

Transition Metal Directed Threading of Molecular Strings into Coordinating Rings

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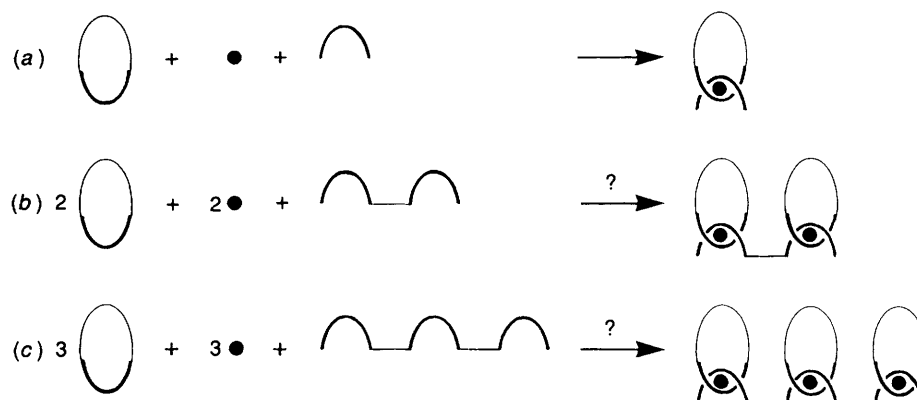
Multicomponent molecular systems consisting of rings, coordinating open-chain fragments and transition metals can be constructed at will; they consist of one or two rings threaded by the acyclic subunit, the various organic components being assembled *via* coordination to copper(I).

Transition metals have been used as assembling and templating species in a variety of processes.¹

The three-dimensional template effect of one or two copper(I) centres has extensively been used to construct topologically non-trivial molecules like catenanes and knots.²

Another approach, based on the formation of electron acceptor-donor aromatic stacks, has recently led to the preparation of various catenanes and rotaxanes.³

In order to make more entangled systems and topologically more complex and attractive chemical objects we investigated the behaviour of multi-chelate threads in the presence of coordinating rings and copper(I). The principle of the problem is indicated in Scheme 1. The driving force for building these multi-component structures is the formation of a bis-chelate complex. In fact, Cu^I and 2,9-diphenyl-1,10-phenanthroline (dpp) derivatives form very stable bis-ligand pseudo-tetrahed-



Scheme 1 Principle of the hypothetical multi-threading reaction. The coordinating fragments are indicated in thick line. The assembling metal centre is a black circle. (a): the well established quantitative threading of a monochelate with formation of a precursor to various catenanes.² (b) and (c): possible generalisation of the reaction to multi-metallic threaded systems.

