Electrochemically Triggerred Swinging of a [2]-Catenate

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Bistability is an essential property for imaging and information storage. Whereas spectacular results have recently been obtained with molecular assemblies and solids,[1,2] the phenomenon at the single molecule level is still very limited.[1,3] In relation to molecular bistability, an inorganic example has recently been described which demonstrates electrochemical hysteresis.[4] Some other related systems of linkage isomerism induced by a redox process have also been reported.[5-7]

We would now like to report a linkage isomerism reaction based on a new principle and utilizing a [2]-catenate, i.e., a transition metal complex whose organic backbone consists of two interlocked coordinating rings.[8] The interconversion between both forms of the complex is electrochemically triggered and corresponds to the sliding motion of one ring within the other. It leads to a profound rearrangement of the compound and can thus be regarded as a complete metamorphosis of the molecule.

The principle of the process is explained in Figure 1. Essential is the difference of preferred coordination number (CN) for the two different redox states of the metal: CN = 4 for copper(I) and CN = 5 (or 6) for copper(II).

The organic backbone of the asymmetrical catenate consists of a 2,9-diphenyl-1,10-phenanthroline (dpp) bidentate chelate included in one cycle and, interlocked to it, a ring containing two different subunits: a dpp moiety and a terdentate ligand, 2,2′,6′,2″-terpyridine (terpy). Depending upon the mutual arrangement of both interlocked rings, the central metal atom (copper, for instance) can be tetrahedrally complexed (two dpp's) or 5-coordinate (dpp + terpy). Interconversion between these two complexing modes results from a complete pirouetting of the two-site ring. It can, of course, be electrochemically induced by taking advantage of the different geometrical requirements of the two redox states of the copper(II)/copper(I) couple. From the stable tetrahedral monovalent complex, oxidation leads to a 4-coordinate Cu(II) state which rearranges to the more stable 5-coordinate compound. The process can be reversed by reducing the divalent state to the 5-coordinate Cu(I) complex obtained as a transient species before a changeover process takes place to afford back the starting tetrahedral monovalent state.

The synthetic strategy and the structures of the compounds made are given in Figure 2. The method is derived from the previously reported procedure developed for making various interlocking ring systems.[8]

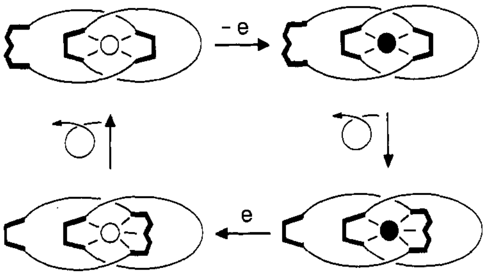

Figure 1. Principle of the electrochemically triggerred rearrangement of an asymmetrical [2]-catenate. The stable 4-coordinate monovalent complex [top left, the white circle represents Cu(I)] is oxidized to an intermediate tetrahedral divalent species [top right, the black circle represents Cu(II)]. This compound undergoes a complete reorganization process to afford the stable 5-coordinate Cu(II) complex (bottom right). Upon reduction, the 5-coordinate monovalent state is formed as a transient (bottom left). Finally, the latter undergoes the conformational change which regenerates the starting complex.

5,5′-Dimethyl-2,2′,6′,2″-terpyridine (**1**) was prepared from 2-acetyl-5-picoline according to a recently described methodology.[9] **2** was generated from **1** and LDA as a deep red compound. It was reacted with 1-bromo-2-(2′-tetrahydropyranyl)ethane to afford **3** (45% from **1**). Deprotection by HCl leads to **4** (81%), which is converted first to the dimesylate **5** in 71% yield by reaction with CH_3SO_2Cl and then to the dibromo derivative **6** by reacting **5** and anhydrous LiBr in acetone (95%).

7[10] and **6** were reacted in DMF (60 °C under argon) in the presence of Cs_2CO_3 under experimental conditions similar to those used previously for making related macrocycles.[10] **8** was obtained as a white solid in 57% yield.

