Multistep N₂ Breathing in the Metal–Organic Framework Co(1,4-benzenedipyrazolate)

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Abstract: A variety of spectroscopic techniques combined with in situ pressure-controlled X-ray diffraction and molecular simulations have been utilized to characterize the five-step phase transition observed upon N₂ adsorption within the high-surface area metal–organic framework Co(BDP) (BDP²⁻ = 1,4-benzenedipyrazolate). The computationally assisted structure determinations reveal structural changes involving the orientation of the benzene rings relative to the pyrazolate rings, the dihedral angles for the pyrazolate rings bound at the metal centers, and a change in the metal coordination geometry from square planar to tetrahedral. Variable-temperature magnetic susceptibility measurements and in situ infrared and UV–vis–NIR spectroscopic measurements provide strong corroborating evidence for the observed changes in structure. In addition, the results from in situ microcalorimetry measurements show that an additional heat of 2 kJ/mol is required for each of the first four transitions, while 7 kJ/mol is necessary for the last step involving the transformation of Co⁰ from square planar to tetrahedral. Based on the enthalpy, a weak N₂ interaction with the open Co⁰ coordination sites is proposed for the first four phases, which is supported by Monte Carlo simulations.

Introduction

Over the past decade, metal–organic frameworks have emerged as one of the most promising classes of microporous materials, particularly in view of their potential applications in catalysis, gas separation/storage, and drug delivery. Within this family, some solids exhibit great flexibility (the so-called ‘breathing’

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Multistep \( \text{N}_2 \) Breathing in Metal–Organic Framework

\[ \text{Co(BDP)} \]

In situ synchrotron powder diffraction patterns were collected at the Swiss-Norwegian Beamlines of the ESRF using a MAR345 image plate detector and a monochromatic beam with a wavelength of 0.700 00 Å. The sample-to-detector distance (250 or 400 mm) and parameters of the detector were calibrated using NIST standard LaB\(_6\). Two-dimensional diffraction images were integrated by Fit2D software. The patterns were indexed using the Dicov software. \(^{11}\) Le Bail fits were then performed with the Fullprof2k software package using its graphical interface Winplot2. \(^{12,13}\) A gas dosing system \(^{14}\) (see Figure S1) was used to admit gases at 1 mbar to 40 bar of pressure into a 0.5 mm quartz capillary filled with a sample and exposed to the X-ray beam. The sample was first outgassed at elevated temperatures using a turbopump \(10^{-4}\) mbar. The temperature was set in the 80–500 K range by Oxford Cryostream 700+. A typical data set at one pressure point was collected during 60 s.

