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Supramolecular reactions of metallo-architectures: Ag₂-double-helicate/Zn₄-grid, Pb₄-grid/Zn₄-grid interconversions, and Ag₂-double-helicate fusion†

Adrian-Mihail Stadler,*^{ab} Juan Ramírez,^c Jean-Marie Lehn^a and Bruno Vincent^d

Supramolecular reactions are of importance in many fields. We report herein three examples where complexes of hydrazone-based ligands are involved. A Ag₂-double-helicate was converted, by treatment with Zn(OTf)₂, into a Zn₄-grid (exchange of metal ions and change of the nature of the initial complex). A Pb₄-grid was converted, upon reaction with ZnCl₂ or ZnBr₂, into a Zn₄-grid (exchange of metal ions, but conservation of the nature of the initial complex). The reverse conversions were also achieved. The fusion of a Ag₂-double-helicate with another Ag₂-double-helicate was performed (exchange of ligands, but conservation of the nature of the complexes) and resulted in a mixture of three helicates (two homostranded ones and one heterostranded one).

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Introduction

Like covalent molecules, supramolecular¹ assemblies may participate in various reactions. The understanding of supramolecular reactions is of much interest because they are involved in many areas such as complex chemical systems and networks,² adaptive³ and stimuli-responsive⁴ chemical systems, fabrication of nanodevices and materials,⁴ biomolecular processes. Thus, in the complexity and diversity of supramolecular chemistry, the reactivity of supramolecules plays a crucial role. It includes the processes:

(a) of (self)assembly (*i.e.* formation of supramolecular architectures through assembly, but also their participation, as subunits, in more complex assemblies), and correlatively, partial or total disassembly;

(b) of partial or total reorganization or exchange (at the supramolecular and, additionally and possibly, at the covalent level), that involves the breaking of several or all of the initial supramolecular connections and formation of new ones;

(c) without breaking or formation of new supramolecular connections (*e.g.* covalent modifications after self-assembly⁵).

Amongst supramolecular architectures, double helices and helicates,⁶ as well as grids⁷ arouse much interest and work. For example, DNA⁸ and the ion channel generated by gramicidine⁹ have a double helical structure, and there are double helical complexes that act as molecular machines¹⁰ or catalysts.¹¹ Gridlike complexes have been studied for their electrochemical and magnetic properties,⁷ for their capacity to encapsulate ions¹² or as starting materials for building more complex architectures (*e.g.* a Solomon link¹³), amongst other things. However, supramolecular interconversions of grids and helicates have not, except several examples,^{14,15} been much explored.

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With these ideas in mind – and using principles such as the displacement of an equilibrium through precipitation, and the preference of Ag⁺ for tetrahedral and of Zn²⁺ for octahedral coordination – we designed, as reported herein, three supramolecular reactions¹⁶ of reorganization and exchange (Fig. 1) involving grids and double helicates. They are related through the ligands¹⁷ (which are pyrimidine-bis-hydrazones;¹⁸ Fig. 2)

$^{i)}_{Ag_2L_2\text{-DH}}$	exchange: metal ion nature changes: yes conformation changes: yes nuclearity changes: yes number of ligands changes: yes
$\overrightarrow{Pb_4L_4-G} \xrightarrow{Tn_4L_4-G}$	exchange: metal ion nature changes: no conformation changes: no nuclearity changes: no number of ligands changes: no
iii) $A_{q_2}L^{1}_{2}$ -DH $A_{q_2}L^{2}_{2}$ -DH $A_{q_3}L^{1}L^{2}_{2}$ -DH	exchange: ligand nature changes: no conformation changes: no nuclearity changes: no number of ligands changes: no

Fig. 1 Stylized representation of the three types of supramolecular reactions reported herein.

