

Synthesis and Characterization of Hexametallic Molecular Hosts Featuring Large Cavity Volumes and Constrained Cavity Port Sizes

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The synthesis and characterization of hexametallic host molecules is described. The new molecules utilize 2,2'-bipyrimidine to bridge rhenium(I) tricarbonyls at three points along the short edge of the cavity, and triply functional pyridine-based ligands (2,4,6-tripyridyl-1,3,5-triazine or 1,3,5-tris(4-ethynylpyridyl)benzene) as a top and bottom. Modeling has been done to determine the volumes of the cavities and the sizes of the entry ports for the host molecules.

Keywords: Inorganic synthesis; host-guest

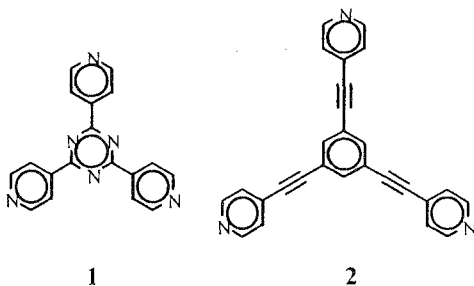
INTRODUCTION

Over the past several years there has been considerable interest in the synthesis of inorganic cyclophanes which use transition metals as an integral part of the framework.^[1,2] While much of the early work focused on making square cavities ("molecular squares"), recent efforts have emphasized other cavity motifs including distinctly 3D cavities based on specialized bridging ligands.^[3-5] Early work in our group complemented the even earlier work in the Fujita and Stang groups on the square motif by replacing the square planar platinum(II) or palladium(II) corners of their assemblies with octahedral rhenium(I) corners.^[6,7] Incorporation of Re(I) added several interesting properties

to the molecules including: a) luminescence from the metal($d\pi$)-to-ligand(π^*) charge transfer states, and b) overall charge neutrality. As seen in single crystal x-ray structures of many of these molecular squares, the cavities of the molecules tend to align so that extended channels are formed. When the component molecules are neutral (i.e. when channel-blocking counterions are absent), the channels provide appropriately-sized guest species with interior access throughout the solid state.

The solid state properties of the Re(I) based molecular squares have subsequently been studied by a variety of atypical, but useful, applications-oriented methodologies (electrochemical permeability, quartz crystal microgravimetry, optically-detected ultrafiltration, etc.). In these studies, the squares and related neutral species were cast as thin films and then examined for their abilities to sieve and separate based on guest size, or for their ability to sense volatile organic compounds (guests).^[8-10] Indeed, the thin films of these materials showed an ability to differentiate between aromatic and aliphatic volatile organic compounds, and the ability to exclude potential guests based on cavity size.

We have recently expanded the synthetic chemistry to utilize the octahedral coordination of the Re(I) to make inorganic cyclophanes with cavity geometries other than squares. Two examples of molecular rectangles and some of their properties were recently described.^[11,12] We reasoned that by incorporating triply functional bridging ligands (for example, ligands **1** and **2**) into the synthetic strategies developed for assembling the rectangles, we could synthesize a host molecule (a "molecular trigonal right prism") which would have a high internal volume, would be very hydrophobic, and would display guest size selectivity based on the cavity port size. In this paper, we report on the synthesis and characterization of the first generation of compounds of this type. Following the "rectangle strategy" in reference [12], these species utilize a 2,2'-bipyrimidine (bpym) to coordinate rheniums along the short edge of the structure.



