

SUPRAMOLECULAR ORGANOMETALLIC ARCHITECTURE VIA SELF-ASSEMBLY

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Introduction

The formation of discrete supramolecular entities driven and held together through metal coordination has remained an intense area of study for the past decade. An attractive feature of this methodology is the rational design of diverse structures of predetermined shape, size, and functionality based on symmetry considerations.¹ Creating new supramolecular architectures tests and refines our understanding of the fundamental principles of molecular self-organization.

Typically comprising a backbone of multi-dentate aromatic bridging ligands joined through transition metals, these inorganic nanostructures have demonstrated promise as a new class of functional receptor molecules. When considering that metal-containing macrocycles often possess magnetic, photophysical, and/or redox properties not accessible to purely organic systems, such studies in basic host-guest chemistry have broad implications for technologies such as molecular sensing, separations, and catalysis.

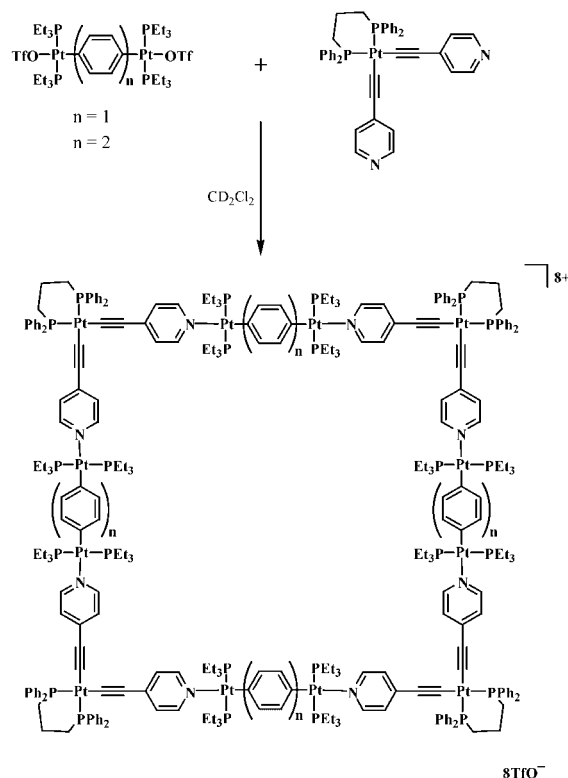
This dissertation presents several new approaches for the rational design and effective synthesis of metal-containing supramolecular species in the form of both discrete and infinite, two- and three-dimensional nanoscopic architectures. The shape, size, and functionality of the resultant structures were pre-determined by the chemical information encoded into the molecular subunits, from which the assemblies were formed.

Chapter 1

This chapter reports a series of molecular squares of unprecedented size and dimensions that were assembled from 90° corner units and dimetallic Pt(II) linear linkers (Scheme 1, iodonium corner units were used as well, but are not depicted).

(1) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2022. (b) Fujita, M.; Umamoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (e) Caulder, D. L.; Brückner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923. (f) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (g) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185. (h) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P., *Transition Metals as Assembling and Templating Species*, In *Comprehensive Supramolecular Chemistry*, Lehn, J.-M., Chair Ed., Atwood, J. L.; Davis, J. E. D.; MacNicol, D. D.; Vögtle, F., Exec. Eds., Pergamon Press: Oxford, 1996, Vol. 9, Ch. 2, p. 43. (i) Baxter, P. N. W., *Metal Ion Directed Assembly of Complex Molecular Architectures and Nanostructures*, In *Comprehensive Supramolecular Chemistry*, Lehn, J.-M., Chair Ed., Atwood, J. L.; Davis, J. E. D.; MacNicol, D. D.; Vögtle, F., Exec. Eds., Pergamon Press: Oxford, 1996, Vol. 9, Ch. 5, p. 165. (j) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417. (k) Uller, E.; Demleitner, I.; Bernt, I.; Saalfrank, R. W., *Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry*, In *Structure and Bonding*, Fujita, M., Ed., Springer: Berlin, 2000, Vol. 96, p. 149. (l) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.-Eur. J.* **1999**, *5*, 102.

