

## Metallosupramolecular Gridlike Structures

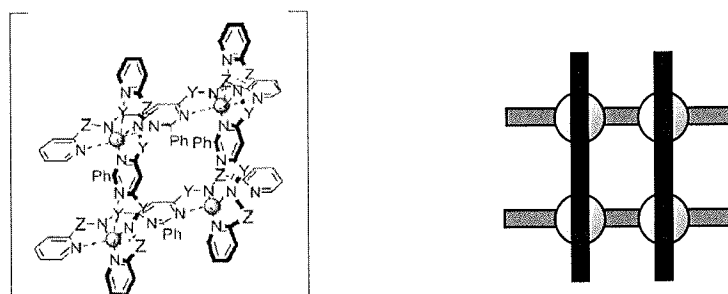
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Inorganic Literature Seminar

September 13, 2004

Supramolecular chemistry encompasses a large class of compounds that are formed through non-covalent interactions between two or more molecules. When a metal is involved in coordination compounds, then we enter upon the realm of metallosupramolecular chemistry. These compounds exhibit a wide variety of shapes, ranging from helicate, catenane and rotaxane architectures to various geometries, such as triangles, cubes, n-sided polygons and n-faceted polyhedra.<sup>1</sup>

Gridlike structures are widespread amongst this class. They are constructed from linear polydentate ligands that have several metal binding sites (see Figure 1).<sup>2</sup> The ligands align themselves into rows and columns, and they coordinate metal ions at their intersections. The final structure of the grid depends on the nature of the metal and the ligand. Grids may be square (nxn) or rectangular (nxm), and (2x2), (2x3), (3x3) and (4x4) grids have been reported (reference 2 and therein). Attempts to prepare larger grids have resulted in incomplete grids where one or more rows or columns were missing. A most remarkable feature of gridlike compounds is their self-assembly. Generally, reactions are performed by adding stoichiometric amounts of the ligand and metal ion in nitromethane or acetonitrile/water. The reactants are typically stirred at room temperature or refluxed.

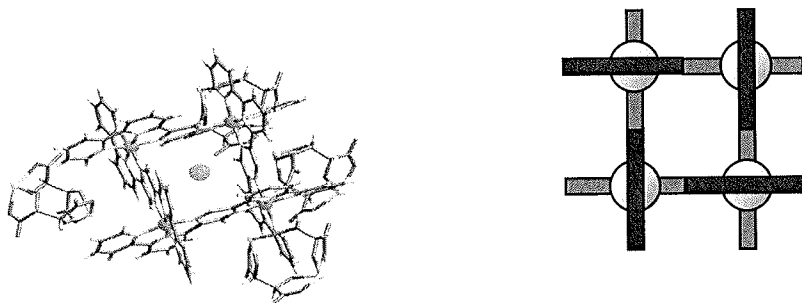


**Figure 1:** Structure of a generic-like (2x2) grid<sup>3</sup> and a schematic representation.

Little information is available on the mechanism of the self-assembly process, although some work towards this direction has been made. Marquis et al. have used <sup>1</sup>H and <sup>109</sup>Ag NMR to study the formation of L<sub>6</sub>Ag<sup>+</sup><sub>9</sub> (3x3) grids.<sup>4</sup> The chemical shifts of “corner”, “edge” and “center” silver ions are different, and hence peak assignments may be made on this basis. Signals attributable to a variety of intermediates were detected, and structures were proposed for them. Distribution curves for the various intermediates were also constructed. The distribution supported positive cooperativity in the final step leading to the product. In general, reaction products cannot be accurately predicted, and a mixture<sup>5,6</sup> or an unexpected product<sup>7</sup> often results. The outcome is also sensitive to the nature of the counterion, solvent and reactant concentration.<sup>7,8</sup>

Much emphasis has been placed on the preparation of grid compounds with novel properties, and the redox chemistry and magnetism of several grids have been investigated.<sup>9-11</sup> Zhao et al. have reported on the electrochemistry of a (3x3) Mn(II) grid.<sup>9</sup> The cyclic voltammogram had five resolved waves, and the redox potentials could be tentatively assigned to the oxidation of the various Mn(II) centers. Grid properties may be fine tuned by varying the substituents on the ligand, and a series of grids have been prepared whose UV-Vis<sup>3</sup> and redox chemistry<sup>11</sup> were pH sensitive.

Intertwined grids are an interesting sub-class of grid structures (see Figure 2). The ligands in these instances are in the transoid configuration and so “wrap” around the metals. Chirality descriptors may be assigned to the metal center using the “Oriented Line Reference System”, and absolute configurations can be assigned to the complexes, which are also chiral.<sup>5</sup> Bark et al. have prepared intertwined grids with Zn(II) and Fe(II).<sup>5,12</sup> Racemic mixtures were obtained with 2,5-bis(2,2'-bipyrid-6-yl) pyrazine as a ligand. The Zn(II) substituted, all- $\bar{A}$  stereoisomer crystallized from solution as the PF<sub>6</sub><sup>-</sup> salt,<sup>7</sup> whereas the Fe(II) substituted, all- $\bar{A}$  stereoisomer was isolated by the addition of antimonyl tartrate, (2R,2'R,3R,3'R)-[Sb<sub>2</sub>(tart)<sub>2</sub>]<sup>2-</sup>.<sup>12</sup> In order to have a stereoselective synthesis, the researchers incorporated pinene moieties into the ligand to render it chiral. Diastereomeric grids were obtained, with one preferred over the other, which crystallized from solution as the PF<sub>6</sub><sup>-</sup> salt.



**Figure 2:** Structure of an intertwined (2x2) grid<sup>18</sup> and a schematic representation.

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