

Metal Insertion in a Microporous Metal–Organic Framework Lined with 2,2′-Bipyridine

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Abstract: Reaction of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with 2,2′-bipyridine-5,5′-dicarboxylic acid (H_2bpydc) affords $\text{Al}(\text{OH})(\text{bpydc})$ (**1**, MOF-253), the first metal–organic framework with open 2,2′-bipyridine (bpy) coordination sites. The material displays a BET surface area of $2160 \text{ m}^2/\text{g}$ and readily complexes metals to afford, for example, $1 \cdot x\text{PdCl}_2$ ($x = 0.08, 0.83$) and $1 \cdot 0.97\text{Cu}(\text{BF}_4)_2$. EXAFS spectroscopy performed on $1 \cdot 0.83\text{PdCl}_2$ reveals the expected square planar coordination geometry, matching the structure of the metal complex (bpy) PdCl_2 . Significantly, the selectivity factor for binding CO_2 over N_2 under typical flue gas conditions is observed to increase from 2.8 in **1** to 12 in $1 \cdot 0.97\text{Cu}(\text{BF}_4)_2$.

Owing to their high surface areas and tunable pore functionality, metal–organic frameworks are currently under investigation for a variety of potential applications, including gas storage,¹ gas separations,² and catalysis.³ Of particular promise are frameworks with surfaces bearing exposed metal centers, since these can dramatically enhance (selective) gas uptake or serve as a source of catalytic activity.⁴ Such metal sites have typically been created either by desolvation of a framework featuring metal-bound solvent molecules or via some form of postsynthetic modification to the organic bridging ligands.⁵ The direct formation of frameworks bearing chelating ligand sites that are open to metal insertion is rare,^{3a,b,6} since typically metal binding at these sites would occur during framework synthesis. In our efforts to generate compounds of this type, we considered the possibility that a hard oxophilic metal cation might preferentially coordinate the carboxylate groups of a mixed donor ligand such as 2,2′-bipyridine-5,5′-dicarboxylate (bpydc^{2-}), leading to a framework with the softer donor groups available to bind metals. Here, we show that this strategy can indeed be successfully employed in generating $\text{Al}(\text{OH})(\text{bpydc})$ (MOF-253), the first metal–organic framework featuring open 2,2′-bipyridine (bpy) ligand sites. Subsequent complexation of Pd^{2+} and Cu^{2+} is demonstrated, with the latter resulting in a material that exhibits a significantly enhanced selectivity for the adsorption of CO_2 over N_2 .

The synthesis of $\text{Al}(\text{OH})(\text{bpydc})$ was accomplished in direct analogy with the recently reported framework $\text{Al}(\text{OH})(\text{bpdc})$ ($\text{bpdc}^{2-} = 4,4'$ -biphenyldicarboxylate).⁷ Reaction of H_2bpydc with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in DMF at $120 \text{ }^\circ\text{C}$ for 24 h afforded $\text{Al}(\text{OH})(\text{bpydc}) \cdot 2.6\text{DMF}$ ($1 \cdot 2.6\text{DMF}$) as a white microcrystalline solid. Thermogravimetric analysis of the product revealed a weight loss of 40% upon heating to

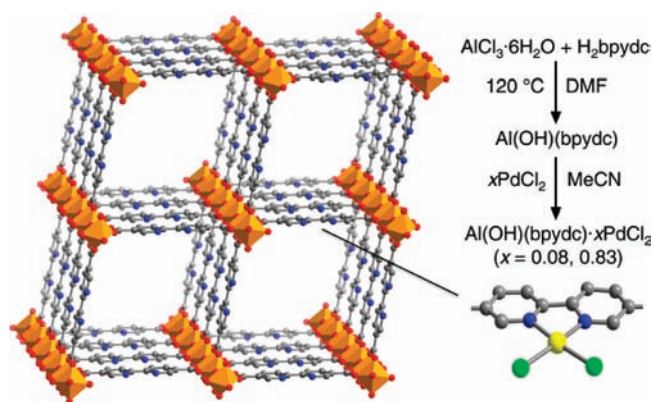


Figure 1. Synthesis and representative structure of $\text{Al}(\text{OH})(\text{bpydc})$ (**1**, MOF-253), with subsequent insertion of PdCl_2 into open bpy ligand sites. Orange octahedra represent Al atoms, while yellow, green, red, blue, and gray spheres represent Pd, Cl, O, N, and C atoms, respectively; H atoms are omitted for clarity.