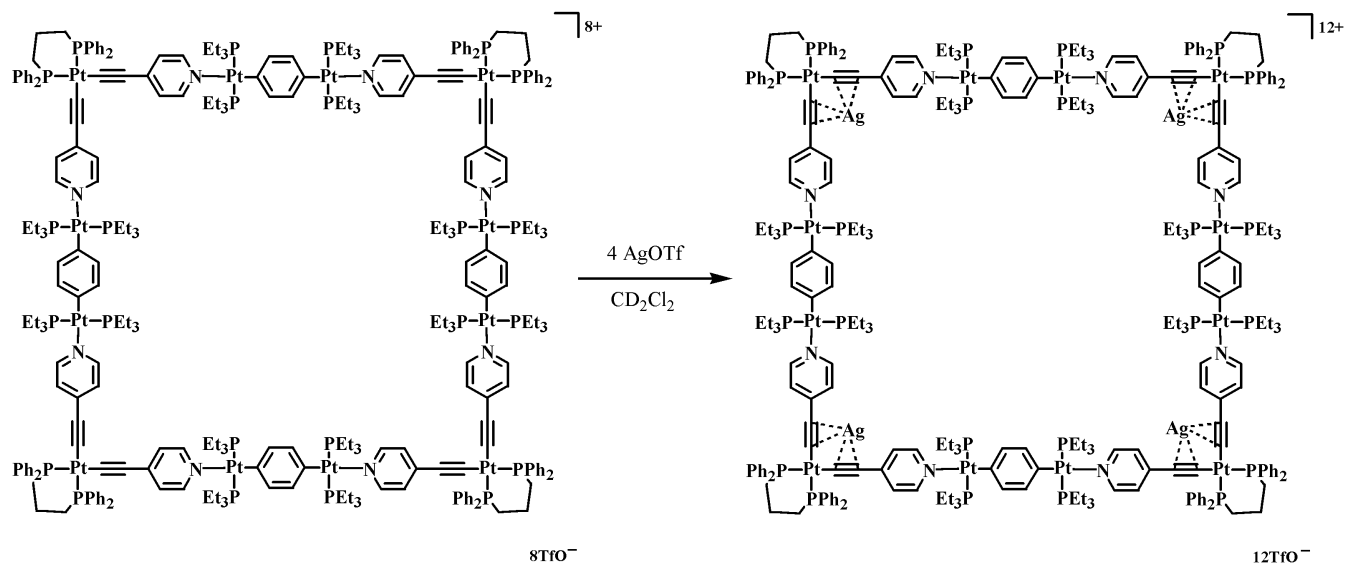
Most hitherto accessible systems had been derived from metal ions having two labile coordination sites available in a *cis* arrangement, and with few exceptions, all had generally been one nanometer or less in size. This limitation was presumably due to the fact that longer linker ligands tend to give inseparable mixtures of triangles and squares because of greater flexibility. The linear building blocks used in this study were obtained by double oxidative addition to simple dihaloaromatics.² The self-assembly reactions were found to be quantitative by NMR, and their tetrameric nature was confirmed by ESI-mass spectrometry. The calculated dimensions of the smallest square assembly were approximately 2.6 nm along the side and 3.5 nm across the diagonal. Additionally, host-guest experiments showed metal π -complexation at the corners of the square led to the uptake of four silver(I) cations (Scheme 2).³



Scheme 1. Self-assembly of nanoscopic molecular squares.

(2) Kuehl, C. J.; Manna, J.; Whiteford, J. A.; Stang, P. J. *Organometallics* **1997**, *16*, 1897.

(3) Kuehl, C. J.; Manna, J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Hofstadler, S. A.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 11611.



