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Subcomponent Assembly and Transmetalation of Dinuclear Helicates**

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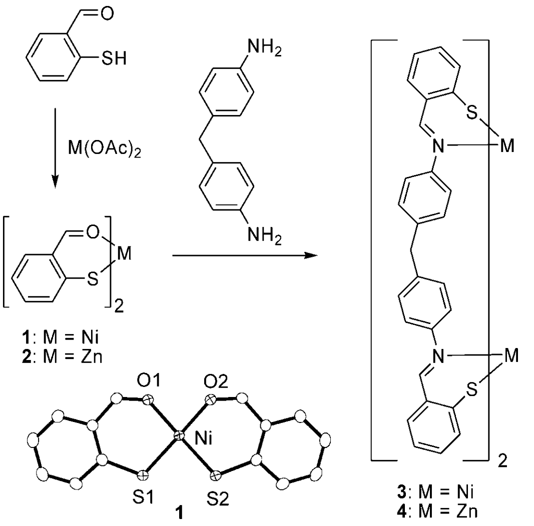
Metallosupramolecular self-assembly strategies and principles have been thoroughly investigated in the past 20 years with the aim of mimicking nature's ability to assemble impressive supramolecular structures.[1] Despite the remarkable metal selectivity and recognition in self-assembly reactions, directed metal exchange (i.e. transmetalation) in such supramolecular structures is still underdeveloped,[2] which is surprising as transmetalation is the missing link between the currently known self-assembly strategies "classical self-assembly" and "subcomponent self-assembly". Classical self-assembly of pre-designed ligands with suitable metal ions is a powerful tool, and is most impressively demonstrated by the synthesis of molecular clusters and their application as hosts,[3] catalysts,[4] and molecular traps.[5] However, this strategy is limited by the often time-consuming synthesis of pre-designed ligands and their intrinsic stability.[6] Developing an alternative approach, Nitschke et al. recently described the "subcomponent self-assembly" strategy, which is based on the reversible condensation of suitable amines at metal-coordinated aldehydes under formation of the thermodynamically most stable product.[7] Although this strategy has led to impressive results, such as the assembly of an unlockable–relockable molecular cage,[8] it is still limited by the need for stable (subcomponent) precursor complexes that allow reversible imine formation within their metal coordination sphere.[8,9]

Transmetalation of supramolecular structures obtained by classical or subcomponent assembly constitutes a promising strategy to overcome these shortcomings. Following this strategy, supramolecular structures containing ligands not accessible by conventional organic synthesis could be obtained by subcomponent assembly, and transmetalation will subsequently allow the use such ligands in classical supramolecular chemistry. Herein, we present the subcomponent self-assembly of dinuclear complexes and the subsequent transmetalation reaction.

Building on our previous work involving sulfur-containing ligands,[10] we investigated the incorporation of the sulfur donor function into Schiff base ligands. In contrast to most Schiff bases, the thiosalicylaldimine (*o*-mercaptobenzaldimine) subunit is not accessible by direct condensation of an amine with the corresponding *o*-mercaptobenzaldehyde, which instead leads to 1,5-dithiocines.[11] However, treatment of a preformed complex bearing 2-thiolatobenzaldehyde ligands with appropriate primary amines leads in a template-controlled reaction to the desired complexes with N,S donor functions.[12] We found that nickel(II) and zinc(II) are excellent templates for this chemistry, as indicated by the facile synthesis and stability of the 2-thiolatobenzaldehyde complexes **1** and **2** (Scheme 1). While the molecular structure of the square-planar nickel complex **1**·$CHCl_3$ (see the Supporting Information) shows the *cis* configuration of the oxygen donors, zinc complex **2** probably has a tetrahedral coordination geometry. These features make **1** and **2** ideal building blocks for a subsequent subcomponent self-assembly reaction by Schiff base formation to obtain the desired dinuclear $[M_2L_2]$ complexes **3** (M = Ni) and **4** (M = Zn), where L is the bis(bidentate) N,S-N,S ligand (Scheme 1).



