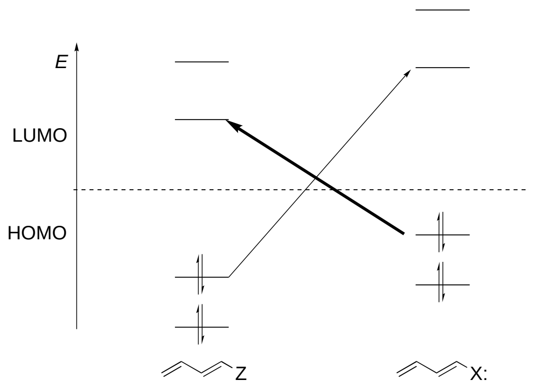

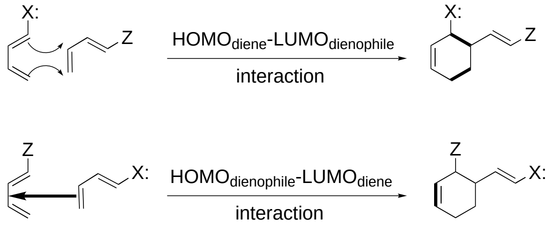

Scheme 5. The dominant interaction in cross-cycloaddition experiments leads to different orbitals in the final cycloadduct depending on the reaction path.

prove useful in predicting more accurately the reactivity of dienes and dienophiles. It will likely have repercussions on predictions of the regio- and stereoselectivity of the process as well.

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Kinetic and Thermodynamic Control in Self-Assembly: Sequential Formation of Linear and Circular Helicates

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Alain Van Dorsselaer

The self-assembly of polynuclear metal coordination compounds has been very actively investigated in recent years, in particular that of complexes presenting a helical arrangement of ligand strands.[1–3] Whereas most of these helicates present linear axes, circular helical architectures have also been reported.[4–6] We recently described the self-assembly of circular helicates based on the octahedral coordination of three tris-bipyridine ligands such as **L** (see Figure 1) with iron(II) ions.[4, 5] On the other hand, with nickel(II) ions ligand **L** had earlier been found to lead to the formation of a complex presenting a triple-helicate structure.[7] Thus, the same ligand yields two different architectures with two metal ions that display the same coordination geometry. In view of these intriguing results we decided to follow more closely the self-assembly process, in order to gain insight into the structural, mechanistic, and physicochemical factors that may be at play.

In particular, whereas in the self-assembly of both synthetic and biological systems the thermodynamic product is usually formed (and should finally result in reversible equilibrium conditions), kinetic products may also be obtained if the shape of the energy hypersurface is such that the system becomes trapped in local minima. Indeed, self-assembly[1] is evidently a time-dependent process, and it may thus display kinetic control.

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An equimolar mixture of ligand **L** (Figure 1) and $FeCl_2$ in ethylene glycol at a concentration of 10^{-3} M was heated to 170 °C for 50 min. Addition of aqueous NH_4PF_6 resulted in precipitation of a red solid, which was isolated by centrifugation. Thin layer chromatography (TLC) showed, beside a very small amount of $[5]^2$**cH**,[8] a single compound which was less polar than $[5]^2$**cH**; it was purified by several recrystallizations from acetonitrile/diethyl ether and analyzed. Its UV/Vis spectrum presents a band at 517 nm typical of the metal-to-ligand charge transfer (MLCT) band of a $[Fe(bipy)_3]$-type complex.[9] The ^1H NMR spectrum displays two singlets (of 2:1 relative intensity due to superposition of two singlets) and six doublet signals in the aromatic region, indicating that all the ligands in the complex are equivalent and that there is an axis of symmetry passing through the central C(2)–C(2′) bond. The CH_2CH_2 bridges give two AA′BB′ multiplets around $\delta = 2.1$ and 3.4. Electrospray mass spectrometry (ES-MS) indicates a complex $[Fe_3L_3](PF_6)_6$; all the signals observed correspond to $[Fe_3L_3]^{6+}$ with zero to four PF_6^- anions. Elemental analysis is also in agreement with the stoichiometry $[Fe_3L_3](PF_6)_6$.