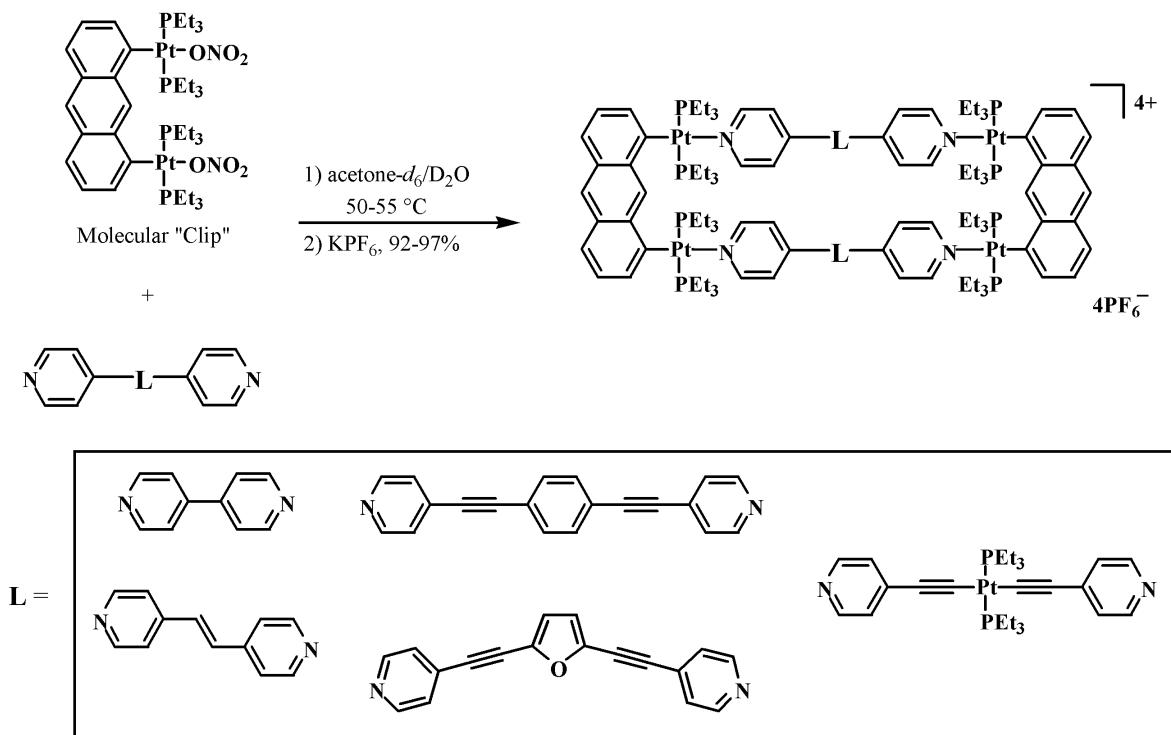
Scheme 2. Macrocylic π -complexation of four silver(I) cations.

Chapter 2

As lower symmetry hosts can ultimately be expected to show enhanced selectivity, especially toward planar aromatic guests, rectangles represent a logical progression in the development of this area. Despite their relative simplicity, molecular rectangles have remained relatively uncommon. A rational basis for this dearth is that mixed ligand species have rarely been observed, i.e., the combination of metals

with different length ligands usually leads to complexes containing only one type of ligand. Hence, the difficulty in the construction of rectangular architectures lies in the necessity of designing a building unit with two parallel coordination sites facing in the same direction.

Chapter 2 describes the spontaneous self-assembly of a series of molecular rectangles that were accessed through the use of a pre-designed molecular “clip” (Scheme 3). Characterization was accomplished with FAB mass



Scheme 3. Self-assembly of molecular rectangles.

