Development of Pyridine Phosphate-based Metal-Organic Frameworks
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Abstract
Metal-organic frameworks (MOFs) are a group of porous crystalline materials formed from coordination complexes between organic and inorganic units. Due to their pores, MOFs can have impressively high surface areas, leading to potential valuable applications in storage, separation, and catalysis. MOFs are typically formed by the growth and accumulation of coordination complex crystals in solution. The goal of this project was to investigate if a crystalline complex could be formed with an organophosphate ligand instead of the more commonly-used carbohydrate-based ligands. To do this, we first synthesized dipyridinediphosphonic acid (DPPDA). Afterwards, we paired the ligand up with a variety of metal ions, solvents, and pH ranges to determine the optimal condition for crystals to grow. We discovered that the best combination involved using 0.0500 mmol of DPPDA with 0.0500 mmol of copper (II) nitrate in 2.0 mL water and 0.10 mL triethanolamine (TEOA) forming blue-green microcrystals. Further tests could be performed with similar conditions to grow larger crystals for use in MOF building.

Background
Metal-organic frameworks (MOFs) are an extensive class of highly-porous coordination polymers with huge internal surface areas. They consist of organic ligands coordinated to metal cations, and due to the enormous variety of compounds and metal ions that could be used as MOF components, a huge amount of different MOFs have been synthesized. Indeed, more than 20,000 different MOFs were reported within the past decade [1].

The most basic units of a MOF is a secondary building units (SBUs) and linkers. SBUs are metal cation clusters or complexes, usually consisting of particular transition metal cations, since these can form a variety of interesting coordination complexes with oxidation numbers ranging from 2 to 7. Linkers are the organic units connecting SBUs to each other. Depending on the structure of the SBU and how it interacts with linkers, the resultant MOF can be one, two, or three-dimensional. See the chart below for how inorganic-organic hybrids are categorized by dimensionality. MOFs have attracted a considerable amount of interest since the 1990s due to their remarkable versatility. Because their features can be fine-tuned after synthesis without significantly affecting underlying topologies, MOFs can be precisely enhanced to suit a particular purpose, a flexibility that has not been achieved with numerous materials like zeolites and carbon-based structures.

Synthesis of MOFs is achieved almost exclusively through hydrothermal synthesis, in which crystals are grown from a solution under high pressure and temperature. The conditions mimic those found deep within Earth that cause natural crystals to form. In this situation, partial or complete dissolution of MOF ingredients is essential, since compounds must be able to easily travel through the solution to aggregate into a “seeded” crystal.

<table>
<thead>
<tr>
<th>Dimensionality of Inorganic Connectivity, f (f = 0–3)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>Molecular complexes</td>
<td>Molecule chains</td>
<td>Hybrid inorganic layers</td>
<td>Hybrid inorganic hybrids</td>
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<td>Coordination polymers</td>
<td>Mixed inorganic layers</td>
<td>Mixed inorganic-organic frameworks</td>
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<tr>
<td>3D coordination polymers</td>
<td>Mixed inorganic-organic frameworks</td>
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Synthesis of Dipyridinediphosphonic acid (DPPDA)

Step 1: 4,4’-bipyridine to N-oxide

To a 250 mL round-bottomed flask was added 15.6 g 4,4’-bipyridine, 43 mL of 30% H2O2, and 80 mL of glacial acetic acid. The mixture was heated while stirring at 80°C for 4 hours. Then another 41 mL of 30% H2O2 was added, and the mixture was heated at 80°C for another 12 hours. After that, the flask was cooled to room temperature, and the unreacted H2O2 and acetic acid were evaporated under reduced pressure. 40 mL of water was added to the residue, and the mixture was evaporated again under reduced pressure. Then 200 mL of acetone was added to form a yellow precipitate that was then filtered and washed with acetone. Finally, 4,4’-pyridine N-oxide was recrystallized from ethanol at an 80% yield.

Step 2: 4,4’-pyridine N-oxide to phosphonate

16 g of 4,4’-pyridine N-oxide was added to a 1000 mL round-bottomed flask with 800 mL CH2Cl2. Then 48.6 mL arsphenyl ethyl chlorophenolate was added and stirred for 10 minutes under nitrogen atmosphere. Following that, 89 mL triethyl phosphate was added dropwise, and the mixture was then stirred for an additional 30 minutes under nitrogen atmosphere. The resulting solution was washed with saturated NaHCO3, water, and then brine, with excess liquid evaporated under reduced pressure. The organic product left behind was dried with silica, run on a column with CH2Cl2, and evaporated under reduced pressure again to form a yellow solid (the phosphonate) at 67% yield.

Step 3: 4,4’-pyridine phosphonate to phosphate

In a 1000 mL round-bottomed flask was placed 24.2 g of 4,4’-pyridine phosphonate and 300 mL of 8 M HCl. The mixture was refluxed over 18 hours, then evaporated under reduced pressure, and then suspended in water and filtered. The resulting product was washed with water twice before to dry at room temperature. The result is an off-white cakey solid, DPPDA, and it was obtained at an 87% yield.

Making the Crystals

Several trials were run, with different metal cations (Mn2+, Cu2+, Ni2+, Zn2+), metal-ligand ratios, pH solvents (water, N-methyl-2-pyrrolidone, methanol, dimethylformamide), and time in oven, before a combination that yields crystals was found. A detailed table of all trials can be found here: https://pesa-utd.udf

In the successful trial, 11.7 mg (0.0500 mmol) of Cu(NO3)2 was added to a screw-top vial containing 15.8 mg (0.0500 mmol) of DPPDA, 2.00 mL deionized water, and 0.10 mL triethanolamine (TEOA). The vial was sonicated until the solution inside became clear. Afterwards, it was heated for 8 hours in a sand bath in an oven at 130°C. After being removed from the oven, the vial was allowed to slowly cool down to room temperature, so the complexes within it would continue to form crystals without disturbance. Finally, the vial was examined under a microscope.

Results

The ligand by itself was insoluble in all solvents used, so base (NaOH or TEOA) was added to deproteinate it. The metal cations did not precipitate as metal hydroxides when TEOA was added, which made it a better base to use than NaOH. Out of all solvents, water was best at keeping both metal and the deproteinated ligand in solution. Also, combinations with copper and nickel dissolved with the most ease.

Most trials were unsuccessful — the ligand may have settled out, or simply remained in solution without binding to the cations, or a powder may have been produced. The trial that produced crystals involved 0.0500 mmol of DPPDA paired with 0.0500 mmol of Cu in 2.00 mL water and 0.10 mL TEOA. The blue-green microcrystals that formed had a diameter of ~10 μm. Since they were so small, however, we could not determine the crystal structure with X-ray crystallography.

References

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