The threaded precursor $\mathbf{9}^+$ was formed quantitatively by mixing stoichiometric amounts of $[Cu(CH_3CN)_4{}^+][PF_6{}^-]$, **8**, and **7** in CH_3CN–CH_2Cl_2–DMF (15:25:25 v/v) at room temperature. $[\mathbf{9}^+][PF_6{}^-]$ is a deep red solid. The cyclization reaction leading to the copper(I) catenate $\mathbf{10}^+$ was carried out by slowly adding a DMF solution of a mixture of $[\mathbf{9}^+][PF_6{}^-]$ and the diiodo derivative of hexa(ethylene glycol), $ICH_2(CH_2OCH_2)_5CH_2I$, to a vigorously stirred suspension of Cs_2CO_3 in DMF, at 60 °C under argon. $[\mathbf{10}^+][PF_6{}^-]$ was obtained in 10% yield as an intense red crystalline solid.[11]

By applying the principle of Figure 1 to $\mathbf{10}^+$, it is clear that for the same oxidation state (either Cu(I) or Cu(II)), the two forms should display significantly different physical properties. In particular, it is expected that the spectroscopic and electrochemical properties of the divalent copper catenates depend strongly on the coordination number of the metal.[12] This could be demonstrated by oxidizing the copper(I) catenate $\mathbf{10}^+$ and subsequently monitoring the absorption spectrum and the redox properties of the divalent complex obtained as a function of time. $\mathbf{10}_{(4)}{}^{2+}$, the tetrahedral Cu(II) species (the subscript *4* indicates the coordination number) obtained immediately after oxidation, either by Br_2 or via electrolysis, is a deep green complex in solution (λ_{max} = 670 nm; ϵ = 830 M^{-1} cm^{-1} in CH_3CN). This is in agreement with previous studies on another copper catenate (Cu(II): λ_{max} = 685 nm; ϵ = 800 M^{-1} cm^{-1} in CH_2Cl_2). The electronic spectrum of the oxidized solution changes with time.

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[11] All the new compounds were characterized by ^1H NMR (200 MHz), UV–vis, and mass spectroscopy. $[\mathbf{10}^+][PF_6{}^-]$: visible absorption spectrum (MLCT band), λ_{max} = 437 nm, ϵ = 2500 M^{-1} cm^{-1}; FAN-MS, molecular ion peak at 1350.2 (calcd for $\mathbf{10}^+$, 1350.47).

[12] For recent studies on 5-coordinate Cu(I) and Cu(II) complexes with imine-type ligands, see: Goodwin, J. A.; Stanbury, D. M.; Wilson, L. J.; Eigenbrot, C. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2979–2991. Goodwin, J. A.; Bodager, G. A.; Wilson, L. J.; Stanbury, D. M.; Scheidt, W. R. *Inorg. Chem.* **1989**, *28*, 35–42. Goodwin, J. A.; Wilson, L. J.; Stanbury, D. M.; Scott, R. A. *Inorg. Chem.* **1989**, *28*, 42–50.

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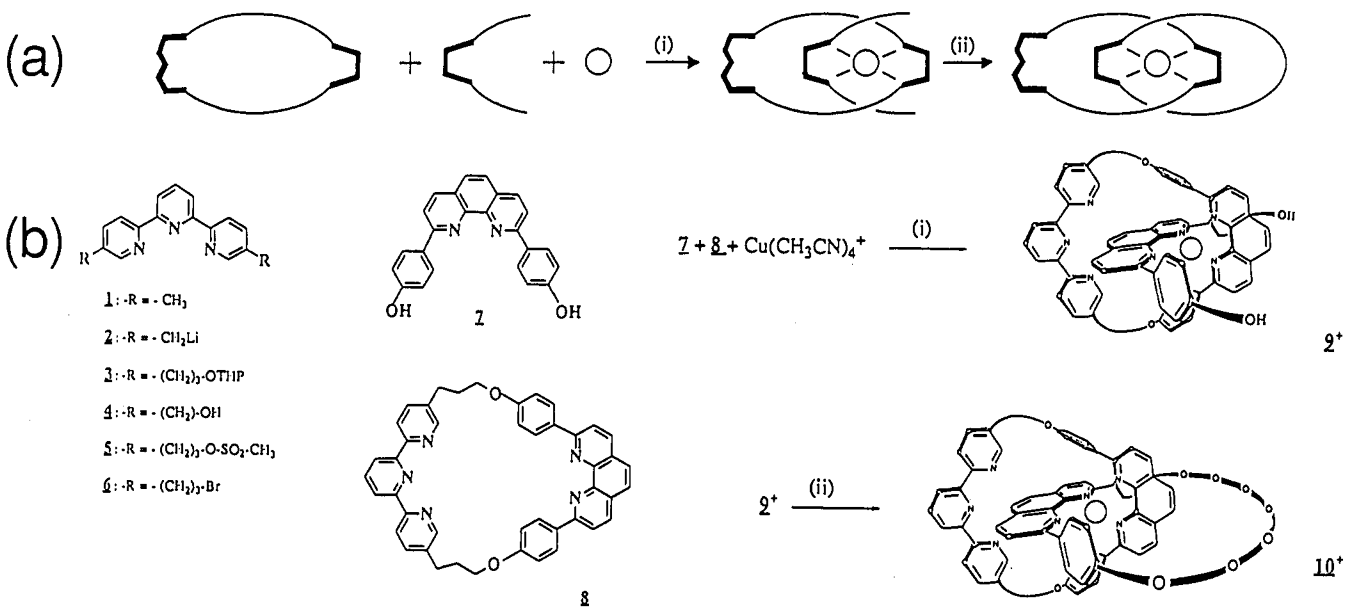