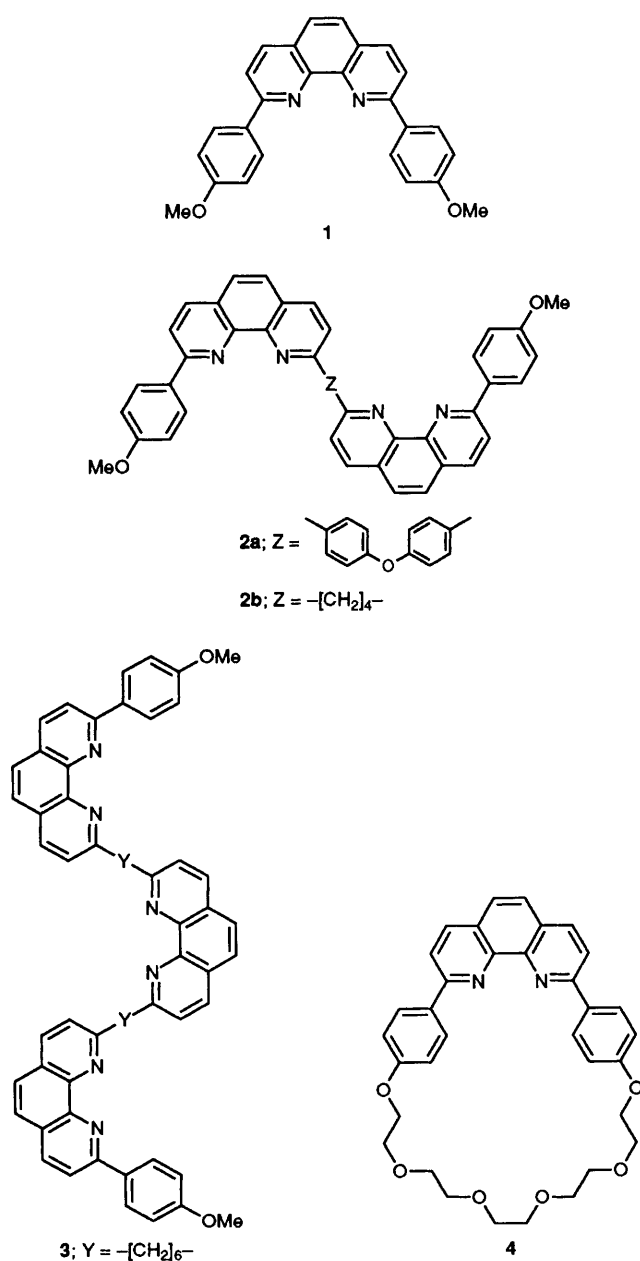


Fig. 1

ral complexes whereas monochelates of the type $\text{Cu}(\text{dpp})^+$ are much less stable.⁴ This has been applied in the simplest case [(a) of Scheme 1] with unambiguous and quantitative formation of the threaded product.² If the string contains several coordination sites, the situation may become more complex and less predictable.

The organic compounds investigated in the present study are represented in Fig. 1. The syntheses of **1**, **2b** and **4** have previously been reported.² **2a**[†] is a rigid bis-chelate fragment whereas **3**[‡] is a flexible three-coordination site thread.

1, **4** and copper(I) behave exactly as schematically represented in (a) of Scheme 1. The validity of principle (b) has also been experimentally demonstrated. By mixing **2a** or **2b** (1 equiv.), **4** (2 equiv.) and $\text{Cu}(\text{MeCN})_4^+\text{BF}_4^-$ in CH_2Cl_2 -MeCN a single complex was formed in both cases as shown by thin-layer chromatography (TLC) and ^1H NMR (Fig. 2). They correspond to the threaded system (b) of Scheme 1. Quantitative formation of these dinuclear compounds is expected since **2a** is too rigid and **2b** is too short to fold up and form a mononuclear copper(I) complex. The chemical reaction is depicted in Fig. 3(a).

The level of complexity increases further in the system containing **3**, **4** and copper(I). When a 1 : 3 : 3 mixture of **3**, **4** and $\text{Cu}(\text{MeCN})_4^+$ was prepared, a mixture of complexes and free ligands was obtained, in contradiction with (c) of Scheme 1. **3** is indeed flexible and should easily accommodate a curled-up conformation in which two of the three binding sites complex the same copper(I) centre intramolecularly. The third 1,10-phenanthroline subunit was then expected to be available for intermolecular reactions. In effect, when **3**, **4** and $\text{Cu}(\text{MeCN})_4^+$ were mixed in a 1 : 1 : 2 proportion, a single compound was formed. It has the formula $[\mathbf{3}, \mathbf{4}, \text{Cu}_2]^{2+}$ [ESMS, $M - \text{PF}_6$: obs. 1756.8 (calc. 1755.9); $M - 2\text{PF}_6$: obs. 805.8 (calc. 805.5)] and, as indicated in Fig. 3(b), it originates from intramolecular bis-chelate copper(I) complex formation and threading of the vacant site into the added ring **4**.

[†] **2a** was prepared from *p*-lithioanisole and phen-*p*- C_6H_4 -*O*-*p*- C_6H_4 -phen (phen = 1,10-phenanthroline). Phen-*p*- C_6H_4 -*O*-*p*- C_6H_4 -phen was obtained by an Ullmann coupling between 2-(*p*-bromophenyl)-1,10-phenanthroline and the sodium salt of 2-(*p*-phenol)-1,10-phenanthroline (overall yield: 40%).

[‡] **3** was obtained by reaction of the corresponding carbanion of 2-methyl-9-(*p*-anisyl)-1,10-phenanthroline with di-2,9-(5-bromopentyl)-1,10-phenanthroline in 78% yield. The dibromide derivative was prepared in three steps from neocuproine (2,9-dimethyl-1,10-phenanthroline) and 4-bromobutyl tetrahydropyran-2-yl ether.