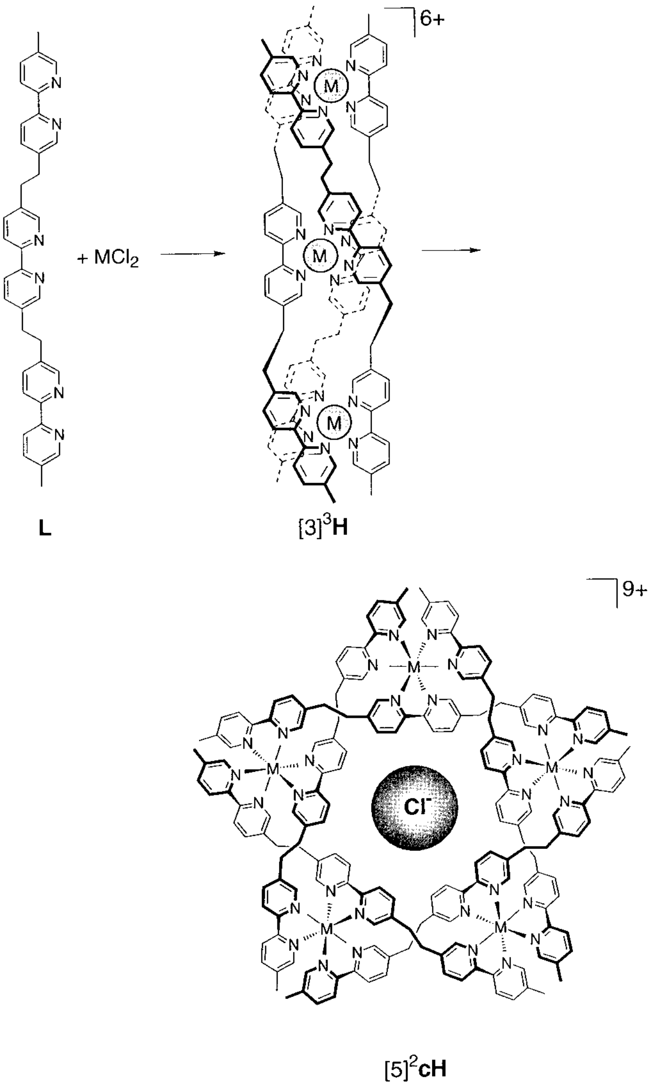

Figure 1. The chronological (but not necessarily mechanistic) sequence of self-assembly processes yielding first a triple helix $[3]^3$**H** and thereafter a circular double helix $[5]^2$**cH** as kinetic and thermodynamic products, respectively. M = Fe^{II} or Ni^{II}.

The cell parameters determined for a single crystal of this complex by X-ray diffraction were found to be identical to those reported for $[3]^3$**H**-Ni^{II},[7] and its structure was therefore not determined. One may conclude that the complex obtained is the iron(II) triple helicate $[3]^3$**H**, which is isostructural to the corresponding nickel(II) helicate.[7] The self-assembly of the ligand **L** and $FeCl_2$ thus yields the triple helicate $[3]^3$**H** after a relatively short reaction time, whereas the circular helicate $[5]^2$**cH** is obtained after prolonged heating.[4] We therefore decided to study the course of the reaction as a function of time.

An equimolar mixture of the ligand **L** with $FeCl_2$ in ethylene glycol ($c = 5 \times 10^{-3}$ M) was heated to 170 °C. At regular intervals, a sample of the solution was added to an aqueous solution of NH_4PF_6, and the red precipitate was isolated and analyzed by ^1H NMR spectroscopy and ES-MS.

Figure 2 shows the evolution of the aromatic part of the ^1H NMR spectra. The formation of $[3]^3$**H** is complete already after 1 min. Thereafter the signals of $[5]^2$**cH** appear, as well as signals belonging to minor intermediate species. After about 24 h all the complexes are converted into $[5]^2$**cH**. This experiment clearly indicates a chronological sequence of self-assembly processes. The initially formed trinuclear $[3]^3$**H** disassembles, at least partially, to allow generation of the pentanuclear $[5]^2$**cH**.