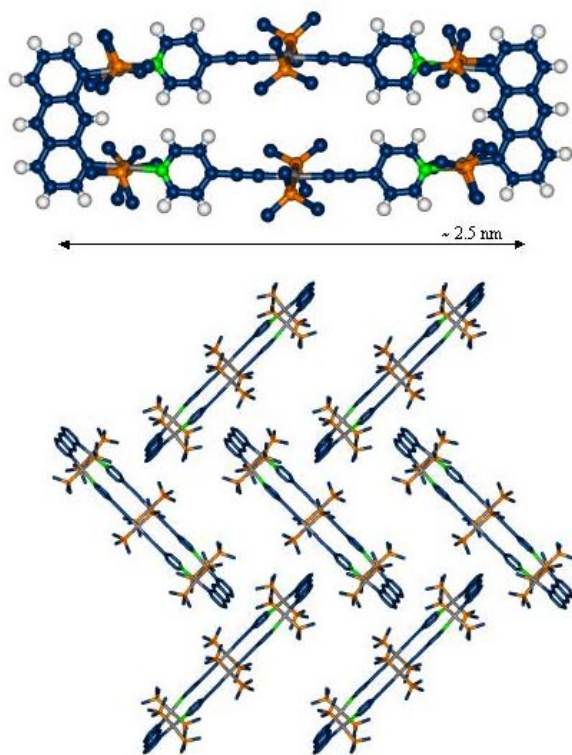


Figure 1. Top: X-ray structure of the molecular rectangle with the platinum-containing bridging ligand. Bottom: Crystal packing diagram. Colors: C, blue; H, white; N, green; P, orange; Pt, gray.

spectrometry, NMR and UV-vis spectroscopy, and the structures firmly established by X-ray crystallography, which showed that the lengths of the rectangles range from 2 to 3 nm. Crystal structures were obtained for four of the five rectangles – a representative example is shown in Figure 1. Mechanistic studies showed the effect that solvent and counterion have on the thermodynamic and kinetic stability of the assemblies, respectively. Additionally, the dynamic behavior of the assemblies was probed by NOESY NMR.⁴ Of particular significance was the observation that, once formed, the structures could be irreversibly locked in place by nonnucleophilic counterion exchange. This result suggested active participation of the counterion as a nucleophile in the self-assembly process, and implies a mechanism for self-correction via associative ligand substitution.⁵

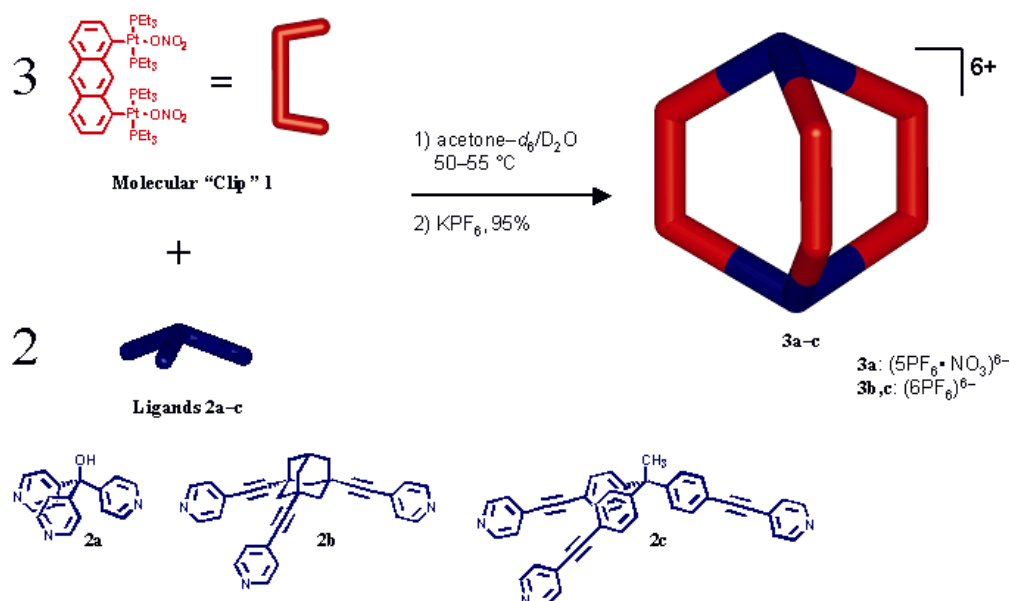
Chapter 3

In the third chapter the utility of the molecular “clip” was extended to three-dimensional constructs in the form of trigonal prismatic cages (Scheme 4). X-ray crystallography showed the cages range from 1 x 2 nm to 1 x 4 nm in size. The assembly of the smallest coordination cage was accompanied by the incarceration of a nitrate anion within its molecular cavity (Figure 2), and could not be exchanged even in the presence of very large excesses of other counterions.⁶ The aesthetic nature of the crystal packing of the largest structure is depicted in Figure 3.

(4) Kuehl, C. J.; Mayne, C. L.; Arif, A. M.; Stang, P. J. *Org. Letters* **2000**, *2*, 3729.

