LIGANDS: A CATENAND WHOSE ROTATION OF ONE RING INTO THE OTHER IS PRECLUDED BY BULKY SUBSTITUENTS.

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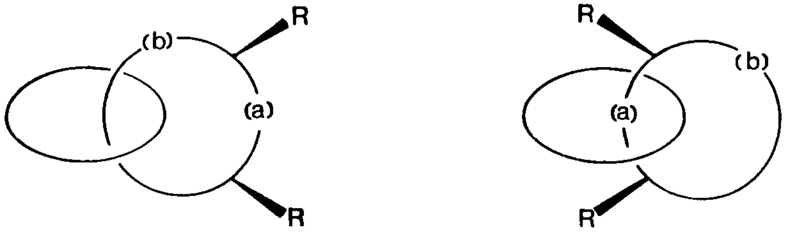
Abstract. A new highly rigid catenand has been synthesized. It contains two interlocked rings whose reciprocal motions are highly restricted, making the topography of the copper(I) catenate similar to that of the free ligand.

Catenanes consist of interlocked rings, usually able to glide freely one into the other[1,2]. Rotaxanes, on the other hand, consist of a cycle and a molecular linear fragment inside it whose gliding out of the ring is prevented by bulky substituents located at its extremities. It is conceivable that, if one of the rings of a catenane bears two bulky groups R, the molecular system will also have a rotaxane character; it might lead to isomers, as represented in Figure 1.



(I) **(II)**

FIGURE 1

Forms (I) and (II) are distinct if the connections (a) and (b) are different. The two isomers cannot interconvert provided the R groups are too voluminous to go through the cycle[4]. In recent years, Schill and his coworkers have reported such "translationally" isomeric [3]-catenanes[5] and rotaxanes[6].

Based on a previously reported three-dimensional template synthesis of coordinating interlocked rings, the **catenands**[7], we have now made molecules equivalent to form (II) of Figure 1. The starting compounds and the synthetic scheme used are represented in Figure 2[8].