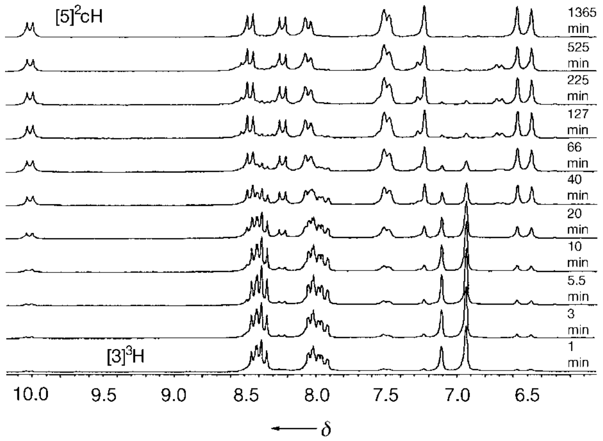

Figure 2. ^1H NMR spectra showing the formation of $[3]^3$**H**-Fe^{II} and its conversion into $[5]^2$**cH**-Fe^{II}. For further details, see the text.

The same samples were also analyzed with ES-MS. The first spectrum shows exclusively the triple helicate $[3]^3$**H**, and the last spectrum the circular helicate $[5]^2$**cH** (Figure 3). The intermediate spectra display the signals of both species. The relative intensities of the signals correlate well with the abundance of the complexes determined by NMR spectroscopy. The minor species observed by NMR spectroscopy correspond to complexes of the composition $[Fe_5L_5]^{10+}$ and $[Fe_5L_5(H_2O)_2]^{10+}$; they probably present a noncyclic arrangement as the ^1H NMR spectrum does not show the signal at $\delta = 9.0$, which is characteristic of the chloride-free cyclic

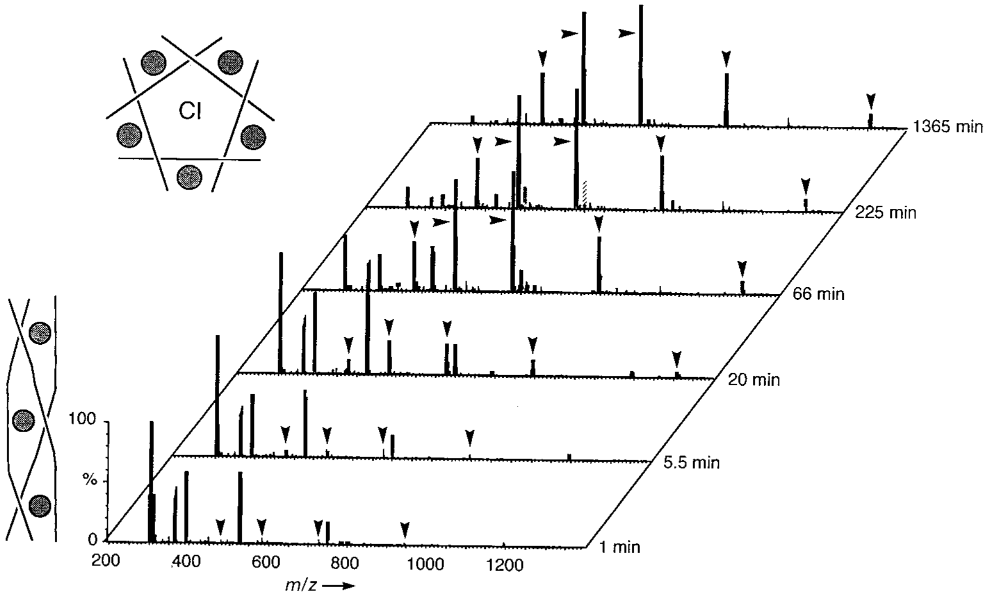

Figure 3. ES mass spectra showing the conversion of $[3]^3$**H**-Fe^{II} into $[5]^2$**cH**-Fe^{II}; the peaks of the latter are indicated by the arrowheads.

species $[5]^2$**cH** obtained by treating the chloride-containing species with a silver salt.

The self-assembly experiment was repeated at different concentrations, and the samples were analyzed by ES-MS. At 10^{-3} M, the formation of the triple helicate $[3]^3$**H** took about 25 min; it transformed slowly into $[5]^2$**cH**, but this conversion was not complete after 22 h. At a concentration of 10^{-2} M, the conversion of $[3]^3$**H** into $[5]^2$**cH** reached 80% already after 60 min, and was quantitative according to the NMR spectrum after 9 h. On the other hand, after 22 h all traces of $[3]^3$**H** had disappeared in the ES mass spectra. Thus, the rate of self-assembly of $[3]^3$**H** and $[5]^2$**cH** increases with concentration, as expected for a multicomponent process. More detailed study of the rate law may provide information about the mechanism of the assembly.