(5) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.

(6) (a) Kuehl, C. J.; Kryshenko, Y. K.; Ukkirampandian, R.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Natl. Acad. Sci., USA* **2002**, in press. (b) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. *Org. Letters* **2002**, in press.



Scheme 4. Self-assembly of prismatic coordination cages.

Chapter 4

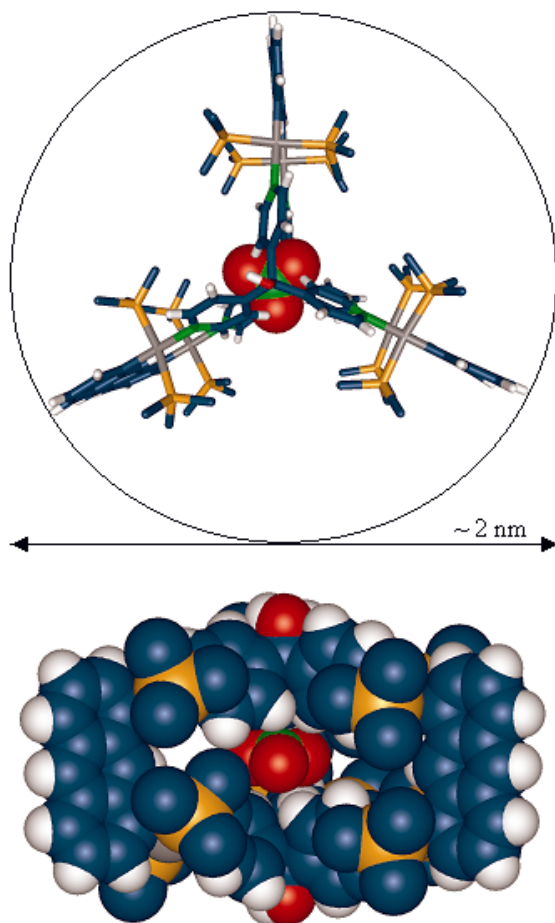


Figure 2. Top: X-ray structure of **3a** viewed along the C_3 axis. Bottom: Space filling representation viewed along the C_2 axis.

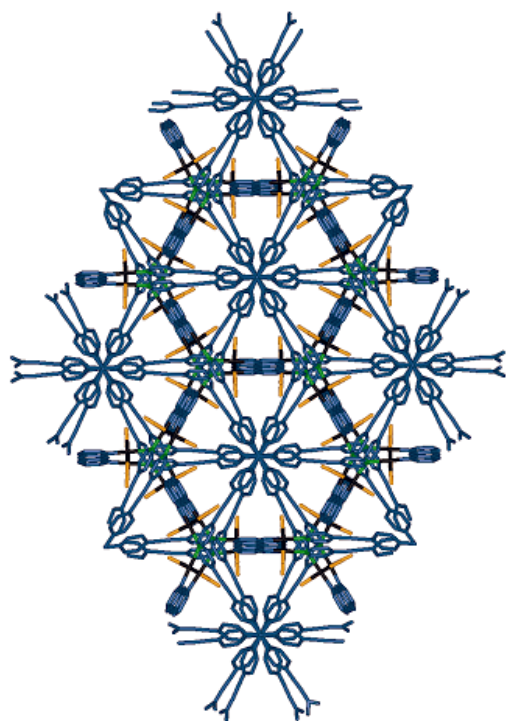
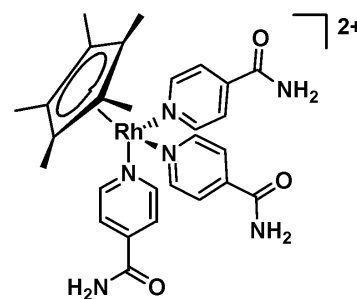
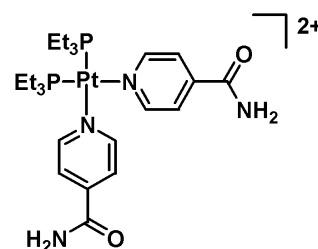


Figure 3. Crystal packing diagram of **3c** as viewed down the $\{001\}$ direction.