Figure 2. (a) Strategy used for constructing a two-binding-mode [2]-catenate. The starting macrocycle incorporates two different chelates: (i) the gathering and threading step and (ii) the cyclization reaction. The circle represents Cu(I). (b) The compounds made in the present work and the catenate formation reaction. (i) Room temperature, CH_3CN; (ii) 60 °C, DMF, Cs_2CO_3, $ICH_2(CH_2OCH_2)_5CH_2I$.

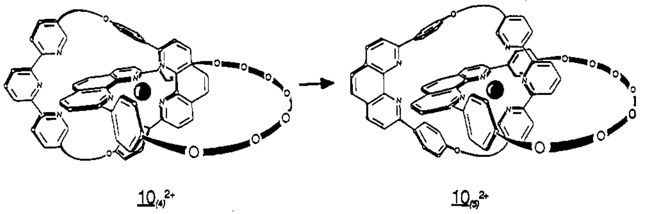

Figure 3. Changeover reaction $10_{(4)}^{2+} \rightarrow 10_{(5)}^{2+}$ [the black circle represents Cu(II)].

A drastic intensity decrease around 670 nm is observed within a few days to give a pale yellow-green complex. This slow process is in agreement with the changeover reaction represented in Figure 3 and leading to the 5-coordinate copper(II) complex $\mathbf{10}_{(5)}^{2+}$, in which a coordinated dpp chelate has been replaced by the incoming terpy unit belonging to the same cycle. The spectral properties of the starting species $\mathbf{10}_{(4)}^{2+}$ and its isomeric product $\mathbf{10}_{(5)}^{2+}$ are in accordance with the coordination number and the geometry assumed around each copper center.[12,13] Interestingly, the transformation of Figure 3 is accompanied by a change in the electrochemical properties of the complex, paralleling the spectroscopic changes. As expected, the tetrahedral copper complex has a relatively high redox potential,

$$\mathbf{10}_{(4)}^{2+}/\mathbf{10}_{(4)}^{+}:\ E^\circ = +0.63\ \text{V vs SCE in}\ CH_3CN$$

whereas the 5-coordinate species has a slightly negative potential, pointing to the greater stabilization of the divalent copper than in the 4-coordinate species,

$$\mathbf{10}_{(5)}^{2+}/\mathbf{10}_{(5)}^{+}:\ E^\circ = -0.07\ \text{V}$$

The electrochemical processes are reversible ($\Delta E\text{p} \sim 60$ mV) for both complexes. Both methods (electrochemical and spectroscopic) afford similar kinetics. The conversion $\mathbf{10}_{(4)}^{2+} \rightarrow \mathbf{10}_{(5)}^{2+}$ is first-order, with a rate constant of $2 \times 10^{-5}\ \text{s}^{-1}$ at 20 °C in CH_3CN.

Finally, reduction of $\mathbf{10}_{(5)}^{2+}$ can quantitatively be carried out by electrolysis to regenerate the starting copper(I) complex:

$$\mathbf{10}_{(5)}^{2+} \xrightarrow{e} \mathbf{10}_{(5)}^{+} \rightarrow \mathbf{10}_{(4)}^{+}$$

Preliminary electrochemical studies indicate that the rearrangement $\mathbf{10}_{(5)}^{+} \rightarrow \mathbf{10}_{(4)}^{+}$, which restores the initial species, is relatively fast in CH_3CN (seconds). The changeover process of the monovalent complex, $\mathbf{10}_{(5)}^{+} \rightarrow \mathbf{10}_{(4)}^{+}$, is much faster than the reverse rearrangement on the divalent copper complex. The sliding process has to involve decoordination of the metal at some stage, and, clearly, this step is expected to be much slower for Cu(II) than for Cu(I) due to the greater charge of the former cation. Previous kinetic studies on the metalation reaction of a catenand and involving related sliding motions pointed to the importance of the nature of the metal center and the oxidation state,[14] in accordance with the present observation. The reaction cycle of Figure 1 could thus be completed. The overall process is related to some other conformational changes involving catenanes and rotaxanes, as recently reported by others on purely organic compounds.[15]

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Supplementary Material Available: Electronic spectra and electrochemical properties of both forms of the copper catenate (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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