The present results indicate that the triple helicate is a kinetic product, formed reversibly from the components, which progressively converts into the thermodynamic product, the circular helicate $[5]^2$**cH**. The higher stability of $[5]^2$**cH** might be attributed to several factors, such as strain in the bound ligand and/or at the coordination centers, or electrostatic interaction with the included chloride anion. On the other hand, while these enthalpic contributions may drive the formation of the pentanuclear complex, it should be entropically less favorable than the trinuclear complex.

Since the Fe^{II} ions form initially the same triple helicate as Ni^{II}, it should in principle also be possible to form the circular pentanuclear architecture with nickel(II), as is the case with iron(II). To facilitate the conversion of $[3]^3$**H** into $[5]^2$**cH**, we searched for a way to accelerate the dissociation of the metal centers. It is known that lowering the pH by inducing protonation of the bipyridine nitrogen atoms increases the rates of decomplexation.[10, 11] An equimolar mixture of $NiCl_2$ and **L** in ethylene glycol was therefore heated to 190 °C in the presence of HCl. Following the initial formation of $[3]^3$**H**-Ni^{II}, ES-MS indicated the appearance of the circular helicate $[5]^2$**cH**-Ni^{II}, containing a single Cl^- ion like $[5]^2$**cH**-Fe^{II}. One may therefore consider that both complexes present an analogous structure. After a reaction time of four days, a 2:1 mixture of $[5]^2$**cH**-Ni^{II} and $[3]^3$**H**-Ni^{II} was obtained, as determined by ES-MS. Further transformation was not observed due to the slow decomposition of the ligand at the high reaction temperatures.

In conclusion, we have shown that both architectures $[3]^3$**H** and $[5]^2$**cH** can be obtained with either iron(II) or nickel(II) ions. The triple helicate is a kinetic product and is formed first and reversibly. It thereafter disassembles, and the system progressively transforms into the circular helicate. Although the formations of $[3]^3$**H** and $[5]^2$**cH** were observed successively, the triple helicate does not necessarily have to lie on the mechanistic pathway leading from the components $FeCl_2$ and **L** to $[5]^2$**cH**.[12] Preliminary kinetic studies show that the disappearance of $[3]^3$**H**-Fe^{II} follows a double-exponential decay. This indicates the possible existence of more than one mechanistic pathway from $[3]^3$**H** to $[5]^2$**cH**.

It is clear that in the self-assembly of complex architectures a number of kinetic products may appear before formation of the thermodynamic product(s). Indeed, self-assembly processes operate on energy hypersurfaces that may present both local and overall minima corresponding to kinetic and thermodynamic products, respectively. Depending on the heights of the related energy barriers a given process may display kinetic and/or thermodynamic control under a given set of conditions. In the present system, both the kinetic and thermodynamic products can be directly observed because of the slow rates of interconversion. Further studies are needed to establish the mechanistic pathways involved and the factors influencing this unique sequence of self-assembly processes. Finally, the intervention of kinetic control also points to extensions involving the role of nonequilibrium features in self-organization processes.[13]

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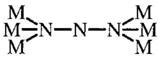
A μ-1,1,1,3,3,3 Azide Anion inside a Trigonal Prism of Silver Centers[**]

Guo-Cong Guo and Thomas C. W. Mak[*]

Dedicated to Professor George A. Jeffrey
on the occasion of his 83rd birthday

Azide compounds have been known for more than a century and continue to attract much current interest.[1] The field has undergone quite spectacular advances in the last decade for three main reasons: 1) covalent inorganic azides are potentially better explosives than lead azide, which is used as a detonator;[2] 2) the μ-azido bridging ligand is undoubtedly one of the most versatile ingredients for the creation of new materials with different magnetic properties, leading to an intensive study of magnetostructural correlations in discrete complexes as well as in polymeric one-, two-, and three-dimensional systems;[3] 3) azido complexes can serve as precursors in preparative materials chemistry as a source of atomic nitrogen.[4] As a sequel to our study on the bonding interaction between silver(I) atoms and the acetylenediide anion, C_2^{2-},[5] we have turned our attention to the isoelectronic cyanide ion CN^-,[6] as well as the azide ion N_3^-, as these species have been well studied together with N_2 in comparative substrate binding to the FeMo cofactor of nitrogenase.[7]