EXPERIMENTAL

Solvents were dried over molecular sieves before use. All other reagents were used as received from Aldrich or Pressure Chemicals. $[\text{Cl}(\text{CO})_3\text{Re}]_2\text{bpym}$ was prepared as we had previously reported.^[12] Ligands **1** and **2** were prepared according to literature methods.^[13,14] UV-vis absorption spectra were recorded on a HP8452 diode array detector and ^1H NMR spectra were recorded using a Gemini 300 spectrometer, using acetone- d_6 or DMSO- d_6 as solvent. Space filling models of **3** and **4** were generated by molecular mechanics based geometry optimization using HyperChem 4 for Windows.¹⁵

Synthesis

3: $[\text{Cl}(\text{CO})_3\text{Re}]_2\text{bpym}$ (69.0 mg) was added to 25 mL of deoxygenated acetone (bubbling with N_2) in a round bottom flask with a teflon stir bar. The silver triflate (47.6 mg) was added and the reaction mixture was heated to 60 °C under flow of N_2 . After four hours, heating was stopped, and the reaction mixture was allowed to cool to room temperature. The precipitated AgCl was removed by passing the reaction mixture through Celite on a glass frit, and the solvent was removed by rotary evaporation to give a dark red film. THF (25 mL) was added to the flask, dissolving the film. Ligand **1** (18.6 mg) was added to the solution, and the resulting mixture was degassed by bubbling N_2 . The reaction mixture was allowed to reflux under flow of N_2 . After two days, heating was stopped, and the flask was allowed to cool to room temperature. A dark red precipitate was collected on a glass frit and washed with several times with THF. The product was dried under vacuum to give 57.4 mg of dark red powder (~52 % yield). ^1H NMR (acetone- d_6 , ppm): 10.34 (d, 12H), 8.74 (t, 6H), 8.66 (d, 12H), 8.46 (d, 12H).

4 was prepared in an identical manner to **3**, except replacing ligand **1** with **2**. The product was isolated as an orange powder, and recrystallized from acetone/hexanes. ^1H NMR (DMSO- d_6 , ppm): 9.95 (s, 12H), 8.50 (t, 6H), 8.34 (d, 12H), 7.65 (s, 6H), 7.30 (d, 12H).

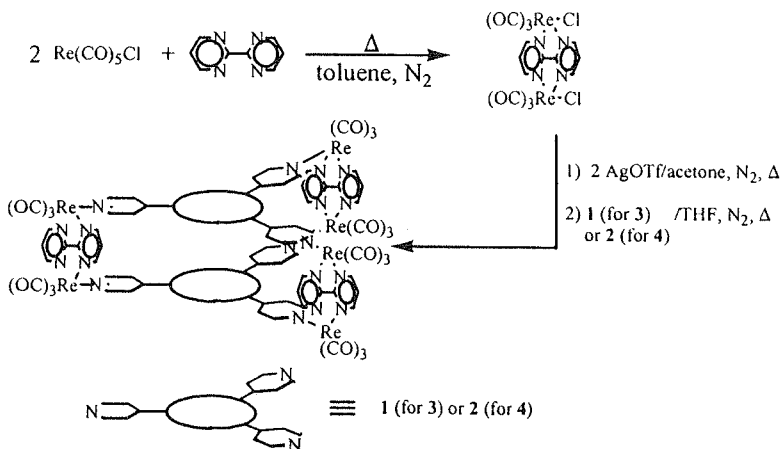
RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis of the molecular-scale trigonal right prisms, as depicted graphically in Scheme 1, is a relatively straight forward extension of our previously reported synthetic strategy. The yields are, as expected, around 50 % because of the orientation of the chlorides on $[\text{Cl}(\text{CO})_3\text{Re}]_2\text{bpym}$: half will be aligned on the same face (syn) with respect to the plane of the bipyrimidine ligand, and can coordinate with the ligand to form a cycle, while half will be aligned on opposite faces (anti), and can form only short chain oligomers. Only the completed cycles precipitate from solution.