**Computationally Assisted Structure Determinations.** The structure of the solid in its dry state was first constructed from scratch in the space group \( \text{C}2\text{c} \) using the cell parameters obtained via the successful indexing of the experimental X-ray powder diffraction pattern. Initially, the fractional coordinates of each atom of the \( \text{Co(BDP)} \) framework were guessed from those of the \( \text{Fe(PO}_4\text{)}\text{BDC} \) \((\text{BDC} = 1,4\text{-benzenedicarboxylate; MIL-53(Fe)})\). \(^{15}\) Indeed, the latter structure is revealed from both cell parameters, volumes, and space group to be topologically similar to the dry form of the \( \text{Co(BDP)} \). This structural model was then energy-minimized by means of density functional theory (DFT) simulations, maintaining fixed the experimental cell parameters obtained at 100 K. These calculations were performed considering the PW91 GGA density functional and the double numerical basis set containing polarization functions on hydrogen atoms \((\text{DNP})\) available in the DMol\(^3\) code, as already successfully used to describe the behavior of other metal–organic frameworks. \(^{16}\) The partial charges of each atom of the framework were also extracted from these DFT calculations using the Mulliken charge partitioning method. Starting from this crystallographic model for the dry state, the structures of the other intermediates (Int.1, Int.2, and Int.3) were then derived from an energy minimization procedure using the classical universal force field \( \text{UFF} \) \(^{17}\) and imposing the unit cell parameters determined experimentally for each phase detected under a nitrogen atmosphere at 100 K. This latter force field has been selected for its ability to successfully determine the structures of many...
metal−organic frameworks, including the structurally analogous phase MIL-53(Fe). Such calculations were performed using the Forcite software. The Ewald summation was employed to evaluate the electrostatic interactions. van der Waals interactions were described by the UFF force field. The N2-Lorentz-Lorentz interactions consisted of a repulsion term and a dispersion term calculated using the mixing rules. The N2 molecule was represented by a three-point charges model developed by Murthy et al., while the atoms of the framework were described by the UFF force field. The N2-framework interactions consisted of a repulsion−dispersion 12-6 Lennard−Jones (LJ) term and a Coulombic contribution. The corresponding LJ parameters were calculated using the mixing Lorentz−Berthelot combination rules. A simulation box of 8 (2 × 2 × 2) was used for the open form, 12 (3 × 3 × 3) for the Int.1 form, and 16 rigid unit cells (1 × 4 × 4) for the dry structure and 2 × 2 × 4 for the Int.2 and Int.3 structures) with typically 2 × 10⁶ Monte Carlo steps was considered in these calculations. Short-range interactions were estimated using a cutoff distance of 12 Å, and an Ewald summation was used to compute the electrostatic interactions.

**Grand Canonical Monte Carlo Simulations.** The absolute N2 adsorption isotherms for the different structures were computed up to 1 bar at 77 K using Grand Canonical Monte Carlo (GCMC) simulations. The N2 molecule was represented by a three-point charges model developed by Murthy et al., while the atoms of the framework were described by the UFF force field. The N2-framework interactions consisted of a repulsion−dispersion 12-6 Lennard−Jones (LJ) term and a Coulombic contribution. The corresponding LJ parameters were calculated using the mixing Lorentz−Berthelot combination rules. A simulation box of 8 (2 × 2 × 2) was used for the open form, 12 (3 × 3 × 3) for the Int.1 form, and 16 rigid unit cells (1 × 4 × 4) for the dry structure and 2 × 2 × 4 for the Int.2 and Int.3 structures) with typically 2 × 10⁶ Monte Carlo steps was considered in these calculations. Short-range interactions were estimated using a cutoff distance of 12 Å, and an Ewald summation was used to compute the electrostatic interactions.

**Adsorption Microcalorimetry at 77 K.** Prior to each adsorption experiment, the sample was outgassed using sample controlled thermal analysis (SCTA). Here, the sample was heated under a constant residual vacuum pressure of 0.02 mbar up to the final temperature of 150 °C for 16 h. The differential adsorption enthalpies were obtained directly using a Tian-Calvet type microcalorimeter coupled to a manometric apparatus built in house. Approximately 50 mg of sample was placed in the microcalorimeter which was immersed within a liquid nitrogen cryostat. A quasi-equilibrium system of gas introduction allowed the determination of the adsorption isotherms and the corresponding microcalorimetric characterization with a high resolution.

**Magnetic Measurements.** A sample of Co(BDP)-2(DEF)-H2O (I) was prepared for magnetic measurements by adding 26.4 mg of microcrystals to a gel capsule with eicosane (52 mg) melted on top of it. The dried compound, Co(BDP) (I), was prepared by washing 1 with anhydrous dichloromethane in a glove bag filled with N2, followed by desolvation at 170 °C under dynamic vacuum. A sample of 1d for magnetic measurements was prepared by adding 22.5 mg of microcrystals to a quartz tube (2.8 mm × 100 mm).