Scheme 1. Synthesis of complexes **1** and **2** and subsequent subcomponent self-assembly to the dinuclear complexes **3** and **4**.

Indeed, reaction of nickel complex **1** with 4,4′-diaminodiphenylmethane at 65 °C (12 h) afforded $[Ni_2L_2]$ **3** as a brown

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solid in 54% yield (m/z 990). The NMR spectra of complex **3** showed only signals for half of each ligand strand, indicating the formation of a highly symmetric compound. The molecular structure of **3**·2DMF·Et$_2$O was established unequivocally by an X-ray crystal structure determination (Figure 1) and shows a dinuclear double-stranded nickel helicate. The two nickel centers in **3** are each coordinated by two thiolato–imine units in a nearly perfect square-planar geometry. Both six-membered C$_3$NSNi rings are significantly bent along the N···S vector, thus placing the parent phenyl groups on opposing sides of the plane defined by the four donor atoms (see coordination environment for Ni2 in Figure 1). The ligand strands are wrapped around the Ni···Ni axis in a helical manner with a twist angle[13] of 159.5°.

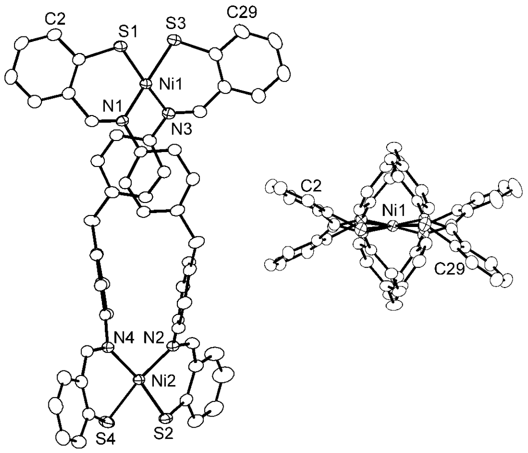
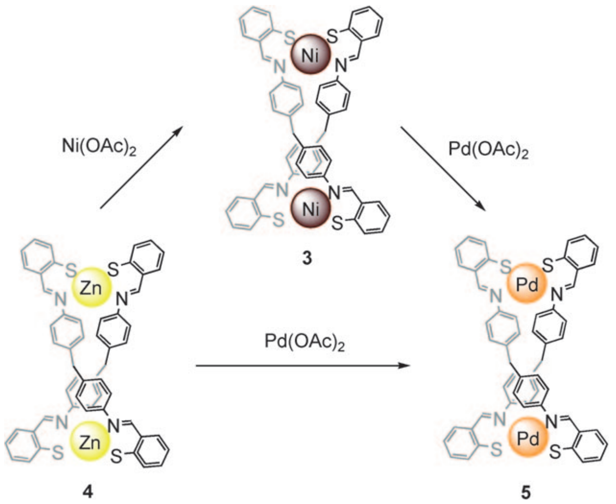


Figure 1. Molecular structure of one molecule of **3** in **3**·2DMF·Et$_2$O (left) and view along the Ni···Ni axis (right). Selected bond lengths (Å) and angles (°): Ni1–S1 2.1616(5), Ni1–S3 2.1787(5), Ni1–N1 1.936(2), Ni1–N3 1.951(2), Ni2–S2 2.1623(5), Ni2–S4 2.1701(5), Ni2–N2 1.936(2), Ni2–N4 1.944(2), Ni1···Ni2 11.884(1); S1-Ni1-N1 93.31(5), S3-Ni1-N3 92.48(5), S2-Ni2-N2 93.17(5), S4-Ni2-N4 92.94(5).

