

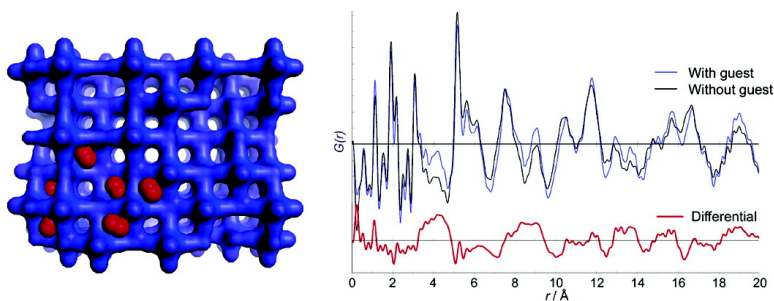
Communication

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## Selective Recovery of Dynamic Guest Structure in a Nanoporous Prussian Blue through in Situ X-ray Diffraction: A Differential Pair Distribution Function Analysis

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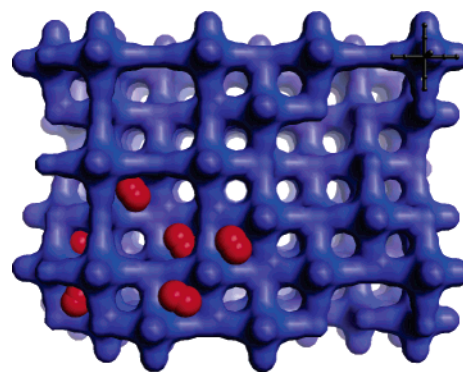
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The functionality of industrially and technologically relevant materials involved in separations, catalysis, and gas storage often relies on the subtle interactions of a guest species reversibly bound/contained within a nanoporous host or substrate.<sup>1</sup> The reversible nature of this interaction is typically associated with weak host–guest interactions, which frequently results in considerable disorder of the guest. Traditional crystallographic techniques, which rely on analysis of Bragg scattering, are often unable to adequately resolve the structure of such disordered components. Therefore, probes of local structure, such as solid-state NMR,<sup>2</sup> XAFS,<sup>3</sup> and vibrational<sup>4</sup> spectroscopy, have often been employed to study these systems. Total scattering methods, including the pair distribution function (PDF), measure the probability of finding two atoms at a distance  $r$  (i.e., atom–atom correlations), including those which may deviate from the *average* long-range structure.<sup>5</sup> In complex structures it is not always straightforward to assign the individual peaks in the PDF to specific pair correlations. Differential PDFs can be acquired to directly probe structure around specific atom types or sites. These experiments are typically performed by exploiting the contrast afforded by anomalous dispersion in X-ray scattering or isotopic substitution in neutron scattering.<sup>6–8</sup> These approaches are time intensive, limited to material compositions with suitable isotopes or accessible K-edges, and in the case of neutron scattering require preparation of isotopically substituted samples.

We demonstrate in this communication a more widely applicable approach for nanoporous host–guest systems, whereby the differential is recovered by direct subtraction of the reference PDF of the vacant host from that of the guest-loaded host. The differential approach to PDF analysis isolates the additional correlations arising from modification of the structure through guest sorption, both guest–guest and guest–host correlations, and hence, recovers the local structure of the guest. Specifically, we use in situ X-ray diffraction to obtain data suitable for such differential PDF analysis, providing unique insight into the structure of weakly bound, dynamic N<sub>2</sub> molecules in the Prussian blue system Mn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>·x{N<sub>2</sub>}. The differential PDF shows a distributed orientation of N<sub>2</sub> molecules constrained to specific sites within the pores.

The Prussian blue analogues, a family of nanoporous molecular framework recently identified for potential gas storage applications, show significant uptake of nitrogen gas up to 20 wt % in Mn<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> (77 K, 1 atm).<sup>9,10</sup> The guest interactions with the pore surface, functionalized with accessible coordination sites, may play an important role in the sorption properties and, therefore, an understanding of the nature of the gas–framework interaction is fundamental to the development of materials with improved capacities. The framework structure itself contains aperiodic



**Figure 1.** Representation of the cubic Prussian blue network with aperiodic lattice vacancies on one-third of the Co(CN)<sub>6</sub><sup>3-</sup> sites. A surface on the structure suggests guest accessible volume. Disordered nitrogen molecules centered at (1/4, 1/4, 1/4) illustrate available guest positions.