After being evacuated, the tube was sealed using a hydrogen/oxygen flame. Variable-temperature dc magnetic susceptibility data were collected from 5 to 300 K at an applied field of 1 kOe using a Quantum Design MPMS2 SQUID magnetometer. All of the data were corrected for the diamagnetic background, including for the gel capsule, eicosane, and quartz tube, with Pascal’s constants that give χ_diam = -0.0001748 emu/mol and -0.0000364 emu/mol for 1 and 1d, respectively. A pressurized sample (1d-N2) was prepared for magnetic measurements by applying a pressure of N2 (100 mmHg) to a sample of 1d in a quartz tube at 77 K using a Micromeretics ASAP2000 gas sorption analyzer, followed by sealing at 77 K. Magnetic data of χ_T values for 1 and 1d were fit to the Fischer equation (eq 1) that expresses the exchange coupling between paramagnetic centers in an infinite chain system.

\[ \chi = \frac{Ng^2S(S+1)}{3kT} \left( 1 + \frac{1}{u} \right) \]

Here, N, \( g \), \( S \), and J represent Avogadro’s number, the Bohr magneton, the Lande g-factor, and the magnetic exchange coupling parameter, respectively. Plots of \( \chi_mT \) versus T are depicted in Figure 5.

**In Situ Infrared Spectroscopy.** The solid dispersed in DEF was deposited on a silicon wafer and then placed in a quartz infrared cell equipped with KBr windows. A movable quartz sample holder allowed the sample to be placed in the infrared beam for measurements or into the furnace for thermal treatment. The cell was connected to a vacuum line for evacuation, calcinations, and the introduction of doses of gas or solvent vapor. In the present study, the sample was activated at 423 K over the course of 1 h under secondary vacuum. In the acetonitrile adsorption experiments, spectra were recorded at room temperature. The integration of the v(CN) bands allowed us to estimate the relative amounts of adsorbed acetonitrile. In the CO adsorption experiment, the temperature of the pellet was decreased to about 100 K by cooling the sample holder with liquid N2 after quenching the sample from the thermal treatment temperature. The probe pressure inside the infrared cell was monitored by two pressure gauges (1−10⁷ Pa and 1−10⁴ Pa range). Transmission spectra were recorded in the 500−5600 cm⁻¹ range at 4 cm⁻¹ resolution on a Nicolet Nexus spectrometer equipped with an extended KBr beam-splitting device and a mercury cadmium telluride (MCT) cryodetector.

**In Situ UV−vis−NIR Spectroscopy.** The UV−vis−NIR spectra were measured in situ in a flow cell (Harrick, Inc.) equipped with a diffuse reflectance accessory. The UV−vis spectra (30 000−12 500 cm⁻¹) were recorded using a Cary 4000 spectrophotometer (Varian Corp.). The NIR spectra (12 500−4000 cm⁻¹) were recorded using a Nicolet 6700 spectrometer equipped with a white light source, a CaF2 beam-splitting device, and an InGaAs detector. Spectra of 1 and 1d were recorded at room temperature under a flow of dry argon gas. Compound 1d was obtained after evacuation of DEF by heating compound 1 at 473 K under argon for 3 h.

**Results and Discussion**

**Collection and Analysis of Powder X-ray Diffraction Data.** The three-dimensional pseudotetragonal (space group P222₁) structure of the as-synthesized solid, Co(BDP)-2DEF-H2O (DEF = N,N-diethylformamide; 1), can be described as a 4⁴ net composed of chains of tetrahedrally coordinated Co₆ centers along [001] linked in the two orthogonal directions by bridging BDP⁻⁻ ligands (see Figure 1). The corresponding square channels along [001] are filled with DEF and water solute molecules, which can be completely evacuated to generate 1d by heating at 160 °C under vacuum. To probe the intriguing five-step isotherm, in situ powder X-ray diffraction studies were performed at 100 K using the Swiss-Norwegian Beamline at
remarkable phase evolution was discovered, which indeed is vapor pressure of N\textsubscript{2} upon warming.

