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# Constitutional Self-Selection of [2 × 2] Homonuclear Grids from a Dynamic Mixture of Copper(I) and Silver(I) Metal Complexes

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This paper describes the controlled self-selection and quantitative parallel amplification of the homonuclear grid architectures derived from the same ligand **1** of different conformational geometries and $Cu^+$ and $Ag^+$ metal ions of different coordination behavior and ionic size.

Self-organization of metallosupramolecular entities may be directed by design and is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry.[1] The selection of one or more components occurs as a function of either internal (such as the nature and geometry of the binding subunits of the ligand, the stoichiometry, etc.) or external factors (such as the nature of the medium, the presence of specific molecules or anions, etc.).[2] One of the key issues in designing complex architectures is the choice of reversible processes that can interconvert the constitutional components. A number of such reactions have been tested including imine exchange, thiol−disulfide exchange, esterification, and ligand exchange in coordination complexes.[3,4] Combinations of two such reversible reactions in dynamic libraries of ligands using “orthogonal”[4b] and “communicative”[4d] exchange processes have been reported.

In view of the lability of the coordination bond, numerous coordination processes may present a number of novel features such as cooperativity, diversity, selection, and adaptation.[4,5] Thus, coordination equilibria might allow the generation of dynamic libraries (mixtures) of metal complexes presenting features such as self-selection,[4] solid-state selection of a constituent of an equilibrating collection of complexes,[4h,6a] and reversible switching between different coordination arrays.[6b,7] Conformational and configurational equilibria are also typical reversible processes.[8] We have generated a double-level dynamic library of grid-type complexes based on metal-ion coordination and cis−trans isomerization processes.

The simple building block **1**,[9a,b] carrying two 2-iminopyridine functionalities, was chosen as the synthetic precursor for the double-level library (Figure 1a). This strategy using 2-iminopyridine groups gives easy access to bifunctional bipyridine-type ligands, which generate grid-type[11] com-

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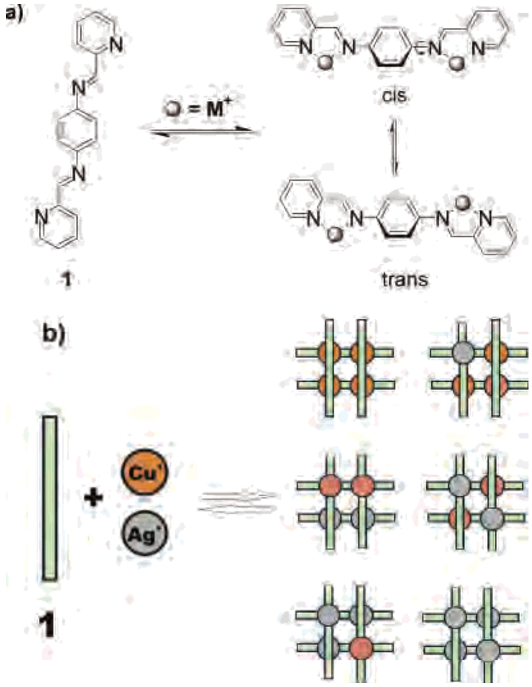

**Figure 1.** (a) Two-level metal-ion coordination/conformational exchange processes and (b) generation of a virtual dynamic library of the [2 × 2] grid complexes from mixtures of **1**:$Cu^+$:$Ag^+$ = 2:1:1 (mol/mol/mol).

pounds in the presence of tetrahedral metal ions ($Cu^+$ and $Ag^+$).[5a,6,10] Metal-ion binding imposes a cisoid arrangement of pyridine nitrogens, as is common in very numerous complexes of bipyridine (bipy).[12] Metal-ion coordination and conformational interconversion between the cis and trans arrangements around the central phenyl moiety of the chelating sites of **1** (Figure 1a) are expected to act simultaneously, leading to the exchanging species in solution. Our strategy was to employ ligand **1** and different tetrahedral $Cu^+$ and $Ag^+$ metal ions in order to generate the interconversion of all possible stoichiometries, thereby forming a library of hetero- and homonuclear grid complexes (Figure 1b).

The self-assembly processes were all performed in the same general manner. The acetonitrile-$d_3$ solutions of **1**:$M^+$ = 1:1 (mol/mol), $M^+ = Cu^+$ (**G1Cu**) or $Ag^+$ (**G2Ag**), and of **1**:$Ag^+$:$Cu^+$ = 2:1:1 (mol/mol/mol)[14] were stirred at 60 °C for up to 24 h. Layering the solutions of **G1Cu** and **G2Ag** in acetonitrile with *i*-propyl ether resulted in the formation of red-brown and yellow crystals, respectively. The crystal structures of **G1Cu** and **G2Ag** showed that the complexes present a [2 × 2] grid-type architecture (Figure 2). The four $Cu^+$ or $Ag^+$ ions form a square and are connected by four ligands; they lie close to an average common plane. The ligands are fully coordinated through all of their nitrogen sites, and the metal ions present a partially flattened tetrahedral coordination geometry.