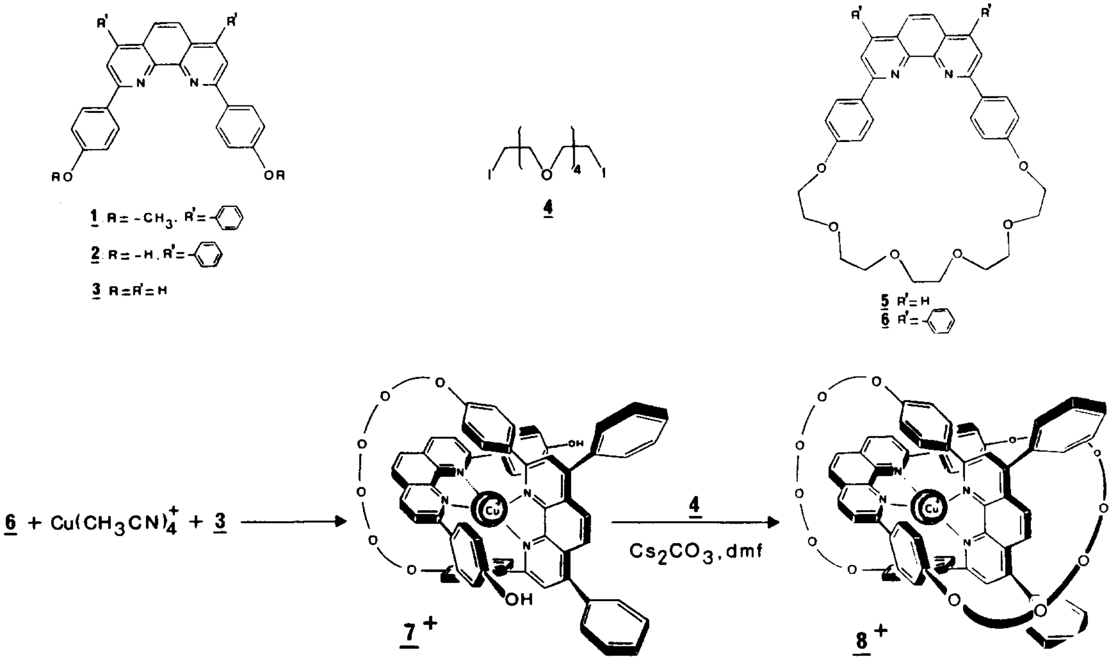


FIGURE 2

1 is prepared (80%; MP = 270°C) by reacting 4,7-diphenyl 1,10-phenanthroline with an excess of lithio-anisole, under conditions similar to those previously described[7]. Selective cleavage of the methyl ethers is performed at 200° in pyridinium chloride: 2 is obtained in 98% yield (MP > 320°C) as a purple compound when dry. Cyclization of 2 to 6 in the presence of 4 is carried out under high dilution conditions[9]: Cs_2CO_3 as base, in DMF at 60°C; yield = 53%; MP = 263°C. 8^+ was prepared according to Figure 2. Stepwise addition of $Cu(CH_3CN)_4^+.BF_4^-$ and 3 (stoichiometric amounts) to a CH_2Cl_2 solution of 6 gives quantitatively the precursor 7^+ as a dark red complex. The latter reacts with the di-iodo derivative 4, in the presence of Cs_2CO_3 (excess), under conditions analogous to those earlier described[7]. After work-up, the catenate 8^+ is isolated as its BF_4^- salt (MP = 289-290°C; yield: 7%); UV-vis absorption: λ_{max}nm (ε) = 247(67000), 300(52000), 454(4200); emission spectrum at room temperature in CH_2Cl_2 (excitation wavelength: 470 nm): λ_{em} = 716 nm, ϕ_{em} $(x10^4)$ = 5. Surprisingly, the catenate containing two of 5 as interlocking rings is also obtained in ~ 4% yield. The formation of this compound indicates that the precursor 7^+ (or its non-catenane alkylation products) is relatively unstable under the reaction conditions used: Cu^+ and 3 are able to dissociate from 7^+ and, subsequently, they can form the complex $Cu(3)_2^+$, precursor of the catenate $Cu(5)_2^+$[7]. The latter compound cannot be separated from 8^+ but it can be selectively decomplexed by KCN (fortunately, it is much less inert to CN^- attack than 8^+). Afterwards, the mixture is subjected to chromatographic separation. The free catenand 9 is obtained as a white solid (MP=298-299°C) in 75% yield from 8^+, by demetallation in the presence of a 20 fold excess of KCN, in CH_3CN/H_2O (6:1). The decomplexation reaction is extremely slow: it requires several days at room temperature and occasional addition of KCN. The decrease in dissociation rate constant for 8^+, as compared to $Cu(5)_2^+$, reflects the

effect of the two phenyl rings introduced in the rear of one phenanthroline (phen): the relative mobility of the two macrocyclic subunits is highly reduced if one polyoxyethylene fragment is confined between the two phenyl nuclei (form (II) of Figure 1). Such a situation allows only limited conformational changes and, as a consequence, makes copper(I) decomplexation particularly unfavourable. Due to the surprisingly high basicity of 9, protonation occurs during chromatographic separation on silica unless a basic eluent is used: CH_2Cl_2/CH_3OH/aq. NH_3 (33%) (90/8/2).