Table 1. Unit Cell Parameters of Co\textsubscript{2}(BDP) under a N\textsubscript{2} Atmosphere at 100 K\textsuperscript{a}

<table>
<thead>
<tr>
<th>phase</th>
<th>space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>V (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>C\textsubscript{2}c</td>
<td>24.87(5)</td>
<td>6.04(2)</td>
<td>7.22(2)</td>
<td>92.8(2)</td>
<td>1084</td>
</tr>
<tr>
<td>Int.1</td>
<td>C\textsubscript{2}c</td>
<td>24.10(4)</td>
<td>10.48(2)</td>
<td>13.90(2)</td>
<td>94.1(1)</td>
<td>2 × 1754</td>
</tr>
<tr>
<td>Int.2</td>
<td>C\textsubscript{2}c</td>
<td>23.17(2)</td>
<td>13.20(1)</td>
<td>6.98(1)</td>
<td>96.2(1)</td>
<td>2123</td>
</tr>
<tr>
<td>Int.3</td>
<td>C\textsubscript{2}c</td>
<td>21.61(2)</td>
<td>15.55(1)</td>
<td>7.02(1)</td>
<td>97.7(1)</td>
<td>2338</td>
</tr>
<tr>
<td>Filled</td>
<td>P\textsubscript{4}2\textsubscript{1}</td>
<td>13.29(1)</td>
<td>13.29(1)</td>
<td>14.82(1)</td>
<td></td>
<td>2618</td>
</tr>
</tbody>
</table>

\textsuperscript{a} As deduced from Dicvolg through the graphical interface Winplot\textsuperscript{11} and further refined (via pattern matching) using Fullprof.\textsuperscript{12}

the European Synchrotron Radiation Facility equipped with a custom-built apparatus to control the N\textsubscript{2} pressure above the sample.\textsuperscript{23} As shown in Figure 2, sequential measurements of the powder X-ray diffraction pattern upon sweeping the N\textsubscript{2} pressure provided a remarkable phase evolution. Notably, the phase transitions occurred reversibly, reflecting the feasibility of repeated pore-opening and pore-closing cycles. Each distinct phase was scrutinized by collecting a diffraction pattern with a longer exposure time at a precise pressure and performing a unit cell indexing. The resulting cell parameters for the successive phases, denoted dry, Int.1, Int.2, Int.3, and filled, indicated a monoclinic cell with space group C\textsubscript{2}c for the first four phases and revealed a remarkable shrinking of the cell volumes upon loss of guest molecules (see Table 1).

A computational strategy based on energy optimization techniques has proven highly effective in assisting with the difficult and time-consuming task of structure determination from powder X-ray diffraction data.\textsuperscript{24} An analogous framework, MIL-53(Fe),\textsuperscript{8,15} served as a starting point for identifying the structure of each phase of Co\textsubscript{2}(BDP).\textsuperscript{10} As a result of the X-ray analysis of 1d coupled with the molecular simulations, a remarkable phase evolution was discovered, which indeed is associated with the change in coordination geometry at the Co\textsuperscript{II} centers (see Figure 3). Notably, the topology and symmetry of the framework in the monoclinic cells remain unaltered from dry to Int.3, demonstrating that Co\textsuperscript{II} adopts a square planar coordination geometry in all phases except filled, wherein it suddenly transforms to a tetrahedral geometry. Since this change is associated with a 90\textdegree{} rotation of two nitrogen atoms out of four while bridging Co\textsuperscript{II} chains, it causes a substantial reorienta-

