Discrete Supramolecular Architecture vs Crystal Engineering: The Rational Design of a Platinum-Based Bimetallic Assembly with a Chairlike Structure and Its Infinite, Copper Analogue

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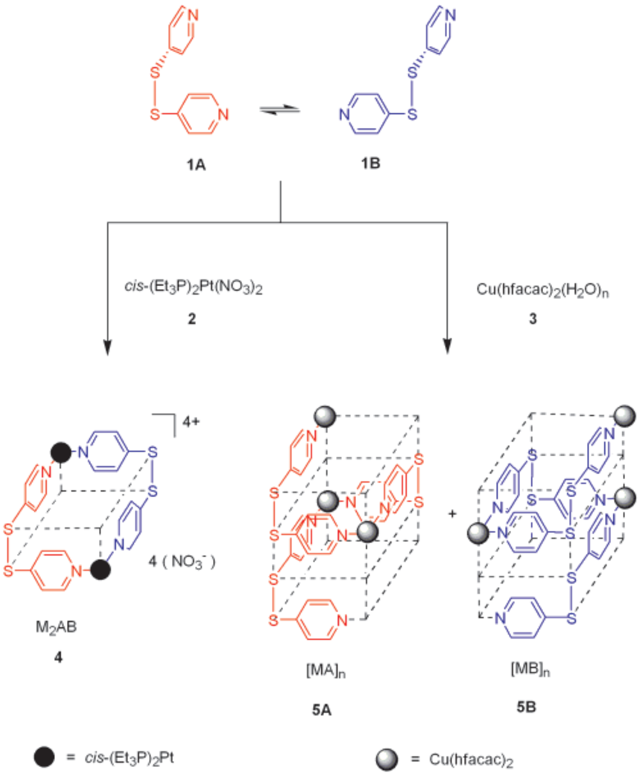
Received March 8, 2001
Revised Manuscript Received June 7, 2001

Over the past decade, the coordination motif has been established as a powerful tool in the design and self-assembly of a wide variety of supramolecular aggregates.[1] This approach has been applied successfully in the development of a vast array of both solution-based, supra-molecules and solid-state, infinite polymers and networks. The former has been termed discrete molecular architecture, while the latter constitutes a branch of crystal engineering.

One sophisticated tactic employed in this type of synthesis is the strategy of rational design, which utilizes building blocks that have been encoded with the information necessary to predetermine the overall structure of the resulting product. Milestones in the still ongoing evolution of this methodology include closed, two-dimensional rings and three-dimensional cage compounds for the discrete systems,[2] as well as a large assortment of coordination polymers, grids, and lattices for the infinite systems.[3] Much of the work done in these areas has relied upon "covalently determined", relatively rigid angles. Here we introduce for the first time the use of a conformationally defined, dihedral angle as a means of pre-programming supramolecular information and investigate its implications in both discrete molecular architecture and crystal engineering.[4] This has the potential for significantly augmenting the "tool-box" of the modern day supramolecular chemist, as well as providing a novel approach to the field of rational design.

In this study, we employed 4,4′-dithiodipyridine (DTDP) **1** as the nucleophilic tecton in self-assembly reactions with metal centers of varying lability. As has been known for over 50 years, acyclic disulfides exist as an equilibrium mixture of two, enantiomeric conformers with idealized dihedral angles (C−S−S−C) of 90°.[5,6] The barrier of rotation between these two forms **1A** and **1B** is known to be relatively low,[7] but, as we will show, served a crucial role in pre-defining the resultant supramolecular species (Scheme 1).

Scheme 1



A priori, the combination of DTDP with an electrophilic, ditopic metal center having a potentially 90° angle between its bonding sites could give rise to three reasonable metal−ligand combinations: chairlike square M$_2$AB (**4**) and helices [MA]$_n$ (**5A**) and [MB]$_n$ (**5B**). The metal centers utilized were the square-planar platinum(II) complex **2**[8] and the octahedral copper(II) complex **3** (hfacac = hexafluoroacetylacetonate), both of which can serve as ∼90°, ditopic linking units.[9] By supplementing the structure-defining C−S−S−C dihedral angle of the DTDP ligand with the proper choice of metal center, the outcome of the self-assembly reactions can be predictably tuned, thus allowing for the unambiguous rational design of both species **4** and **5**.

When platinum(II) subunit **2** (47.6 mg, 0.09 mmol) was allowed to react with DTDP **1** (18.9 mg, 0.09 mmol) in methanol-d_4, M$_2$AB (**4**) was formed in 90% yield. Formation of a closed, highly symmetrical system was indicated by ^{31}P{^{1}H} and ^{1}H NMR.[10] By the slow diffusion of diethyl ether into a methanol solution of **4**, crystals suitable for X-ray analysis were grown.

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(6) Crystals of DTDP **1** were grown out of a diethyl ether/hexanes solvent mixture by slow evaporation. The dihedral angle C−S−S−C (84°) of the disulfide unit and the S−S bond length (2.03 Å) were found.

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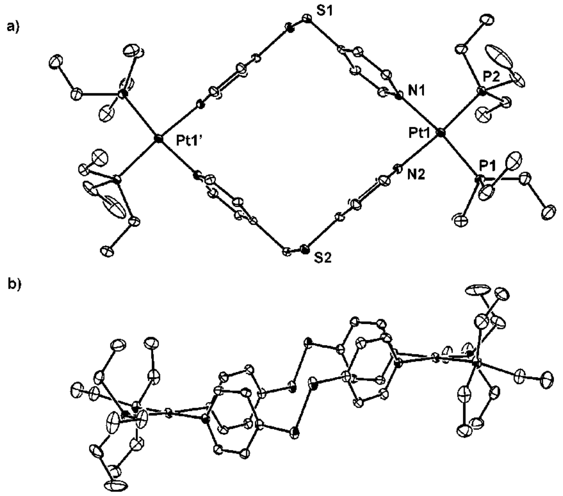

Figure 1. Crystal structure of M_2AB complex **4**: (a) top view and (b) side view. Solvent, counterions, and protons were omitted for clarity.