$200 \text{ }^\circ\text{C}$, consistent with loss of 2.6 solvent molecules per formula unit, with no further weight loss up to $400 \text{ }^\circ\text{C}$. Accordingly, the solid was soaked in methanol and then heated at $250 \text{ }^\circ\text{C}$ under dynamic vacuum for 24 h to yield the fully desolvated framework $\text{Al}(\text{OH})(\text{bpydc})$ (**1**).

X-ray powder diffraction data show **1** to be isostructural with $\text{Al}(\text{OH})(\text{bpdc})$.⁷ A full-pattern decomposition of the data was performed through a Pawley refinement using the $\text{Al}(\text{OH})(\text{bpdc})$ unit cell parameters as a starting point, resulting in refined orthorhombic unit cell parameters of $a = 23.59(10) \text{ \AA}$, $b = 6.91(3) \text{ \AA}$, and $c = 19.84(8) \text{ \AA}$. Based upon the refinement, it is clear that $\text{Al}(\text{OH})(\text{bpydc})$ crystallizes as an **sra** net with a rod-shaped secondary building unit in an extended MIL-53 structure. A crystal model of the structure was built by replacing the biphenyl moiety of $\text{Al}(\text{OH})(\text{bpdc})$ with bipyridine (see Figure 1). Here, one-dimensional chains of hydroxide-bridged, octahedrally coordinated Al^{3+} cations are linked via bpydc^{2-} ligands to give a three-dimensional framework with rhombic channels running along the b axis. Note that the pyridine rings should have only a small energy barrier associated with rotation away from the coplanar configuration depicted, thereby enabling insertion of up to one metal center per bpy unit.

NMR spectroscopy was employed to confirm the bulk composition of **1** (see Supporting Information, Figures S5–S7). As in the activated form of MIL-53,⁸ the ^1H MAS NMR spectrum exhibits two broad peaks, attributable to the aromatic and bridging hydroxide protons. The six sharp resonances in the ^{13}C cross-polarization MAS NMR spectrum confirm the presence of bpydc^{2-} in the structure. Most importantly, the ^{27}Al MAS NMR spectrum shows a solitary

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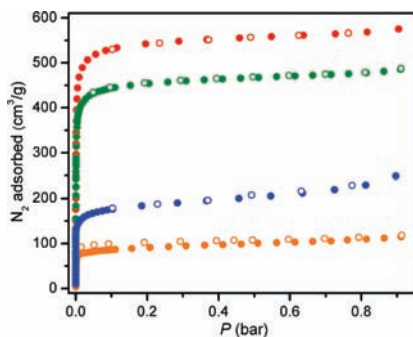


Figure 2. Isotherms for the adsorption of N₂ at 77 K in **1** (red), **1**·0.08PdCl₂ (green), **1**·0.97Cu(BF₄)₂ (blue), and **1**·0.83PdCl₂ (orange). Filled and open circles represent adsorption and desorption data, respectively.

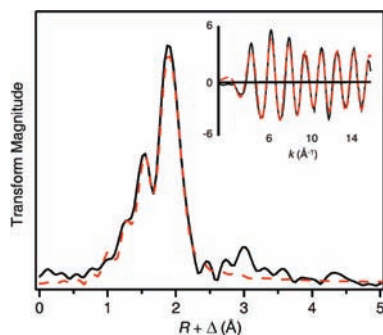


Figure 3. Pd K-edge EXAFS Fourier transforms and EXAFS spectrum (inset) for **1**·0.83PdCl₂. Solid lines show the experimental data, and dashed red lines show the best fits.

signal at $\delta = -7.38$ ppm, consistent with the presence of a single six-coordinate Al³⁺ site. The observation of just one ²⁷Al resonance indicates that the bpy ligands are not coordinated by aluminum and should therefore be available for the postsynthetic chelation of various other metal centers.