The dihedral angle between pyrazolate rings (denoted α in Figure 3) estimated from the simulated structures corresponds to the large angle of the rhomb defining the channels within the monoclinic frameworks. With the progression of the pore-opening, α changes by decreasing from 152\textdegree{} to 108\textdegree{} for dry to Int.3, respectively. Also, the angle between two neighboring Co\textsubscript{II} square planes along a chain increases from 133\textdegree{} in dry to 146\textdegree{} in Int.3 by increments, reflecting the transformation toward parallel alignment. In addition, a reorientation of the benzene rings is accompanied by every transition, which contributes to the small changes in the powder X-ray diffraction patterns (see Figure S2). Indeed, \textit{in situ} infrared spectra for Co(BDP) recorded at 100 K confirmed that the C−N stretching vibrations for the pyrazolate rings have undergone transitions from dry to Int.1 and Int.1 to Int.2 upon increasing the N\textsubscript{2} pressure to 0.01 and 0.023 bar, respectively (see Figure 4, right). Since α turns strictly to 90\textdegree{} with the pair of pyrazolates aligned parallel in the filled phase, a pseudotetragonal symmetry is defined.

In terms of topology, the four monoclinic phases (dry−Int.3) are closely related to the MIL-53(Fe) structure type.\textsuperscript{6,25} In a previous paper,\textsuperscript{8} we showed that the evolution of the unit cell volume (V) in this class of materials can be analytically described as a function of the two diagonals of the lozenge (d and D, corresponding here to the unit cell parameters b and a, respectively):

\[ V = k \sin[2 \arctan(d/D)] \] (2)

Indeed, the observed volumes of the different structures of Co(BDP) fit perfectly with the theoretical curve (see Figure S4). Accordingly, the four steps involving dry to Int.3 correspond to displacive transitions upon pore opening, whereas the last step to form the filled phase is a reconstructive transition (see Figures S5 and S6).

\textbf{In Situ UV−vis−NIR and IR Spectra.} The expected geometry change at the Co\textsuperscript{II} centers in Co(BDP) during breathing is accompanied experimentally by a color change between purple for the dry phase and pink for the filled phase. UV−vis−NIR diffuse reflectance spectra recorded at room temperature for 1 and 1d are shown at the left in Figure 4 and confirm the conversion from a tetrahedral to a square planar geometry for the Co\textsuperscript{II} centers upon desolvation through the disappearance of the shoulder at 10 500 cm\textsuperscript{-1} in the \textit{A}_\text{2g} \rightarrow \textit{T}_\text{1g} transition manifold.\textsuperscript{26} Analogous color changes arise upon cooling a sample of 1d under a N\textsubscript{2} atmosphere. A quartz tube containing 1d was cooled to 77 K, filled with 0.13 bar of N\textsubscript{2}, and sealed. Upon immersion of the tube in liquid nitrogen, the color of the solid was observed to change from purple to pink and then back to purple upon warming (see Figure S7).

\textbf{Magnetic Susceptibility Data.} Magnetic susceptibility measurements were performed on 1 and 1d in anticipation of observing the differences between the Co\textsuperscript{III} centers adopting a high-spin (\(S = \frac{5}{2}\)) tetrahedral geometry in 1 versus a low-spin (\(S = \frac{1}{2}\)) square planar geometry in 1d. As depicted in Figure 5, compound 1 displays a \(\chi T\) value of 1.96 emu·K/mol at 300 K, near the spin-only value of 1.875 emu·K/mol expected for the ligands, although the simulated Co−N bond distances remain unchanged (mean Co−N = 1.955 Å) (see Figures S5 and S6).


isolated metal centers with $S = \frac{3}{2}$. Upon cooling, the value of $\chi_MT$ drops steadily to near zero at 2 K, suggesting the presence of an antiferromagnetic exchange coupling between neighboring Co$^{II}$ centers along the pyrazolate-bridged chains. Accordingly, the data were fit using Fisher’s equation, which expresses the exchange coupling between paramagnetic centers linked in an infinite chain.\(^\text{(27)}\) The best fit resulted in an exchange constant of $J = -9.2 \text{ cm}^{-1}$ and $g = 2.130$, in agreement with previous reports of antiferromagnetic exchange in pyrazolate- or tetra-zolate-bridged Co$^{II}$ compounds.\(^\text{(28)}\) In contrast, 1d exhibits a much lower magnetic moment at 300 K, with the value of $\chi_MT = 0.848 \text{ emu} \cdot \text{K/mol}$ indicating an $S = \frac{1}{2}$ ground state with a $g$ value significantly higher than 2.00. Such a large $g$ value is in fact typical for low-spin Co$^{II}$, as assessed for various four- and five-coordinate complexes via EPR spectroscopy.\(^\text{(29)}\) Indeed, the result is in good agreement with the square planar geometry.