^aUniversité de Strasbourg, CNRS, UMR 7006, ISIS, 8 Allée G. Monge, Strasbourg, France. E-mail: mstadler@unistra.fr

^bInstitute of Nanotechnology (INT), Karlsruhe Institute of Technolgoy (KIT), 76344, Eggenstein-Leopoldshafen, Germany

Institut Pasteur Paris, 28 Rue du Docteur Roux, 75015 Paris, France

^dService de RMN, Faculté de Chimie, 1 Rue B. Pascal, Strasbourg, France

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Fig. 2 Structural formulae and stylized representations of ligands 1 and 2, and of grids and double helicates.

that produce the supramolecular complexes, as well as through the nature of complexes, and occur due to the dynamic character of the present metal-ligand connections. These reactions (Fig. 1) can be seen as:



Fig. 3 Stylized representation of: (a) the conversion of $Ag_2 1_2$ -DH double helicate into the Zn_41_4 -G grid; (b) the interconversion Aq_21_2 -DH/Zn₄ $\mathbf{1}_4$ -G; (c) the conversion of Ag₂ $\mathbf{2}_2$ -DH double helicate into the Zn_42_4 -G grid; (d) the conversion of Zn_42_4 -G grid into Ag_22_2 -DH double helicate. Charges and stoichiometric coefficients are omitted for simplicity.



Fig. 4 Stylized representation of: (a) reaction of Pb₄1₄-G grid with $ZnCl_2$, $ZnBr_2$, and $Zn(OTf)_2$ and $Bu_4P^+Br^-$ (solvent CD_3CN); (b) Zn_4I_4 -G/Pb₄1₄-G and Pb₄1₄-G/Zn₄1₄-G conversions. Charges and stoichiometric coefficients are omitted for simplicity



Fig. 5 Stylized representation of the fusion (conproportionation) reaction of double helicates Ag_21_2 -DH and Ag_22_2 -DH with formation of heterostranded species Ag₂(1)(2)-DH. Charges are omitted for simplicity.

(i) a change of the nature of the supramolecular architecture, from a Ag⁺ dinuclear double helicate (DH) into a Zn²⁺ tetranuclear grid (G), induced by replacement of Ag^+ by Zn^{2+} (Fig. 3). In this reaction, not only the nature of the complex and that of the metal ion change, but also the conformation of the ligand (helical \rightarrow unfolded), the charge (2⁺ \rightarrow 8⁺) and the nuclearity of the complex $(2 \rightarrow 4)$ and the number of ligands per complex $(2 \rightarrow 4)$. In regard to this last change, this process can be compared with the conversion or the equilibrium between supramolecular dimer and tetramer of bioactive proteins,19 or between other homo-oligomers²⁰ with influence on the protein functions.

(ii) a substitution²¹ (metal ion exchange or transmetallation), in a sole operation, of the four Pb²⁺ ions of a grid-like²² complex by Zn^{2+} ions (Fig. 4);

(iii) a fusion (conproportionation)²³ between two Ag⁺ double helicates²⁴ (Fig. 5).

While in case (ii) the equilibrium is shifted towards the Zn²⁺ grid through the precipitation of Pb²⁺ as its halides (chloride and bromide), in cases (i) and (iii), the conversions can be done without precipitation.

Results and discussion

(i) The conversion Ag_2L_2 -DH $\rightarrow Zn_4L_4$ -G (L = 1, 2) through transmetallation is a dramatic reorganization of the nature of the metallo-supramolecular architecture induced by the replacement of Ag^+ by Zn^{2+} (Fig. 3a and c): 2 Ag_2L_2 -DH + 4 Zn^{2+} \rightarrow Zn₄L₄-G + 4 Ag⁺. Ag⁺ prefers a tetrahedral coordination geometry which is, in the case of ligands 1 and 2, achieved from 2 two-Nsp²-atom bidentate pyridine-hydrazone sites. In this

way, Ag^+ induces the formation of double helicates with ligands 1 and 2. Zn^{2+} prefers an octahedral coordination environment that results from 2 three-Nsp²-atom tridentate sites of type pyridine-hydrazone-pyrimidine, thus generating a grid.