Up to now the known coordination modes of the azido ligand in transition metal complexes are terminal monodentate or bridging bidentate (μ-1,1; μ-1,3), tridentate (μ-1,1,1; μ-1,1,3), and tetradentate (μ-1,1,3,3; μ-1,1,1,3).[8] Herein we report a novel compound $AgN_3\cdot 2AgNO_3$ in which the azide unit exhibits an unprecedented bridging hexadentate (μ-1,1,1,3,3,3) coordination mode as an encapsulated species inside a trigonal prism (Scheme 1).



Scheme 1. Schematic representation of the μ-1,1,1,3,3,3 coordination mode of the azido ligand in the Ag_6 prisms of $AgN_3\cdot 2AgNO_3$.

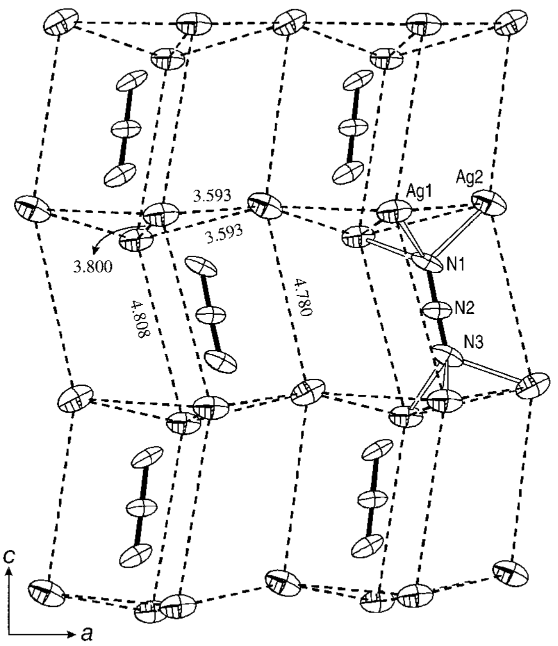


Figure 1. Layer-type framework in $AgN_3\cdot 2AgNO_3$ built of filled and empty trigonal prisms viewed along the b direction. The lengths [Å] of the edges of a prism are shown. For clarity, the nitrate anions have been omitted, and Ag–N bonds are shown only for one of the encapsulated azide ions. Selected bond lengths [Å] and angles [°]: Ag1–N3^{i} 2.409(1), Ag1–N1 2.503(1), Ag2–N1 2.278(2), Ag2–N3^{ii} 2.351(2), N1–N2 1.239(2), N2–N3 1.174(2); N2-N1-Ag(2) 122.09(15), N2-N1-Ag1 118.21(8), N3-N2-N1 179.4(2), N2-N3-Ag2^{iii} 120.0(2), N2-N3-Ag1^{iv} 119.80(7). Symmetry codes: i: $-x, -y, z+1/2$; ii: $-x-1, -y, z+1/2$; iii: $-x-1, -y, z-1/2$; iv: $-x, y, z-1/2$.

The layer-type framework in $AgN_3\cdot 2AgNO_3$ can be regarded as constructed from a stacking of slant trigonal prisms each composed of silver atoms at its vertices with azide units imprisoned within half of them (Figure 1). The filled and hollow prisms are stacked on their trigonal faces to form a zigzag column extending along the c direction. Such prismatic columns share rectangular faces and edges alternately along the a direction to generate a grooved slab, with pendant η^1-nitrate anions attached to Ag1 atoms on both sides (Figure 2). In any filled trigonal prism, the Ag2 atoms and the encapsulated azide unit all lie on the same mirror plane. The azide unit in $AgN_3\cdot 2AgNO_3$ is linear and asymmetrical (N1–N2 1.239(2), N2–N3 1.174(2) Å), which is consistent with its Raman spectrum. The terminal N atoms of the azide ligand are each asymmetrically bound to two Ag1 and one Ag2 atoms (Ag1–N1 2.503(1), Ag2–N1 2.278(2), Ag1–N3 2.409(1), Ag2–N3 2.351(2) Å), and the bond angles Ag-N1-N2 and Ag-N3-N2 lie in the range of 118.2 to 122.1°. It is

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