The low-coverage enthalpy of adsorption for a rigid microporous material, such as a zeolite. The result is obviously distinguishable from a typical plot of an enthalpy of adsorption for a rigid microporous material, such as a zeolite. Notably, significant valleys appear between each step, which is indicative of additional heat required for the phase transition concomitant with adsorption. While that energy is estimated as ca. 2 kJ/mol for the dry through Int.3 transitions, it significantly increases to 7 kJ/mol for the last transition, reflecting the higher activation barrier associated with the transformation of the Co(II) coordination geometry from square planar to tetrahedral. To the best of our knowledge, this is the first time such a complex transformation involving significant enthalpy changes has been measured directly during a gas adsorption at low temperature. Less complex behavior arose for CH₄ adsorption in 1d, where only two steps were observed. Interestingly, four-step transitions from dry to Int.3 were also apparent in the infrared spectra of 1d exposed to various CO pressures at 100 K (see Figure S8). Moreover, adsorption of acetonitrile below 0.013 bar at room temperature revealed a two-step isotherm characterized as the dry and Int.2 phases by infrared spectroscopy, with no evidence for the intervening Int.1 phase (see Figure S9). Thus, occurrence of the guest-dependent phase transitions appears to be associated with both the binding ability and size of the adsorbate molecule.

Monte Carlo simulations were undertaken in an attempt to identify the locations of the N₂ binding sites at 77 K for each form of Co(BDP). Adsorption of just one N₂ molecule per formula unit was found for the dry structure, wherein the adsorbate binds a Co(II) center in a side-on fashion with a Co···N contact of 2.6 Å. This is a longer distance than typically observed for dinitrogen coordination complexes, indicating a rather weak interaction with N₂. At higher loadings, the larger pore size results in N₂ molecules that are even further from the metal sites, with Co···N contacts falling in the range 3.2–3.4 Å for phases Int.1 through Int.3 (see Figures S10 and S11). Notably, N₂ molecules are primarily located near the open Co(II) metal sites, with Co···N contacts falling in the range 3.2–3.4 Å for phases Int.1 through Int.3 (see Figures S10 and S11). Notably, N₂ molecules are primarily located near the open Co(II) coordination sites in all of the phases except for the filled phase where the full capacity was somewhat underestimated (see Figure S12).

**Outlook**

The aforementioned results provide the first in-depth study of the structural and thermodynamic origins of an unprecedented sequence of five phase transitions during N₂ adsorption in a

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flexible porous framework. This remarkable multistep breathing behavior, which is supported by a variety of in situ spectroscopic techniques, can be attributed to a combination of structural changes involving the orientation of the benzene rings relative to the pyrazolate rings, the dihedral angles for the pyrazolate rings bound at the metal centers, and a change in the metal coordination geometry from square planar to tetrahedral. In future work, an understanding of the nature of the phase transitions induced within Co(BDP) by various other adsorbates will be the focus, with an eye toward the development of potential applications in selective gas adsorption and molecular sensing.

**Acknowledgment.** This research was supported in the U.S. by the Department of Energy under Contract No. DE-AC02-05CH11231 and in France by ANR ‘SAFHS’ (ANR-07-BLAN-0284-02), ‘NOMAC’ (ANR-06-CO2-008), and the Region Lower-Normandy. We acknowledge the Swiss-Norwegian Beamlines for the in-house beamtime allocation and H. Leclerc for experimental assistance.

**Supporting Information Available:** Complete experimental details and refs 4b and 24b. This material is available free of charge via the Internet at http://pubs.acs.org.