Reaction of 1 equiv. of Ag_2L_2 -DH^{15c} with 2 equiv. of $Zn(OTf)_2$ (OTf⁻ = CF₃SO³⁻) produces – without the need to precipitate Ag⁺ as a halide – the corresponding grid Zn_4L_4 -G^{15b,22a} (solvent: CD₃NO₂ with 6–14% CD₃CN; ESI, pp. S9–S11†). Where ZnCl₂ is used in the reaction with Ag₂1₂-DH, two equivalents of AgOTf per equiv. of DH are required according to the equation (ESI p. S8†):

$$2Ag_2I_2-DH + 4ZnCl_2 + 4Ag^+ \rightarrow Zn_4I_4-G + 8AgCl_2$$

On treatment of the double helicate Ag_22_2 -DH in CD_3NO_2 with 2 equiv. of Zn(OTf)2 - added as a solution in a small volume of CD_3CN , or as a solid – the grid Zn_42_4 -G was obtained. When the double helicate $Ag_2 \mathbf{1}_2$ -DH in CD_3NO_2 was treated with 2 equiv. of Zn(OTf)₂, added as a solution in a small volume of CD_3CN (about 6–14% of the CD_3NO_2 volume), the grid Zn_41_4 -G was obtained. When $Zn(OTf)_2$ was added as a solid, without CD_3CN , was obtained a mixture without the Zn_41_4 -G grid; addition of a small volume of CH₃CN (about 6-14% of the CD_3NO_2 volume) to this mixture produced the expected grid Zn₄1₄-G. A possible explanation could be that, in the case of the reaction $Ag_2 \mathbf{1}_2$ -DH \rightarrow Zn₄ $\mathbf{1}_4$ -G, the CH₃CN acts as a coordinating species for the Ag⁺ ions and so contributes to the displacement of the equilibrium from the double helix towards the grid. The grid Zn_42_4 -G should be – due to the π -stacking aromatic interaction between a phenyl ring and the two ligands between which that phenyl is located within the grid - more stable than the grid $Zn_4 I_4$ -G. This stability may be sufficient to make possible the formation of the grid Zn₄2₄-G from the corresponding double helicate without, unlike in the case of the grid Zn_41_4 -G, the assistance of CH_3CN .

DOSY NMR was also used to study the conversion Ag_2L_2 -DH \rightarrow Zn₄L₄-G (L = 1, 2). As expected, the volume of the grid species obtained from double helicates on treatment with Zn(OTf)₂ was found in agreement with that of the grid prepared from the free ligands L and Zn(OTf)₂.

The reverse conversion Zn_4L_4 -G $\rightarrow Ag_2L_2$ -DH can be done as follows: after treatment of the grid with KOH, the solvent (CD₃CN or CD₃NO₂) is removed, and the ligand is extracted with CDCl₃ and separated from the solid residue (by centrifugation or filtration); after removal of CDCl₃, CD₃NO₂ is added, then AgOTf is added to form the helicate. In order to simplify the procedure, we used ligand **2** and a mixture of CDCl₃ and CD₃NO₂ where ligand **2**, as well as the corresponding grid and double helicate were soluble. After precipitation of Zn²⁺ with KOH, the mixture was centrifuged (the ligand **2** being soluble in the mixture of solvents), and to the recovered liquid phase AgOTf was added to produce the Ag₂2₂-DH (ESI, p. S13[†]).

In a pH-dependent system (Fig. 3b), the interconversion between Ag_21_2 -DH and Zn_41_4 -G was achieved as follows (ESI, p. S10†): the grid was generated from the double helicate by reaction with Zn^{2+} ; then, Zn^{2+} was complexed with hexacyclen, and the double helicate was regenerated; partial protonation of hexacyclen with TfOH caused release of Zn^{2+} and formation of the grid (incomplete yield); finally, addition of triethylamine reactivated the hexacyclen that again encapsulated Zn^{2+} and resulted in the reformation of the double helicate.