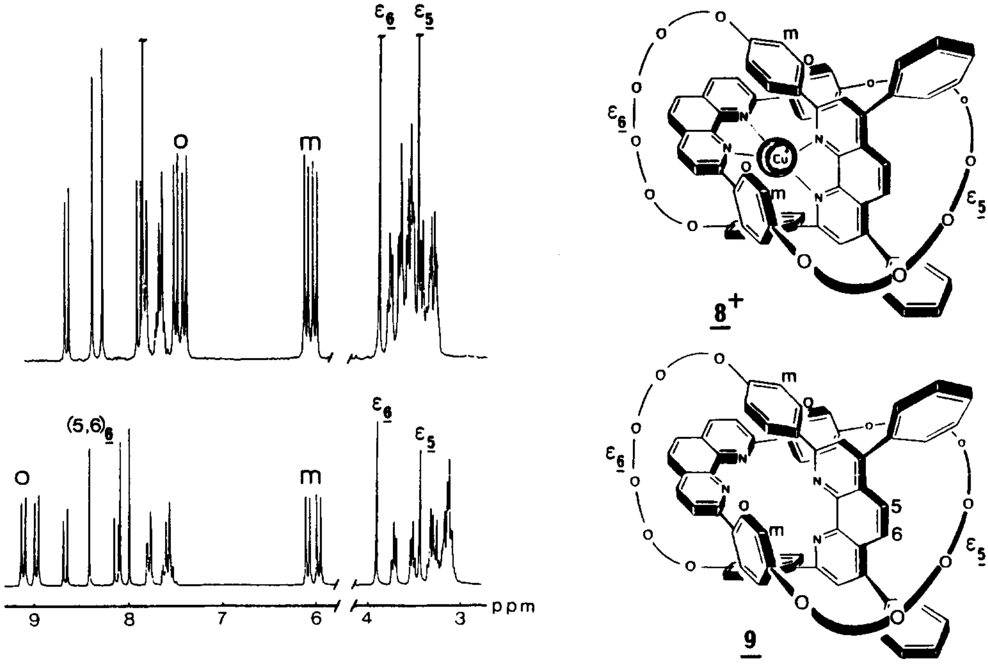


FIGURE 3

The ^{1}H-NMR spectra of $\underline{8}^+$ and 9 are represented in Figure 3. (200 MHz in CD_2Cl_2; reference: $CHDCl_2$ at 5.32 ppm). A comparison between the two spectra of Figure 3 confirms the restricted mobility of the catenand 9. In the latter, the two 2,9-diphenyl 1,10-phenanthroline (dpp) fragments are still entwined, although no gathering transition metal is present. This situation is drastically different from that observed when there are no phenyl rings in the back of one phenanthroline: in the catenand consisting of two interlocking 5 rings, the two dpp fragments are fully disentangled either in solution[7] or in the solid state[10]. The entwined geometry of 9 is clearly demonstrated by the chemical shift values of signals corresponding to some particular protons. For instance, the H_m protons appear at 5.96 and 6.08 ppm in 9 whereas for the analogous protons in 5, $\delta = 7.23$ ppm. The topography of 9 was confirmed by Nuclear Overhauser Effects (NOE). A large NOE value (4.2%) between the $CH_2\varepsilon$ protons of the 5 subunit and $H_{5,6}$ of the 6 component of 9 demonstrates that indeed the two dpp fragments of the latter are tightly entwined and that the polyoxyethylene link of 5 is in close proximity with the back of the phen nucleus of the other macrocyclic subunit. In the rigid catenand 9, predisposition of the coordination site should lead to novel complexing properties with respect to flexible catenands.

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4. It is noteworthy that (I) and (II) are **topographically** distinct (different shapes in euclidian geometry) due to the rigidity imposed by restricted rotation of one of the rings, but they are **topologically** identical. The bond connectivity (or the graph defined by the vertices and edges of the molecular system) is the same for both representations (I) and (II). It follows that the term "topo-isomer" is ambiguous, as shown in the present case: (I) and (II) are **topographical isomers** but are **topologically** indistinguishable. For a deeper discussion of the latter notions: see D.M. Walba, in "Chemical Applications of Topology and Graph Theory", R.B. King, Ed., Elsevier, Amsterdam, 1983; Tetrahedron, **41**, 3161 (1985).
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