The compounds show similar electronic absorption spectra in DMSO as solvent. Both feature a relatively intense absorption with a λ_{max} near 325 nm and a much weaker and broader shoulder which tails out to ~ 575 nm with no clearly defined maximum. While Re(I) polypyridyl complexes are typically luminescent, species which utilize the bpym as a bridge are nonemissive due to the greatly lowered energy of the bpym-based π^* orbital upon coordination of a second metal, and the resulting increase in energy-gap-dependent nonradiative decay.^[12,16]

Scheme 1



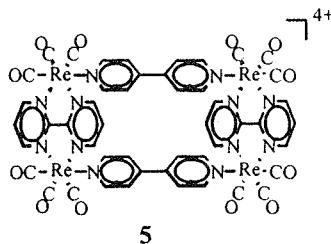
Mass spectrometry studies using electrospray ionization were utilized to confirm formation of the hexametallic species **3** and **4**. While the parent ion was not observed for **3** ($m/z = 3615$), two ions were observed which were assigned as a doubly charged ion ($m/z = 1659$), corresponding to the loss of two triflates, and a triply charged ion ($m/z = 1056$), corresponding to the loss of three triflate counterions. For **4** ($m/z = 3753$) however, a weak signal for the parent ion minus one triflate ($m/z = 3604$) was observed, in addition to a stronger signal which was assigned as doubly charged ion, indicating the loss of two triflates ($m/z = 1728$).

Host-Guest Interactions

The interaction of **3** and **4** with potential guests was monitored by ^1H NMR. Unfortunately, we were unable to use either D_2O or a $\text{D}_2\text{O}/\text{DMSO}-d_6$ mixture as solvent because, upon addition of charged guests (benzene sulfonic acid, sodium salt or naphthalenedisulfonic acid, disodium salt, for example), **3** or **4** quantitatively precipitates out of solution. When the precipitate is redissolved and examined in $\text{DMSO}-d_6$, signals from protons on both the guest molecule and the host are observed. While the precipitation certainly suggests that there is an interaction between the host and guest, attempts to observe the interaction in these systems in pure $\text{DMSO}-d_6$ as solvent were ambiguous because any changes in host signals were small (>0.05 ppm) or were hidden by NMR signals associated with the guests.

Modeling and Volume Calculations

The systems developed should provide access to relatively large cavities, with respect to internal volume as compared to one of our molecular rectangles, **5**. Calculations based on the crystal structure of the molecular rectangle and modeling of **3** and **4** with HyperChem have allowed us to estimate both the increase in cavity volume and the size of the port which gives access to the cavity. For **5**, the data from the crystal structure gives a cavity with approximate dimensions of $5.9 \times 11.5 \times 8.8 \text{ \AA}^3$ ($\sim 600 \text{ \AA}^3$). Figure 1 shows a tilted side view of the results of geometry optimization for



4. To find the internal volume for **3**, the area of the top edge was idealized as a hexagon (as seen in Figure 2, the top view of **3** shows a hexagonal shape with the bipyrimidines serving as one set of edges, and the distance between the closest protons on the bipyrimidines serving as a second set), whose area was then multiplied by the Re-Re distance along the bpym edge (this distance was taken from the crystal structure of **5** as

HyperChem consistently underestimates the Re-N bond distance by a couple of tenths of Å). A cavity volume of 1200 Å³ was obtained. A similar procedure was used to obtain the internal volume of **4** (See Figure 3), which gave a result of ~1800 Å³; almost three times larger than the rectangular host, **5**.

A second feature of the triangular structures should be an ability to select guests according to size by controlling the size of the entry ports. Rough estimations show that for **3** the minimum port size is ~9 Å, while for **4**, it is closer to 13 Å. It is easy to envision further constriction of the entry ports by addition of substituents to the bpym bridges at the 5 and 5' positions. Another option would be to impart

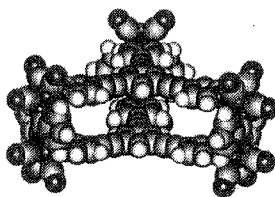


Figure 1. A tilted view of the spacefilled model of **4**, as generated by HyperChem 4, using molecular mechanics to generate a geometry optimized structure.

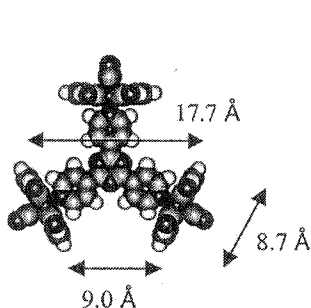


Figure 2. A molecular model of **3** showing the hexagonal dimensions.