Interestingly, the subcomponent self-assembly of zinc precursor **2** with 4,4′-diaminodiphenylmethane proceeds more easily, enabling an efficient one-pot synthesis of **4** at room temperature. In situ preparation of zinc complex **2** from o-mercaptobenzaldehyde and the corresponding metal acetate (2 h, room temperature) was followed by addition of 4,4′-diaminodiphenylmethane (12 h, room temperature) to generate [Zn$_2$L$_2$] (**4**), which was isolated as a yellow solid (52% yield, m/z 1004; Scheme 1). Along with the expected signals for a dinuclear double-stranded zinc helicate, a second set of signals with lower intensity (ca. 10%) was observed in the ^{1}H NMR spectrum of **4**, which can be assigned to the corresponding trinuclear [Zn$_3$L$_3$] species according to MALDI MS (m/z 1506). 2D EXSY NMR experiments (see the Supporting Information) confirmed the presence of an equilibrium between the dinuclear and trinuclear zinc species, in analogy with those reported by Hannon et al. for dimeric–trimeric copper complexes bearing related Schiff base ligands.[14]

The subcomponent self-assembly is not applicable to the synthesis of the corresponding dipalladium helicate **5**, which is most likely due to the reduced reactivity of the mononuclear palladium bis(2-thiolatobenzaldehyde) complex towards diamines. Fortunately, both dinuclear helicates **3** and **4** undergo complete metal exchange with palladium(II) by the simple addition of two equivalents of palladium acetate at ambient temperature (12 h), affording [Pd$_2$L$_2$] **5** in 32% and 36% yield, respectively (m/z 1086; Scheme 2). These transmetalations in metallosupramolecular chemistry can be followed visually by the fast color change from either dark brown (**3**; absorption of the {NiN$_2$S$_2$} chromophore at $\lambda_{max} = 501$ nm) or bright yellow (**4**; $\lambda_{max} = 426$ nm) to deep orange for dipalladium species **5** ($\lambda_{max} = 463$ nm).



Scheme 2. Transmetalations involving dinuclear helicates **3**–**5**.

A single-crystal X-ray analysis of **5**·3CH$_2$Cl$_2$ confirmed the formation of the dinuclear double-stranded palladium complex **5** (Figure 2), which shows comparable structural features to nickel analogue **3**. Both palladium atoms are

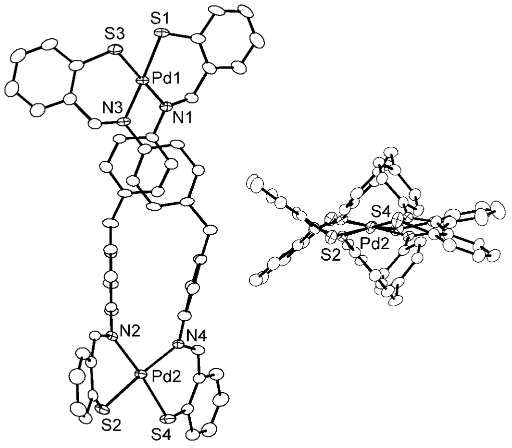


Figure 2. Molecular structure of one molecule of **5** in **5**·3CH$_2$Cl$_2$ (left) and view along the Pd···Pd axis (right). Selected bond lengths (Å) and angles (°): Pd1–S1 2.2496(14), Pd1–S3 2.2718(14), Pd1–N1 2.087(4), Pd1–N3 2.092(4), Pd2–S2 2.2687(14), Pd2–S4 2.2589(14), Pd2–N2 2.087(4), Pd2–N4 2.091(4), Pd1···Pd2 12.175(1); S1-Pd1-N1 93.75(12), S3-Pd1-N3 89.26(12), S2-Pd2-N2 89.43(12), S4-Pd2-N4 91.53(12).

coordinated in a slightly distorted square-planar fashion, and the helical twist angle[13] is 152.1°. The chelate rings are not planar, but rather bent along the N···S vector. Although both molecular structures, **3** and **5**, are stabilized by intra- and intermolecular interactions,[15] the latter play a more important role for the dipalladium complex **5**, leading to a C-shaped bending of this helicate along the Pd···Pd axis (for a detailed discussion, see the Supporting Information).

