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Reversible Transformations of P-N Coordination Networks upon Interactions with Solvent

Jason Kositarut
DePaul University, jkosi@mac.com

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INTRODUCTION
Self-assembling crystalline networks of metals and organic compounds have received significant attention from the research community. The area of guest-host chemistry of metal-organic frameworks (MOFs) is of particular interest as it shows great promise as a technology for storing gases that are important for future energy technologies. Many MOF structures feature large pores within their structure. These pores greatly increase the surface area of the molecule providing numerous adsorption sites. This is of particular interest for the automotive industry as it looks for alternatives to hydrocarbon fuels. Hydrogen is widely considered to be the best candidate for replacing gasoline and ethanol but faces significant hurdles before widespread adoption can occur. One of those hurdles is a storage system for the hydrogen fuel. The most common storage methods at this time involve compressing it in gaseous form or cryogenically condensing it to a liquid. Both methods, while effective, provide significant engineering challenges when applied to an automobile.

In theory, this could be solved by storing the hydrogen as a guest molecule inside the structure of a metal-organic framework.

This work focuses on metal-organic networks that result from the reaction of cuprous chloride, CuCl, and closo-tetraphosphorohexamethylimide, \( \text{P}_4(\text{NCH}_3)_6 \), ligand in the presence of different solvents. The goal was to explore the ability of these compounds to exchange guest ligands through solvent exchange. This research has shown that it is possible to convert these two structures into each other, and re-form the original structure by simply soaking the solid material in a different solvent. In one experiment, a MOF with a structure consisting of alternating layers of ruffled sheets was found to have channels roughly 16Å across. These channels were found to contain molecules of the solvent used in the MOFs creation. The guest solvent molecules were successfully replaced through immersion in another solvent or removed through heating under vacuum.
A metal-organic network with the same large-scale structural features was recently discovered. As with the previous structure, it was found to host molecules of the solvent in which it was created. This is the sixth structure found using the combination of \( \text{P}_4(\text{NCH}_3)_6 \) cage ligand and cuprous chloride. The first five networks are assembled in acetonitrile with the structure dependant on the ratio of ligand to metal. One of these networks (2) assembled in acetonitrile results from a ligand/metal ratio of 1:1. The sixth structure (1) is assembled in benzonitrile and the shape is the same at ligand/metal ratios greater than 1:1 and features stacking 2-D sheets with a distinct ruffled shape. When 1 is treated with acetonitrile, the structure is reassembled to match that of 2. When 2 is treated with benzonitrile, the structure is reassembled to that of 1. This process is reversible and does not depend on the provenance of the starting material. The general outline of the reactions can be seen in Figure 2.

**EXPERIMENTAL**

**GENERAL CONSIDERATIONS**

All reactions were carried out in a glove box under nitrogen atmosphere unless otherwise stated. Anhydrous benzonitrile, acetonitrile and diethyl ether were purchased from Sigma-Aldrich and used without additional refinement. Powder XRD analysis was performed using a Rigaku GiegerFlex D-Max/B X-ray diffractometer with power settings of 35kV, 25mA, using glass specimen holders with a well-depth of 0.5mm. Diffraction intensities were collected using step-scan acquisition over a 2-\( \theta \) range of 5° to 35° with a step size of 0.02° and a dwell time of 4 seconds. Diffraction patterns were then compared to calculated patterns derived from single-crystal data using the crystallographic program Mercury. \(^1\text{H}, \, ^{13}\text{C} \) and \(^{31}\text{P} \) NMR analyses were done using a Bruker Avance 300MHz NMR spectrometer. Thermogravimetric analyses were performed with a Thermal Advantage 2050 with a temperature range of 30-600°C at 10°C/minute with 60mL/minute of \( \text{N}_2 \) gas.

**PREPARATION OF \( \text{P}_4(\text{NCH}_3)_6 \) LIGAND**

\( \text{P}_4(\text{NCH}_3)_6 \) cage ligand was prepared as described by Holmes and Forstner.\(^{12}\) Anhydrous methylamine was condensed into the reaction vessel at -78°C. Phosphorous trichloride was added while being mechanically stirred. The mixture was allowed to warm overnight and crude product was recovered by extraction with hexanes, filtration and evaporation. Pure ligand was isolated by vacuum sublimation at 90°C.

**SYNTHESIS OF \( \text{P}_4(\text{NCH}_3)_6\text{CuCl} \cdot 0.3\text{C}_6\text{H}_5\text{CN} \) (1)**

Compound 1 was synthesized from cuprous chloride and \( \text{P}_4(\text{NCH}_3)_6 \) in the following procedure. A solution of \( \text{P}_4(\text{NCH}_3)_6 \) cage ligand was prepared by adding 10mL of benzonitrile to 0.385g (0.129M) of ligand in a 20mL scintillation vial. The solution of cuprous chloride was prepared by adding 10mL of benzonitrile to 0.105g (0.106M) of CuCl. After both solutions were prepared, the cuprous chloride solution was added drop-wise to the scintillation vial containing the ligand solution. Wispy, white precipitate formed and redissolved during the addition of the first 1.5mL of metal solution. The precipitate persisted after 1.5mL and the solution became progressively cloudier with further additions. The solution was stirred overnight and suction filtered to yield a fine, white powder (0.405g, 82.6%).