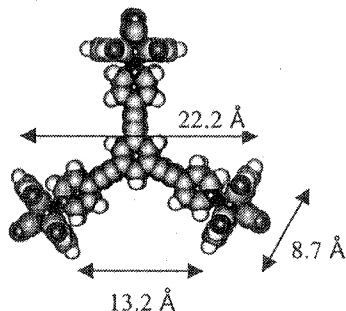


Figure 3. A molecular model of **4** showing the hexagonal dimensions.

specific chemical or enantiomeric selectivity by modifying the bpym with chemically functional or chiral groups which can act as gatekeepers to allow or deny access to the cavity for guests which have desired functionalities.

CONCLUSION

The synthetic chemistry for the first two members of a family of hexametallic host molecules has been developed. The large cavity volumes of the host molecules **3** and **4** ought to allow the sequestering of several potential guests and should provide a more completely encapsulating, and thus more hydrophobic, cavity than possible with the simple molecular rectangles — although this has yet to be demonstrated experimentally. In addition, the structure of bpym bridges should allow functionalization of the host at the entry ports of the cavity which will allow further chemical and size selectivity of potential guests. Finally, by analogy to the most recent developments in molecular rectangle chemistry,^[17] we hope to gain useful synthetic access to closely related neutral assemblies. These assemblies could serve as building blocks for additional molecular materials capable of sensing and/or sieving.

Acknowledgments

We gratefully acknowledge financial support from the U.S. National Science Foundation (grant number CHE-9810483) and from the National Oceanic and Atmospheric Administration.

References

- [1] M. Fujita, G. Ogura *Bull. Chem. Soc. Jpn.* **69**, 1471 (1996), and references therein.
- [2] P. J. Stang, B. Olenyuk *Acc. Chem. Res.* **30**, 502 (1997), and references therein.
- [3] M. Fujita, S. Nagao, K. Ogura *J. Am. Chem. Soc.* **117**, 1649 (1995).
- [4] N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita *Nature* **398**, 794 (1999).
- [5] B. Olenyuk, J. A. Whiteford, A. Fechtenkötter, P. J. Stang *Nature* **398**, 796 (1999).
- [6] R. V. Slone, J. T. Hupp, C. L. Stern, T. E. Albrecht-Schmitt *Inorg. Chem.* **35**, 4096 (1996).
- [7] R. V. Slone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei, A. L. Rheingold, *Coord. Chem. Rev.* **171**(1), 221 (1998).
- [8] S. Bélanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson, T. G. Carrell, *J. Am. Chem. Soc.* **121**, 557 (1999).
- [9] S. Bélanger, J. T. Hupp, *Angew. Chem., Int. Ed. Engl.* **38**, 2222 (1999).
- [10] M. H. Keefe, R. V. Slone, J. T. Hupp, K. F. Czaplewski, R. Q. Snurr, C. L. Stern *Langmuir*, submitted (1999).
- [11] K. D. Benkstein, J. T. Hupp, C. L. Stern *Inorg. Chem.* **37**, 5404 (1998).

- [12] K. D. Benkstein, J. T. Hupp, C. L. Stern *J. Am. Chem. Soc.* **120**, 12982, (1998).
- [13] A. J. Amoroso, A. M. W. C. Thompson, J. P. Maher, J. A. McCleverty, M. D. Ward *Inorg. Chem.* **34**, 4828 (1995).
- [14] H. L. Anderson, S. Anderson, J. K. M. Sanders *J. Chem. Soc. Perkin Trans. I* 2231 (1995).
- [15] *HyperChem* Release 4 For Windows; HyperCube: Waterloo, Ontario, 1994.
- [16] R. Lin, T. F. Guarr *Inorg. Chem. Acta* **167**, 149 (1990).
- [17] K. D. Benkstein, J. T. Hupp, C. L. Stern, unpublished results.