To complete the metallosupramolecular transmetalation, the reaction of dizinc complex **4** with nickel acetate was also investigated (Scheme 2). The initially yellow reaction mixture turned brown within minutes, and after 12 h at room temperature, dinickel complex **3** was isolated in 45 % yield.

The thermodynamic driving force for these metal exchange reactions can be attributed to the preferred coordination of the soft N,S binding groups to the softer metal center available,[16] as shown earlier for transmetalations involving mononuclear zinc, nickel,[17] and palladium[18] complexes with sulfur/nitrogen ligation. To gain more insight into the principles of the transmetalation, exchange reactions involving helicates **3**, **4**, and **5** were investigated.

Figure 3 shows the characteristic CH_2 region of the ^1H NMR spectra of a 1:1 mixture of the dinickel helicate **3** and the dizinc helicate **4** (including traces of the trinuclear species) 30 min (A) and 18 h (B) after the two complexes were dissolved in [D_7]DMF. Spectrum (A) is dominated by the signals for the homodinuclear complexes, with a weak resonance at $\delta = 3.90$ ppm appearing for the heterodinuclear [$NiZnL_2$] complex. The intensity of this signal increases with time, and becomes the dominant resonance in spectrum (B) after 18 h. Formation of the heterodinuclear complex is consistent with the MALDI MS data for this reaction and the analogous reactions involving the metal exchanges of **3** or **4** with **5** (see the Supporting Information).

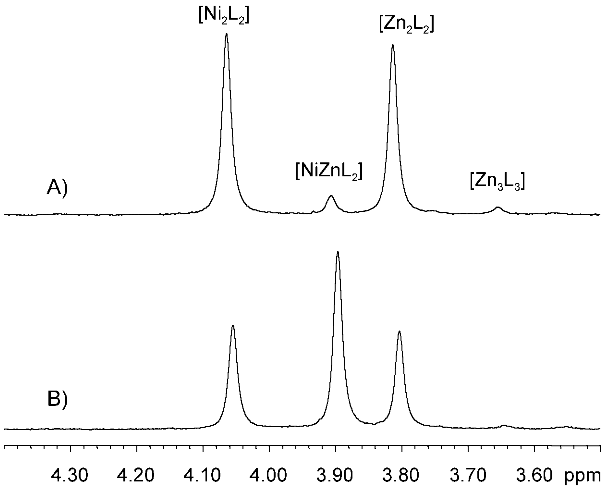


Figure 3. The CH_2 signals in the ^1H NMR spectra of a 1:1 mixture of **3** and **4** after 30 min (A) and 18 h (B) in [D_7]DMF at room temperature.

The formation of the heterodinuclear species from the reaction of two homodinuclear helicates verifies that the corresponding helicates interact and exchange metals while in equilibrium and thereby confirms the reversibility of the metal exchange. This reversibility is the essential criterion for self-assembly processes and enables formation of the thermodynamically most stable product from a number of possible aggregates. Thus we conclude that a self-assembly pathway is operative for the transmetalations.

In summary, we have generated complexes bearing thiosalicylaldimine (N,S) donor groups in a metal-template-controlled reaction from complexes bearing two 2-thiolatobenzaldehyde ligands and 4,4′-diaminodiphenylmethane. The template-controlled formation of the N,S donor groups proceeds concurrently with a subcomponent self-assembly reaction, leading to the dinuclear double-stranded complexes **3** and **4**. Both **3** and **4** react with palladium acetate by transmetalation to afford the dinuclear palladium complex **5** in a self-assembly reaction with formation of the thermodynamically most stable product. Formally, this reaction sequence can be seen as a template-synthesis of N,S ligands followed by release of these ligands to serve in a self-assembly reaction or as subcomponent self-assembly reaction of dizinc or dinickel helicates followed by a transmetalation self-assembly to the dipalladium helicate. This reaction sequence will give access to new supramolecular structures not accessible by classical self-assembly or subcomponent supramolecular synthesis alone.

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