**CONVERSION OF (1) TO (2)**

A 0.297g sample of 1 was stirred in 10mL of acetonitrile. This resulted in a clear, colorless solution over powdery white solid. The mixture was stirred for 90 minutes and then allowed to sit undisturbed overnight. The mixture was vacuum evaporated with a stir bar. The remaining white solid material was left under vacuum for 20 minutes before the product was recovered from the flask yielding a fine, white powder (0.199g 67.0%).

Additional experiments were conducted where the acetonitrile was separated from the solid product through filtration instead of evaporation. In these experiments, the filtrate was evaporated separately and white, needle-like crystals were observed to form.
Compound 2 was synthesized following the procedure outlined by Leser, et al. CuCl (0.092g, 9.3x10^{-4} mol) and cage ligand (0.277g, 9.3x10^{-4} mol) were combined yielding a fine white powder (0.228g, 61.7%).

CONVERSION OF (2) TO (1)
A 0.119g sample of 1 was stirred in approximately 10mL of benzonitrile for 90 minutes. The vial was left undisturbed for four days resulting in a clear, colorless liquid over white solid. The solid mixed readily when the vial was gently stirred. The contents of the vial were transferred via pipet to a fritted glass funnel for vacuum filtration. After filtration, the contents of the funnel were washed with 1.5 mL of diethyl ether. The product was a fine white powder (0.105g, 88.2%).

RESULTS
XRD PATTERN ANALYSIS
Powder patterns of all products were compared against patterns calculated from single-crystal data using Mercury 2.0 performed by Pickering. The observed powder patterns for 1 and 2 were consistent with the calculated pattern for 1 and 2, respectively. The observed pattern for 1, after being soaked in acetonitrile, was consistent with the calculated pattern for 2. The observed pattern for 2, after soaking in benzonitrile, was consistent with the calculated pattern for 1.

DISCUSSION
Structure 1, a two-dimensional metal organic network, is normally synthesized by reacting P₄(NCH₃)₆ with cuprous chloride in benzonitrile. Compound 2, a three-dimensional network, is synthesized from the same reactants but using acetonitrile as the solvent. When 1 is treated with acetonitrile, the structure is rearranged to match that of 2. To reverse this process, the newly reorganized 2 is treated with benzonitrile and the network is returned to its original structure. This process has been observed to occur regardless of whether the starting material was synthesized directly or the product of prior conversion.

The difference in stoichiometry between 1 and 2 suggests there should be an excess of ligand left over after conversion of 1 to 2. Compound 1 has a ligand-to-metal ratio [P₄(NCH₃)₆:CuCl] of 1:1 while 2 has a ratio of 2:3. As a result, it is expected that excess ligand would remain after converting 1 to 2. Though not observed in the diffraction patterns, white needle-like crystals form after evaporating the filtrate from step 1 of the reaction, represented by (c) in Figure 2. Proton and phosphorus NMR spectroscopy identified these crystals as pure P₄(NCH₃)₆ ligand. NMR analysis of the acetonitrile filtrate also indicated the presence of trace amounts of benzonitrile, the guest molecule in the pores of compound 1. An excess of CuCl is also expected after converting from 2 to 1 but this has yet to be confirmed.

CONCLUSION
Transformation of the two-dimensional sheets of compound 1 into the three-dimensional network of compound 2 can be accomplished by soaking the material in a different solvent. Without significant loss of material, the reverse transformation takes place by switching the solvent system back to the original benzonitrile. The reversible uptake of solvent guests, and subsequent release of those guests to a different solvent, illustrates the idea of using these networks as storage and delivery systems for guest molecules. In this case, two equivalents of acetonitrile are captured during the conversion from compound 1 to 2 in acetonitrile. The guest acetonitrile molecules can be released in another location by treating compound 2 with benzonitrile. Since the X-ray diffraction patterns are so distinct, the progress of capture or release can be monitored through XRD analysis. This process can also be considered “green” as the process of capture and release occurs without consuming the storage medium.

This experiment is significant because it illustrates a reversible process by which molecules can be easily stored, transported and released in a reusable storage medium.
P4(NCH3)6 ligand, left, and the two different compounds studied in this work 1 and 2 respectively. Pink atoms are phosphorus, blue-nitrogen, gray-carbon, dark blue-copper, green chlorine. Hydrogen atoms removed for clarity. The solvent channels in structure 1 are highlighted in pink.

**FIGURE 1**

The synthesis and conversion of two metal-organic networks synthesized from P4(NCH3)6 and CuCl.

**FIGURE 2**

Powder XRD pattern data showing the conversion of 1 to 2. The starting material for this reaction was taken from the product of the conversion of 1 to 2.

**FIGURE 3**

Powder XRD pattern data showing the conversion of 2 to 1. The starting material for this reaction was taken from the product of the conversion of 1 to 2.
REFERENCES