The ORTEP representation of **4** clearly revealed that the anticipated structure was realized (Figure 1).

With the gauche conformation and dihedral angle (91.6°) of the disulfide unit, as well as the S−S bond length (2.03 Å), largely retained, an unstrained, chairlike configuration for the supramolecular entity was achieved. Platinum compounds with **2** as a subunit are especially known to form closed rings in solution.[11] To create such a closed system in **4**, one of each enantiomer **1A** and **1B** was necessary, as was evident. The dimensions of the internal cavity were 11.0 Å (Pt1−Pt1′ distance) and 8.7 Å (S1−S2 distance). These were quite similar to previously published rhomboids.[11] The rhomboids were designed as planar species via the "covalently determined " building blocks employed. Our unique, conformationally controlled design strategy, however, has allowed for an added dimension in the final product, drawing a stark distinction between itself and previously known systems.

In contrast, when a more labile metal center, such as copper(II) complex **3** (50.3 mg, 0.10 mmol), was treated with DTDP **1** (22.1 mg, 0.10 mmol) under similar reaction conditions, a racemic mixture of helices $[MA]_n$ (**5A**) and $[MB]_n$ (**5B**) resulted in the solid state.[12] The crystals suitable for X-ray structural determination were obtained by slow evaporation of the methanol solvent.

The crystal structure of **5** clearly demonstrated that the gauche conformation of the DTDP unit was very similar to both the starting material **1** and platinum complex **4** [dihedral angle 92.2°, S−S bond distance 2.03 Å], as expected (Figure 2). The distinguishing characteristic between **5** and **4**, however, was that **5** existed in the solid state as infinite, polymeric helices. Only a single enantiomer, either **1A** or **1B**, was present in any given helix, which can be viewed as a form of enantiomeric resolution for each distinct species **5A** and **5B**.

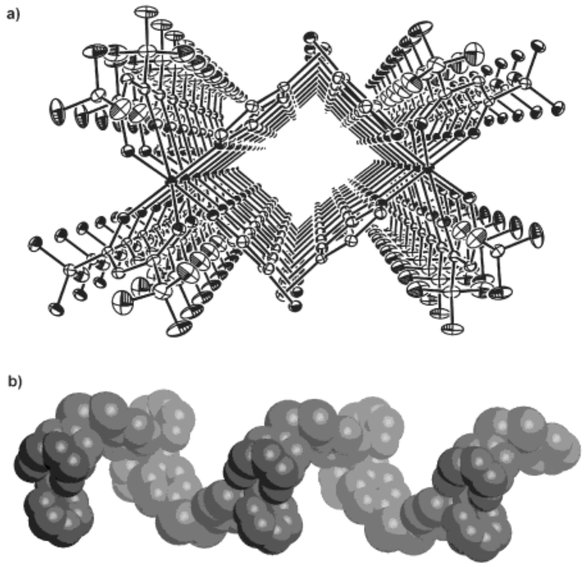

Figure 2. (a) Stacking diagram of helix **5B** protons omitted for clarity. (b) Segment of helix **5B**. Protons and CF_3 groups were omitted for clarity.

The assumption can be made that the differences arising between **4** and **5** were a direct result of the fact that platinum aggregate **4**, with its more inert dative bonds, assembled in solution, while copper assembly **5**, having a much more labile interaction with the ligand, formed at the solvent−crystal interface. With **4** having been produced in solution, such factors as entropy may have driven the formation of a closed system. In **5**, which existed only in the solid state, crystal packing forces may have predominated and dictated the overall product.

In conclusion, we present here the first example in which a conformationally defined, dihedral angle was employed as a means of pre-programming supramolecular information in the self-assembly of both a bimetallic supramolecular square and a helical coordination polymer. With the more inert platinum−pyridyl bond, we believe that the closed system resulted from solution-based thermodynamics. The polymeric system, with the more labile copper−pyridyl bond, was derived primarily from organizational forces in the solid-state. This potentially considerable extension of already intriguing rational design methodologies supplies a unique predictive power over these systems and may lead to new horizons in the fields of both discrete supramolecular architecture and crystal engineering.

Acknowledgment. Dedicated to Academician O. M. Nevedov on the occasion of his 70th birthday. We thank the National Science Foundation for financial support of this research (CHE-9818472). We are also grateful to the A. v. Humboldt Foundation for a Feodor Lynen Fellowship for F. M. Tabellion.

Supporting Information Available: Crystallographic data of **1**, **4**, and **5** and experimental preparations for **4** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015784A

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(10) $^{31}P\{^1H\}$ NMR (methanol-d_4) δ 0.57 (s, $^1J_{Pt-P} = 3073$ Hz); ^1H NMR (methanol-d_4) δ 8.70 (m, 8H, δ-pyridyl proton), 8.07 (m, 8H, δ-pyridyl proton), 1.71 (m, 24H, CH_2-P), 1.13 (m, 36H, CH_3-CH_2-P). A minor biproduct was observed via NMR (~5%). ESMS data could not be obtained for 4, perhaps, in part, due to its thermal instability.

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