Low-pressure N₂ adsorption measurements performed on **1** at 77 K revealed a type I adsorption isotherm characteristic of a microporous solid (see Figure 2, red circles). Fits to the data gave a pore volume of 0.89 cm³/g, together with BET and Langmuir surface areas of 2160 and 2490 m²/g, respectively. The latter value is in good agreement with the Langmuir surface area of 2335 m²/g reported for Al(OH)(bpd).⁷

The accessibility of the chelating bpy units within the framework of **1** was confirmed by soaking the solid in acetonitrile solutions of PdCl₂ and Cu(BF₄)₂ to afford **1**·xPdCl₂ ($x = 0.08, 0.83$) and **1**·0.97Cu(BF₄)₂, as confirmed by elemental analyses. Thermogravimetric analysis showed these metal-loaded samples to exhibit weight losses at 125 °C of 28%, 15%, and 25%, respectively, with no additional loss occurring up to 350 °C (see Supporting Information, Figure S8). As evidenced by powder X-ray diffraction, NMR spectroscopy, and infrared spectroscopy, the underlying framework structure is maintained upon metal complexation. Consistent with the formulations of **1**·0.08PdCl₂, **1**·0.83PdCl₂, and **1**·0.97Cu(BF₄)₂, N₂ adsorption measurements at 77 K resulted in type I adsorption isotherms with reduced BET surface areas of 1780, 355, and 705 m²/g, respectively (see Figure 2). In addition, the estimated pore volumes for the samples were lowered to 0.65, 0.13, and 0.39 cm³/g, respectively.

Extended X-ray adsorption fine structure (EXAFS) spectroscopy was performed on **1**·0.83PdCl₂ to establish the coordination environment of the Pd atom upon insertion within the framework (see Figure 3). The data were best fit using the usual square planar

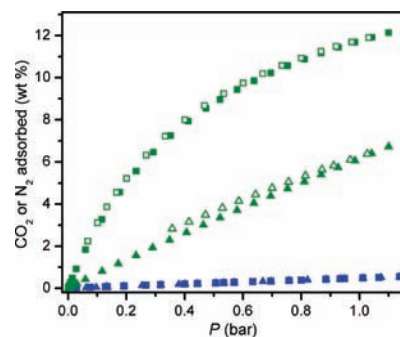


Figure 4. Adsorption isotherms collected at 298 K for the uptake of CO₂ in **1** (green triangles) and **1**·0.97Cu(BF₄)₂ (green squares) and for the uptake of N₂ in **1** (blue triangles) and **1**·0.97Cu(BF₄)₂ (blue squares). Filled and open symbols represent adsorption and desorption, respectively.

geometry, with two Cl⁻ ions and two N atoms from bpy binding the Pd²⁺ center at distances of 2.296(1) and 2.038(3) Å, respectively (see Figure 1). Note that these bond distances are in good agreement with crystallographic data obtained for the analogous molecular complex (bpy)PdCl₂.⁹

Insertion of metal salts within **1** can be expected to create electric dipoles on the surface that render the material suitable for gas separations.² Indeed, as shown in Figure 4, **1**·0.97Cu(BF₄)₂ was found to display a significantly enhanced selectivity for the adsorption of CO₂ over N₂ under conditions relevant to its capture from flue gas. Specifically, at 298 K, the selectivity factor, calculated as the mass of CO₂ taken up at 0.15 bar divided by the mass of N₂ taken up at 0.75 bar, is seen to increase from 2.8 in **1** to 12 in **1**·0.97Cu(BF₄)₂. Consistently, the average isosteric heat of CO₂ adsorption, as calculated using isotherm data collected at 298, 303, and 308 K, was found to increase from 23 to 30 kJ/mol upon insertion of Cu(BF₄)₂ into the bpy sites of **1** (see Supporting Information, Figures S10 and S11). Thus, metal-loaded variants of **1** are well worthy of further study as CO₂ capture materials.

The foregoing results demonstrate the ability of mixed donor ligands to select for hard metal cations during framework assembly, resulting in the first bpy-lined microporous material. Given the ubiquitous role of the bpy ligand in coordination chemistry, we anticipate that this framework will provide a platform for the insertion of a wide variety of metal centers, leading to a broad range of properties and applications.

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Supporting Information Available: Detailed synthetic procedures and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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