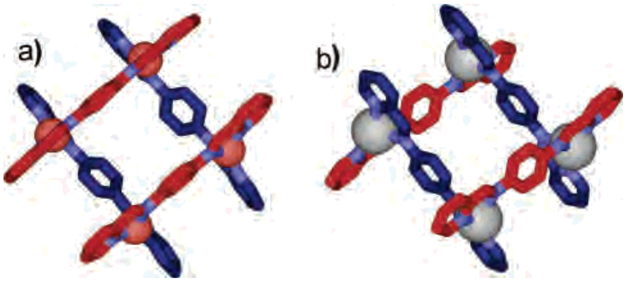

**Figure 2.** Crystal structure of the grid complexes (stick representation): (a) **G1Cu** and (b) **G2Ag**: $Cu^+$, red-brown spheres; $Ag^+$, gray spheres.

**Table 1.** Ionic Diameter, Distances, and Angles of the Coordination Geometries of $Cu^+$ and $Ag^+$ in Complexes **G1Cu** and **G2Ag**

| compd | $D_{M^+}$ [Å] | $d_{M^+-NPy}$ [Å] | $d_{M^+-NIm}$ [Å] | $N-M^+-N$ angles [deg] |
|---|---|---|---|---|
| **G1Cu** | 1.15 | 2.02 | 2.02 | 84.0−128.8 |
| **G2Ag** | 1.55 | 2.25 | 2.40 | 72.5−149.3 |

The geometries of $Cu^+$ and $Ag^+$ metal ions coordinated by two iminopyridine motifs are very different in the complexes **G1Cu** and **G2Ag** (Table 1). In **G1Cu**, the $Cu^+$ metal ion is symmetrically coordinated by the pyridine and imine moieties, presenting a unique $Cu^+-N$ bond length. The four ligands of **G1Cu** are arranged in a cis conformation and are disposed into two perpendicular sets (Figure 2a). In **G2Ag**, the $Ag-N_{Pyridine}$ distances are significantly shorter than the $Ag-N_{Imine}$, imposing an asymmetrical coordination geometry of $Ag^+$, consistent with other bond lengths reported for similar compounds.[10] This imposes a grid torsion of the four ligands of **G2Ag**, which are arranged in two different parallel pair sets. The first set consists of two ligands twisted in a trans conformation. The second set is composed of two ligands in a cis conformation, which lie on opposite sides of the grid, one above and one below the mean plane through the four $Ag^+$ ions (Figure 2b). The **G2Ag** entity is reminiscent of the multinuclear [5 × 5] $Ag^+$ grid described by Lehn in which cisoid and transoid conformations of the ligand are combined to maximize the strong Ag−N interactions.[6b]

Nitschke and Lehn have reported the elegant use of double-level libraries of grids where the imine and coordination processes can be processed in an independent way.[4c,5a] The **G1Cu** and **G2Ag** grid-type architectures are based on two encoded features: (1) the cis and trans relative conformations of the bipy-type sites of the ligand **1** can be reversibly interexchanged and (2) a double set of metal ions of tetrahedral coordination geometry could be exchanged during exchange processes. This two reversible processes can be expressed in a mixed fashion by reading molecular information stored in the ligand **1** and the metal ions.[13] These facts encouraged us to study the equilibrium composition of the mixture of conformationally dynamic ligand **1** and mixtures of metal ions as building blocks of a dynamic collection of grids resulting from a combination of different connectivities and geometries (Figure 1).

The $^1H$ NMR spectra of **G1Cu** and **G2Ag** could be fully assigned and showed a deshielding of terminal pyridine

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(14) A mixture of **1**:$Ag^+$ = 1:1 and **1**:$Cu^+$ = 1:1 was also experienced, leading to the same NMR and ESI-MS spectra, which are not evolutive for 2 weeks. We assume that the thermodynamic equilibrium was reached by stirring at 60 °C for up to 24 h. The NMR spectra are similar whether they are recorded in a coordinating solvent like $CD_3CN$ or in a noncoordinating solvent like $CD_3NO_2$.

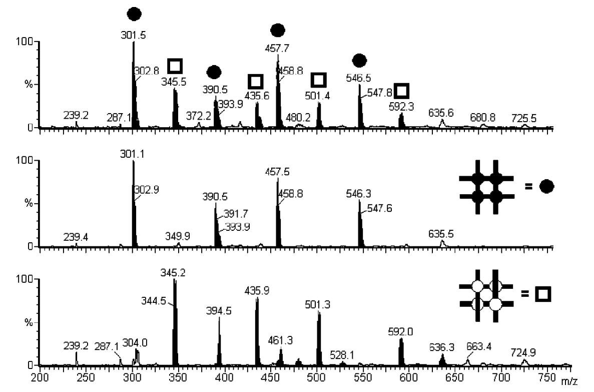

**Figure 3.** ESI-MS spectra of **G1Cu** (●), **G2Ag** (□), and a 1:1 (mol/mol) mixture of **G1Cu** and **G2Ag**.

protons due to the metal-ion complexation. The phenyl proton signals overall were shielded with respect to the ligand, suggesting that in solutions the complexes adopt a very compact grid-type structure where the phenyl rings are in close contact with terminal pyridines.