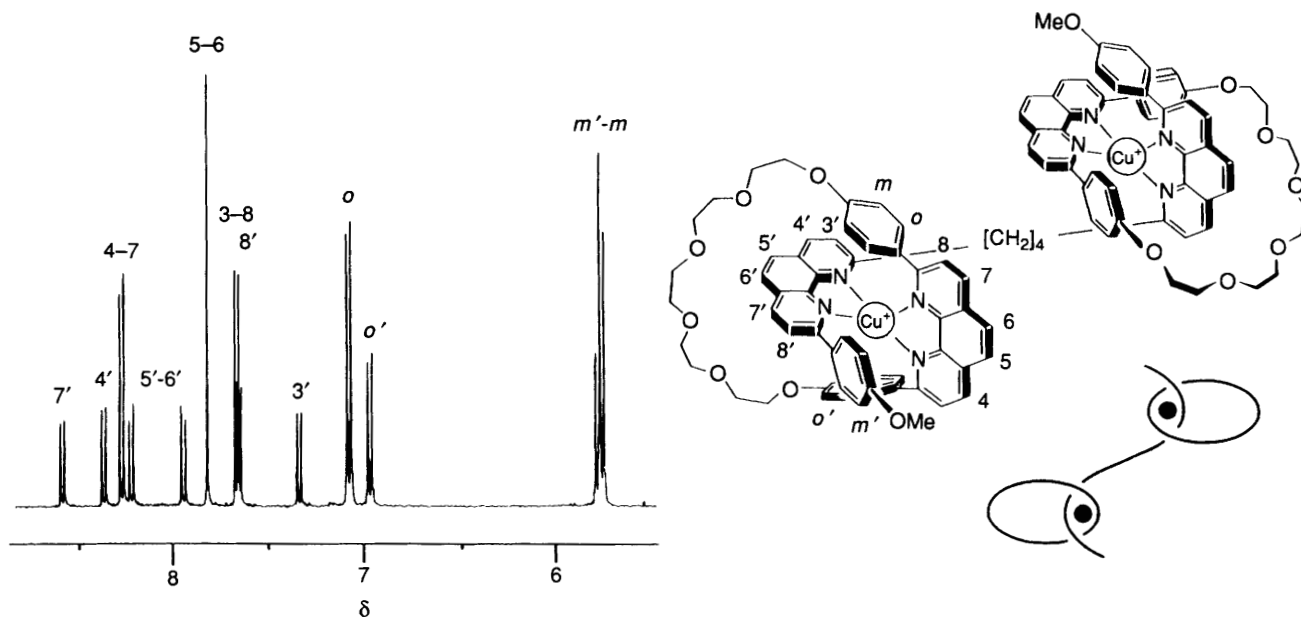


Fig. 2 400 MHz ^1H NMR spectrum of $[\mathbf{2b}, (\mathbf{4})_2, \text{Cu}_2]^{2+}$ (aromatic region) in CD_2Cl_2

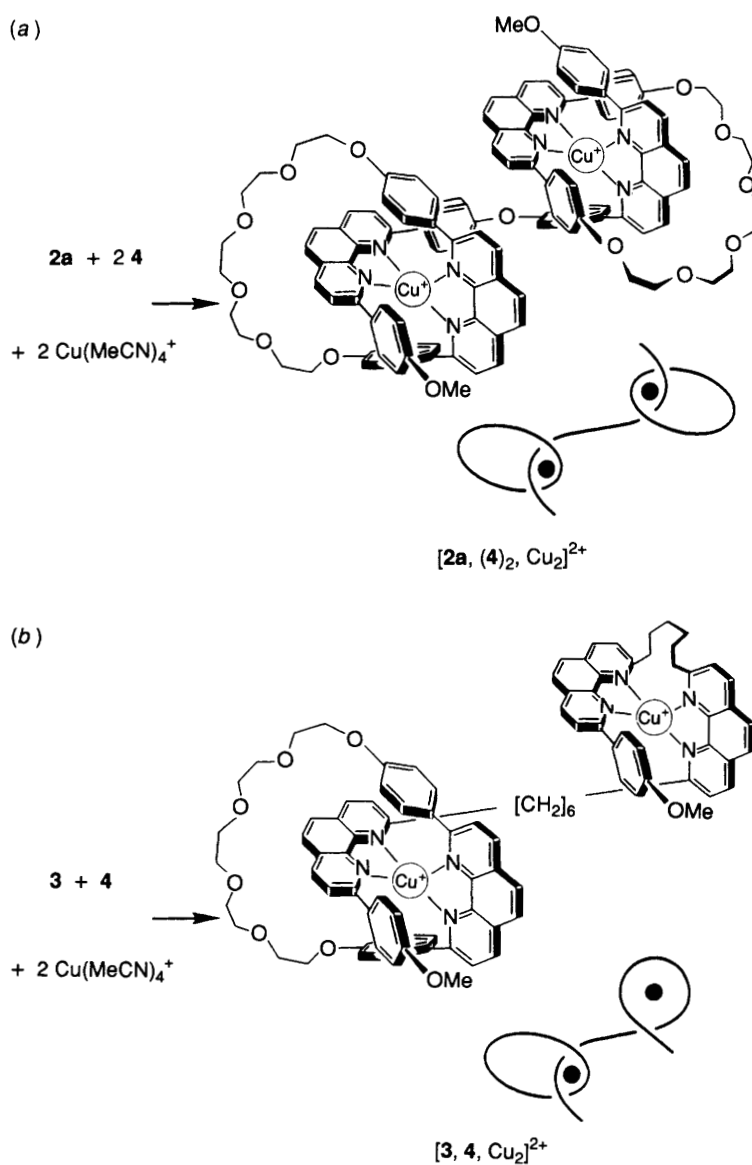


Fig. 3

In conclusion, it could be shown that the course of transition metal directed assembling and threading processes can be oriented by the proportion of components and structural parameters such as rigidity/flexibility of the strings to be threaded.

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