Supramolecular reactions of metallo-architectures: Ag$_2$-double-helicate/Zn$_4$-grid, Pb$_4$-grid/Zn$_4$-grid interconversions, and Ag$_2$-double-helicate fusion†

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Supramolecular reactions are of importance in many fields. We report herein three examples where complexes of hydrazone-based ligands are involved. A Ag$_2$-double-helicate was converted, by treatment with Zn(OTf)$_2$, into a Zn$_4$-grid (exchange of metal ions and change of the nature of the initial complex). A Pb$_4$-grid was converted, upon reaction with ZnCl$_2$ or ZnBr$_2$, into a Zn$_4$-grid (exchange of metal ions, but conservation of the nature of the initial complex). The reverse conversions were also achieved. The fusion of a Ag$_2$-double-helicate with another Ag$_2$-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).

Introduction

Like covalent molecules, supramolecular 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, adaptive and stimuli-responsive chemical systems, fabrication of nanodevices and materials, 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-assembly).

Amongst supramolecular architectures, double helices and helicates, as well as grids, arouse much interest and work. For example, DNA and the ion channel generated by gramicidine have a double helical structure, and there are double helical complexes that act as molecular machines or catalysts. Grid-like complexes have been studied for their electrochemical and magnetic properties, for their capacity to encapsulate ions or as starting materials for building more complex architectures (e.g. a Solomon link), amongst other things. However, supramolecular interconversions of grids and helicates have not, except several examples, been much explored.

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 Zn$^{2+}$ for octahedral coordination – we designed, as reported herein, three supramolecular reactions of reorganization and exchange (Fig. 1) involving grids and double helicates. They are related through the ligands (which are pyrimidine-bis-hydrazones; Fig. 2)

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

(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 Zn²⁺ (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 / unfolded), the charge (2⁺ / 8⁺) and the nuclearity of the complex (2 / 4) and the number of ligands per complex (2 / 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-like complex by Zn²⁺ ions (Fig. 4);

(iii) a fusion (conproportionation)²² between two Ag⁺ double helicates²³ (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 Ag₂L₂-DH → Zn₄L₄-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 Zn²⁺ (Fig. 3a and c): 2 Ag₂L₂-DH + 4 Zn²⁺ → 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-hydrazones sites. In this case...
way, Ag⁺ induces the formation of double helicates with ligands 1 and 2. Zn²⁺ 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 Ag₂L₂-DH with 2 equiv. of Zn(OTf)₂ (OTf⁻ = CF₃SO₃⁻) produces – without the need to precipitate Ag⁺ as a halide – the corresponding grid Zn₄L₄G⁴⁺₂⁻ₐₔ (solvent: CD₃NO₂ with 6–14% CD₃CN; ESI, pp. S9–S11†). Where ZnCl₂ is used in the reaction with Ag₂L₂-DH, two equivalents of AgOTF per equiv. of DH are required according to the equation (ESI p. S8†):

\[ 2\text{Ag}_2\text{L}_2\text{DH} + 4\text{ZnCl}_2 + 4\text{Ag}^+ \rightarrow \text{Zn}_4\text{L}_4\text{G} + 8\text{AgCl} \]

On treatment of the double helicate Ag₂L₂-DH in CD₃NO₂ with 2 equiv. of Zn(OTf)₂ – added as a solution in a small volume of CD₃CN, or as a solid – the grid Zn₄L₄-G was obtained. When the double helicate Ag₂L₂-DH in CD₃NO₂ was treated with 2 equiv. of Zn(OTf)₂, added as a solution in a small volume of CD₃CN (about 6–14% of the CD₃NO₂ volume), the grid Zn₄L₄-G was obtained. When Zn(OTf)₂ was added as a solid, without CD₃CN, was obtained a mixture without the Zn₄L₄-G grid; addition of a small volume of CH₃CN (about 6–14% of the CD₃NO₂ volume) to this mixture produced the expected grid Zn₄L₄-G. A possible explanation could be that, in the case of the reaction Ag₂L₂-DH → Zn₄L₄-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 Zn₄L₄-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 Zn₄L₄-G. This stability may be sufficient to make possible the formation of the grid Zn₄L₄-G from the corresponding double helicate without, unlike in the case of the grid Zn₄L₄-G, the assistance of CH₃CN.

DOSY NMR was also used to study the conversion Ag₂L₂-DH → 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 Zn₄L₄-G → Ag₂L₂-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 Ag₂L₂-DH (ESI, p. S13†).

In a pH-dependent system (Fig. 3b), the interconversion between Ag₂L₂-DH and Zn₄L₄-G was achieved as follows (ESI, p. S10†): the grid was generated from the double helicate by reaction with Zn²⁺; then, Zn²⁺ was complexed with hexacyclen, and the double helicate was regenerated; partial protonation of hexacyclen with TfOH caused release of Zn²⁺ and formation of the grid (incomplete yield); finally, addition of triethylamine reactivated the hexacyclen that again encapsulated Zn²⁺ and resulted in the reformation of the double helicate.

(ii) The Pb₄L₄-G → Zn₄L₄-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 Pb₂L₄-G with 4 equiv. of Zn(OTf)₂ produces a mixture which no longer contains the grid-like species Pb₂L₄-G or Zn₄L₄-G (ESI p. S2†). This suggests that the affinity of Zn²⁺ for the ligand, as well as its preference for octahedral coordination are not sufficient to displace the equilibrium towards Zn₄L₄-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 Bu₄P⁺Br⁻) to the above mixture, or treatment of Pb₂L₄-G with four equivalents of ZnBr₂ or ZnCl₂ produced – along with the formation of PbX₂ (X = Br, Cl) which precipitates and, doing so, shifts the equilibrium – the expected Zn₄L₄-G grid (solvent: CD₃CN; ESI pp. S3–S4†). Pb₂L₄-G + 4 ZnX₂ → Zn₄L₄-G + 4 PbX₂.

The reverse conversion Zn₄L₄-G → Pb₄L₄-G grid was achieved in several steps (Fig. 4b). Treatment of Zn₄L₄-G (in CD₃CN) with KOH led to the precipitation of Zn²⁺ (as Zn(OH)₂ or K₂[Zn(OH)₄]), as well as of the free ligand L. After removal of CD₃CN, the free ligand 1 was extracted with CDCl₃ and used further for the preparation of Pb₄L₄-G (see ESI, p. S5†).

Thus, in addition to its self-assembly from Zn²⁺ and a ligand, the same Zn²⁺ grid, Zn₄L₄-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 Ag₂L₂-DH with 1 equiv. of Ag₂L₂-DH (Fig. 5) according to the equation

\[ \text{Ag}_2\text{L}_2\text{DH} + \text{Ag}_2\text{L}_2\text{DH} \rightarrow \text{Ag}_2\text{L}_2(\text{1/2})\text{DH} \]

produces a mixture that contains each of the three helicates, namely two homoletic (homoestranded) 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 Ag₂L₂-DH, 25% for Ag₂L₂-DH and 50% for Ag₂L₂(1/2)DH. For characterization of the new compound Ag₂L₂-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 ESL†

Conclusions

To summarize, three supramolecular reactions were investigated: (i) a Ag₂L₂-DH double-helicate into Zn₄L₄-G grid...
conversion, where the exchange of metal ions changes the nature of the metallo-supramolecular architecture, (ii) a Zn$_2$L$_1$-G grid into Pb$_4$L$_1$-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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