At room temperature, the $^1$H NMR spectrum of the copper complex **G1Cu** is broad, indicative of the presence of slow-exchanging species in solution. The $^1$H NMR spectrum of silver complex **G2Ag** shows a single set of sharp proton resonances, consistent with a fast exchange at room temperature. The $^1$H NMR and $^{13}$C NMR spectra of the solution mixture of **G1Cu**:**G2Ag** $=$ 1:1 (mol/mol) result from the superposition of the NMR spectra of the two species that are in slow exchange on the NMR time scale. The line-broadening and coalescence effects within each spectrum over the temperature range of $-50$ to $+50$ °C indicate that the dominant species are pools of complexes exchanging slowly over the temperature range covered.

Further evidence for the structures of grid-type complexes was obtained with electrospray ionization mass spectrometry (ESI-MS). The ESI-MS spectra were consistent with the presence of $[\mathbf{1}_4\mathrm{M}_4]^{4+}$, M $=$ $\mathrm{Cu}^+$- and $\mathrm{Ag}^+$-type complexes in solution (Figure 3). After equilibration of a solution of $\mathbf{1}$:$\mathrm{Ag}^+$:$\mathrm{Cu}^+$ $=$ 2:1:1 (mol/mol/mol) or by simple mixing of the 1:1 (vol/vol) solutions of **G1Cu** and **G2Ag**, despite the possibility of forming different grids, resulting from the combination of different ratios of **1** and $\mathrm{Ag}^+/\mathrm{Cu}^+$ (Figure 1b), the mass spectrum showed the formation in a high yield and near-quantitatively of an equimolar mixture of **G1Cu** (50%) and **G2Ag** (50%) grids, through the selection of cis and trans arrangements of the chelating sites of ligand **1** driven by metal-ion coordination. Assuming that the ESI-MS detection limit error under the experimental conditions used is about 1% (estimated from five repetitive calibration experiments; see also Figure 1S of the Supporting Information), the formation of **G1Cu** and **G2Ag** grids must display amplification factors of about 100%, reported to the statistical distribution of the mixture of grids.[15]

The present system is able to select the appropriate conformation of the ligand, required by the metal ions to form near-quantitatively the *homonuclear* grid-type complexes **G1Cu** and **G2Ag**. The heteronuclear grid compounds combining different metal ions require one to adapt the conformation of their ligands to the very different coordination geometries of $\mathrm{Cu}^+$ and $\mathrm{Ag}^+$ (Table 1). The symmetrical ($\mathrm{Cu}^+$/iminopyridine) and unsymmetrical ($\mathrm{Ag}^+$/iminopyridine) coordination geometries may be unfavorably associated within the same grid entity. The homocomplexation process represents the best compromise of the combination of ligand **1** with $\mathrm{Cu}^+$ and $\mathrm{Ag}^+$ metal ions, resulting in the formation of the symmetrical **G1Cu** grid and the interwoven **G2Ag** grid.

The above results describe the controlled self-selection and *quantitative parallel formation of homonuclear* metallosupramolecular grid architectures derived from the same ligand of different conformational geometries and different metal ions of different coordination behavior and ionic size. Using a simple chemical mechanism, it is possible to select the metal-adapted geometry of the ligand in order to amplify the *homonuclear* grid architectures. These results represent a new and original example of constitutional self-selection, reminiscent of other reported processes of the generation of specific architectures displaying “positive cooperativity” or “induced-fit” concepts, to generate bisterpyridines,[4b,h] grid-type architectures,[4c] and double- or triple-stranded[4e,f] or heteroduplex[4g] helicates.

A further step toward processes of increasing complexity could involve the ligands of different dimensionality or the library diversification by ligands undergoing structurally reversible interconnections by chemical exchange.

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**Supporting Information Available:** NMR spectroscopic data, ESI-MS data, crystallographic data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] From a $\mathbf{1}$:$\mathrm{Cu}^+$:$\mathrm{Ag}^+$ $=$ 2:1:1 (mol/mol/mol) solution, a statistical distribution mixture of grids might result: 6.25:12.5:25:25:12.5:6.25 $=$ $[\mathbf{1}_4\mathrm{Cu}_4]^{4+}$:$[\mathbf{1}_4\mathrm{Cu}_3\mathrm{Ag}]^{4+}$:$[\mathbf{1}_4\mathrm{Cu}_2\mathrm{Ag}_2]_{\mathrm{sim}}{}^{4+}$:$[\mathbf{1}_4\mathrm{Cu}_2\mathrm{Ag}_2]_{\mathrm{asim}}{}^{4+}$:$[\mathbf{1}_4\mathrm{CuAg}_3]^{4+}$:$[\mathbf{1}_4\mathrm{Ag}_4]^{4+}$.