Both coordination-driven self-assembly and hydrogen bonding have proven to be powerful tools for the formation of a wide variety of discrete supramolecular species. Far less common, however, have been studies directed toward the simultaneous use of these two distinct bonding motifs. Of fundamental interest are network solids assembled with combined structural themes. Here the attractiveness of such a design principle lies not only in the synthesis of materials with new and potentially useful properties (e.g., magnetic, optical, mechanical, etc.), but to further our understanding of the significance of particular intermolecular interactions and arrangements. Specifically, a hybrid motif benefits from the generally predictable three-dimensional arrangement of metal-ligand interactions while offering the versatility of organic functionality as a means to drive and preserve the assembly.

The final chapter describes infinite supramolecular structures that were obtained by allowing metal complexes with two and three pendant *cis* functionalities capable of multiple hydrogen-bonding interactions to crystallize (*vide infra*). The first structure, derived from Pt(II) ions, resulted in infinite, single-stranded chains (Figure 4), while the second structure, a Rh(III) complex, gave infinite, inter-woven double-stranded chains (Figure 5). In contrast to purely organic hydrogen bonded networks based on neutral building blocks, these structures owe their stability to the convolution of hydrogen bonding interactions in the presence of ionic forces. Incorporation of metal atoms may allow us to not only exploit new topologies, but also to endow the target structures with distinctly inorganic properties. Although a high degree of predictability as of yet remains unrealized, these observations confirm that the ligand domain may be manipulated to as to influence the microstructure of inorganic/organic hybrid materials.⁷



(7) Kuehl, C. J.; Tabellion, F. M.; Arif, A. M.; Stang, P. J. *Organometallics* **2001**, *20*, 1956.

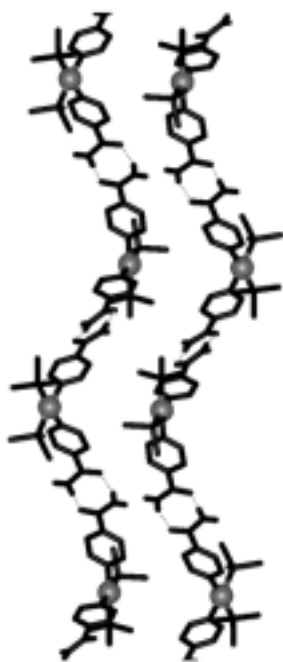


Figure 4. Infinite zigzag chains formed by head-to-head amide-amide hydrogen bonding interactions in the Pt(II) complex.

Conclusion

Several novel architectural types were successfully characterized and studied, namely nanoscopic molecular squares, rectangles, prisms, and infinite inorganic structures propagated via hydrogen bonding interactions. The study presented here contributes to ongoing work in an exciting new area at the forefront of supramolecular chemistry. The development of this field has been fueled by the promise of new materials with potentially useful properties and by the purpose of gaining a better understanding of the fundamental principles of molecular self-organization.

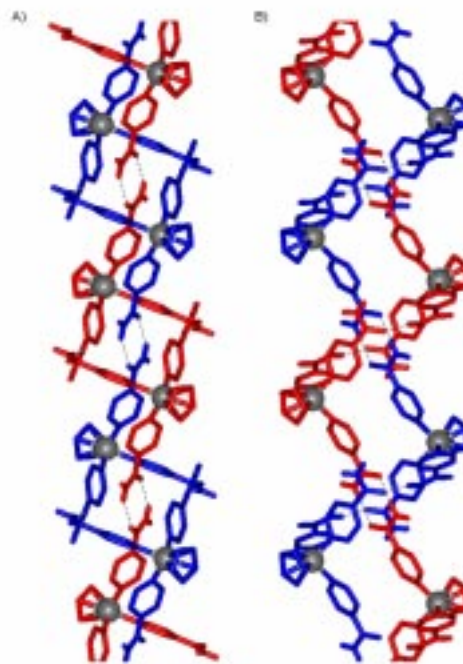


Figure 5. Two different perspectives (A and B) illustrating the interwoven strands of the supramolecular structure of the Rh(III) complex.

Acknowledgement

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