

Review

Heteroleptic copper phenanthroline complexes in motion: From stand-alone devices to multi-component machinery

Abir Goswami, Michael Schmittel*

Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany

ARTICLE INFO

Article history:

Received 31 May 2018

Received in revised form 7 July 2018

Accepted 13 August 2018

Keywords:

Copper
Phenanthroline
Diimine
Kinetics
Rate
Molecular machines
Devices
Switches

ABSTRACT

Two and a half decades of copper phenanthroline-based switches, devices and machines have illustrated the rich dynamic nature of these metal complexes. With an emphasis on the metal-ligand dissociation as the rate-determining step the present review summarizes not only spectacular examples of machinery, but also highlights rate data collected during a variety of investigations. Copper-ligand exchange reactions are mostly triggered by redox processes, addition of metal ions or addition of ligands. While the rate data spread over >8 orders of magnitude, individual effects of solvent, steric bulk, flexibility, σ -basicity and the trajectory (intra- vs. intermolecular dissociation) have large impact. Unfortunately, in many cases the exact mechanism in the rate-determining step (nucleophile-induced vs. monomolecular metal-ligand dissociation) has not been determined, suggesting to invest further efforts in the physical (in)organic chemistry of such coordination-driven systems.

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* Corresponding author.

E-mail address: schmittel@chemie.uni-siegen.de (M. Schmittel).

1. Introduction

This review focuses on heteroleptic copper(I) phenanthroline and some selected diimine complexes because of their eminent role in coordination-based molecular machines. The reason for this exceptional standing is three-fold: (a) among the large amount of thermodynamically strong metal complexes, the copper-phenanthroline interaction is highly labile, thus allowing motion-based devices via rate-determining metal-ligand dissociation. (b) Moreover, several strategies are known (*vide infra*) that allow the clean preparation of heteroleptic complexes, which is a key prerequisite for structurally diverse molecular machinery. (c) Since NMR characterization is imperative, the diamagnetic nature is another factor suggesting use of copper(I) ions. We are grateful to Jean-Pierre Sauvage for initiating the field and providing continued inspiration over several decades through the demonstration of fascinating copper(I)-based catenane and rotaxane machines [1].

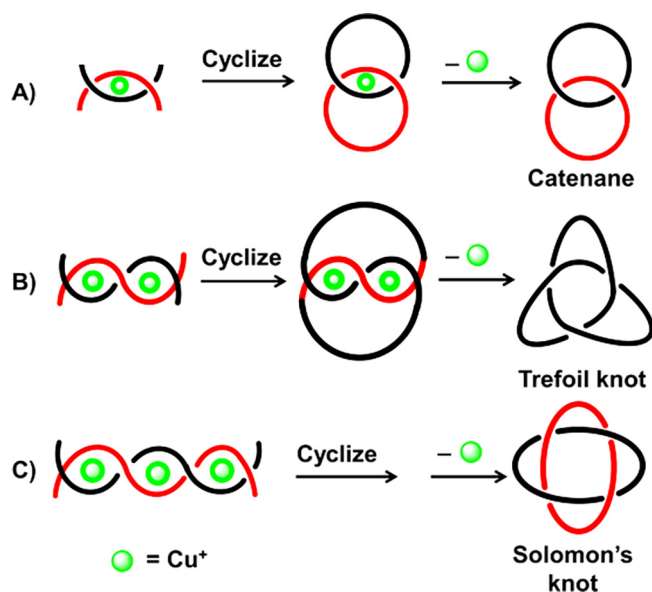


Fig. 1. Strategies for making mechanically interlocked molecules.

As distinct states of switches, devices and machines sometimes go along with major constitutional change(s) we will use different numbers for the very same multifunctional ligand & metal ion ensemble depending on the connected binding site(s). The $N_{\text{phen}} \rightarrow$ copper(I) phenanthroline interaction (with phen representing any phenanthroline) has been exploited in a variety of mechanically interlocked molecules, nanoswitches and nanorotors in the past decades [1]. We will denote this general complexation motif as $[\text{Cu}(\text{phen})_2]^+$, with the superscript expression in brackets describing the coordination number of the metal ion.

2. Selected examples of stand-alone switches, devices and machines

2.1. Topological control

Interlocked structures, in particular rotaxanes or catenanes, are ideally suited for designing molecular machines due to the fact that motion is possible without dissociation of components. Moreover their preparation is facilitated by the template effect [2] as impressively demonstrated by Sauvage in 1983. Over the years this method has developed into a highly successful strategy for preparing copper(I) phenanthroline-based catenanes (Fig. 1), and several other types of interlocked molecule, such as rotaxanes [3], molecular knots [4] etc., equally became accessible by this approach. In the 80s and early 90s, control and variation of the topological outcome was a main focus of Sauvage's work [5]. In particular for the fabrication of knots, a series of fascinating designs were developed, but throughout this work the lability of copper(I) phenanthroline complexes was not used for machine-type of motions, rather only to remove the copper for preparing the metal-free structures.

Use of the intrinsic lability of the $[\text{Cu}(\text{phen})(\text{L})]^+$ complex ($\text{L} =$ any ligand) for machine-type function was elaborated by Sauvage in 1994 [6]. The electrochemically triggered swinging in the $[\text{Cu}(\text{phen})_2]^+$ -based [2]-catenate $[\text{Cu}(\mathbf{1})]^+$ (Fig. 2) relies on the different coordination preferences of copper(I) vs. copper(II) and follows a four-step mechanism. First, the stable tetracoordinated copper(I) complex $[\text{Cu}(\mathbf{1})]^+$ is oxidized to the intermediate tetrahedral species $[\text{Cu}(\mathbf{1})]^{2+}$. However, since this complex contains the copper (II) ion in a thermodynamically less favorable tetracoordination, it

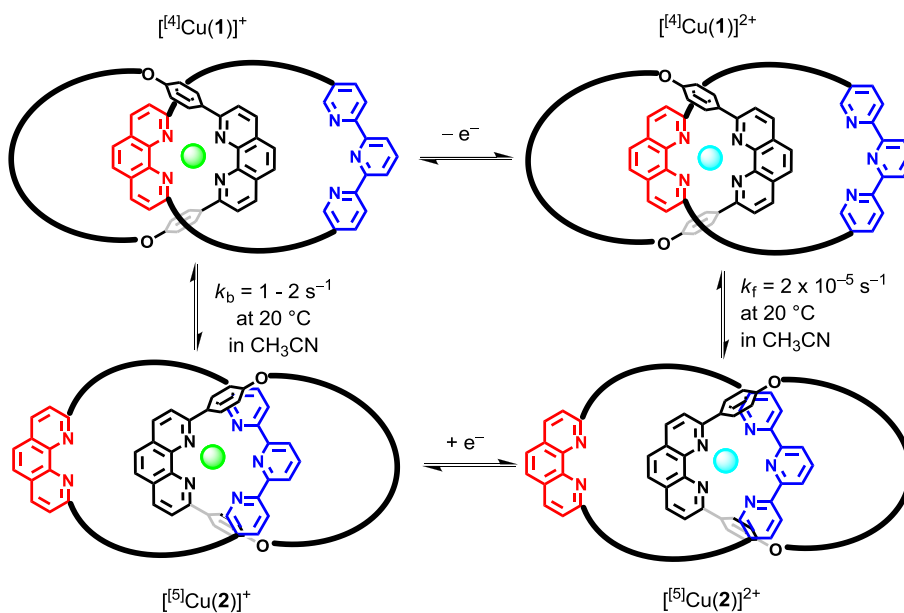


Fig. 2. Electrochemically triggered dynamics in an [2]-catenate [6].

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