(ii) The Pb₄**1**₄-G \rightarrow Zn₄**1**₄-G conversion (Fig. 4a) can formally be seen as a substitution of Pb²⁺ by Zn²⁺ ions, although the real mechanism, involving breaking and formation of supramolecular bonds, must be more complex. Reaction of Pb414-G15b with 4 equiv. of Zn(OTf)2 produces a mixture which no longer contains the grid-like species Pb414-G or Zn414-G (ESI p. S2⁺). This suggests that the affinity of Zn^{2+} for the ligand, as well as its preference for octahedral coordination are not sufficient to displace the equilibrium towards Zn₄1₄-G. We considered that the involvement of Pb²⁺ ions in a weakly dissociating or sparingly soluble compound should displace the equilibrium. Indeed, addition of Br⁻ (as $Bu_4P^+Br^-$) to the above mixture, or treatment of Pb_41_4 -G with four equivalents of ZnBr₂ or ZnCl₂ produced - along with the formation of PbX_2 (X = Br, Cl) which precipitates and, doing so, shifts the equilibrium – the expected Zn₄1₄-G grid (solvent: CD₃CN; ESI pp. S3–S4[†]): Pb₄1₄-G + 4 ZnX₂ \rightarrow Zn₄1₄-G + 4 PbX₂.

The reverse conversion $Zn_4\mathbf{1}_4$ - $G \rightarrow Pb_4\mathbf{1}_4$ -G grid was achieved in several steps (Fig. 4b). Treatment of $Zn_4\mathbf{1}_4$ -G (in CD₃CN) with KOH led to the precipitation of Zn^{2+} (as $Zn(OH)_2$ or $K_2[Zn(OH)_4]$), as well as of the free ligand **1**. After removal of CD₃CN, the free ligand **1** was extracted with CDCl₃ and used further for the preparation of Pb₄\mathbf{1}_4-G (see ESI, p. S5[†]).

Thus, in addition to its self-assembly from Zn^{2+} and a ligand, the same Zn^{2+} grid, $Zn_4\mathbf{1}_4$ -G, can be obtained, in reactions (i) and (ii), from a Ag⁺ dinuclear double helicate or from a Pb²⁺ tetranuclear grid (exchange of metal ions and reorganization of the architectures).

(iii) The fusion (conproportionation) reaction of double helicate Ag_21_2 -DH^{15c} with 1 equiv. of Ag_22_2 -DH (Fig. 5) according to the equation

$$Ag_21_2$$
-DH + Ag_22_2 -DH $\rightarrow 2Ag_2(1)(2)$ -DH

produces a mixture that contains each of the three helicates, namely two homoleptic (homostranded) ones and one heteroleptic (heterostranded) one. Ligands **1** and **2** equally participate to homo- and heteroleptic helicates, and so the observed molar percentages are of approximately 25% for Ag_21_2 -DH, 25% for Ag_22_2 -DH, and 50% for $Ag_2(1)(2)$ -DH. For characterization of the new compound Ag_22_2 -DH, see ESI pp. S14–S20;† for ¹H, ¹³C and DOSY of the mixture of three helicates, see ESI pp. S25–S31.†

For the reactions described above it might appear necessary, in practice, to slightly (2–10%) increase the amounts of reagents with respect to those theoretically calculated.

Experimental

For experimental details, see the ESI.†

Conclusions

To summarize, three supramolecular reactions were investigated: (i) a Ag_2L_2 -DH double-helicate into Zn_4L_4 -G grid conversion, where the exchange of metal ions changes the nature of the metallo-supramolecular architecture, (ii) a Zn_41_4 -G grid into Pb_41_4 -G grid conversion driven by a halide-induced precipitation and where the nature of the metallo-supramolecular architecture is conserved, and (iii) a double exchange of ligands during the fusion of two double helicates.

The grid/grid and double-helicate/grid conversions were made reversible by precipitation of Zn^{2+} with KOH and subsequent reaction of the free ligand with Ag^+ or Pb^{2+} , or, for one DH/G interconversion, in a pH-dependent way.

In perspective, such ligands could be introduced in larger and more complex, suitably decorated, architectures where such supramolecular reactions can act as actuators of various properties (charge, volume, multivalency).

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