Co(CN)<sub>6</sub><sup>3-</sup> lattice vacancies (Figure 1) associated with accessible Mn<sup>II</sup> sites of average coordination MnN<sub>4</sub>. As the nanoporous Prussian blue framework remains relatively unperturbed by the gas sorption–desorption process, the vacant apo-host can provide a reference PDF, making this system ideally suited to differential PDF analysis.

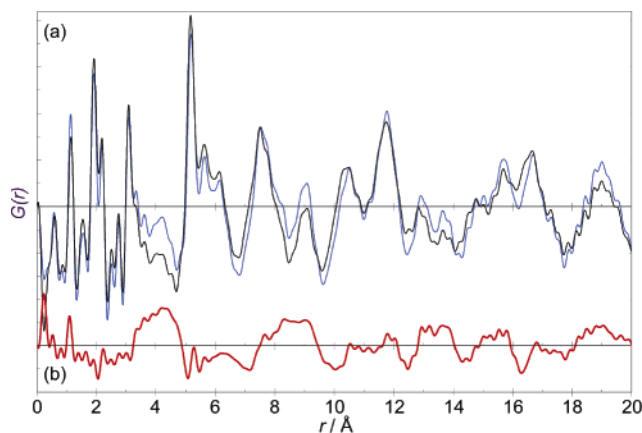
A sample of the hydrated phase, Mn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>[H<sub>2</sub>O]<sub>6</sub>·xH<sub>2</sub>O, was desolvated in situ at 423 K under continuous helium (UHP) flow using an apparatus that allows simultaneous heating and gas flow.<sup>11</sup> The desolvated sample was cooled to 85 K using an Oxford Cryostreams Cryostream 700 and data were collected in both nonadsorbing helium and nitrogen (UHP) gas atmospheres. The high energy X-rays (90.48 keV,  $\lambda = 0.13702$  Å) available at the 11-ID-B beamline at the APS at Argonne National Laboratory, were used in combination with a MAR-345 image plate detector to record diffraction patterns to high momentum transfer ( $Q \approx 23$  Å<sup>-1</sup>). Raw images were processed using Fit-2D<sup>12</sup> and the PDFs ( $G(r) = 4\pi r[\rho(r) - \rho_0]$ ) were extracted as described previously.<sup>13,14</sup> The sample-to-detector distance was increased for images used in Rietveld analysis to improve  $Q$  resolution. Rietveld and PDF refinements were performed using the GSAS and PDFfit programs, respectively.<sup>15,16</sup>

The Rietveld refinement of the structural model for Mn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> was consistent with the known topology ( $R_{wp} = 3.76$ ). Upon loading of N<sub>2</sub>, a minor expansion (0.36%) in the cubic lattice parameter and significant changes in peak intensities are evident, with reduced intensity of the 111 reflection due to filling of the pores.

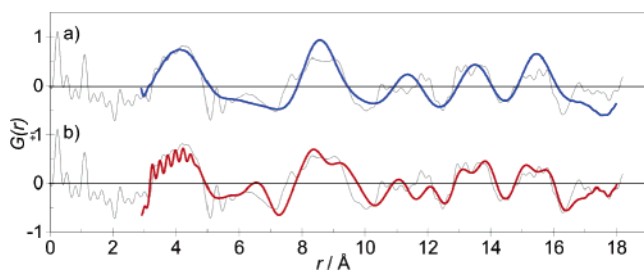
The PDFs,  $G(r)$ , show subtle differences for the vacant and N<sub>2</sub> loaded framework (Figure 2). The differential PDF isolates structural information derived from atomic correlations involving the guests, both N<sub>guest</sub>–N<sub>guest</sub> and N<sub>guest</sub>–framework, and guest-induced framework perturbations. The generally broad features in

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**Figure 2.** PDFs,  $G(r)$ , extracted for the vacant (black) and loaded (blue) framework (a) and the corresponding differential PDF (b).



**Figure 3.** Calculated differential PDFs for the simple host-guest model (a) and the model accounting for lattice expansion effects (b). The experimental differential PDF is shown for comparison (gray line).

the differential PDF, compared to that of the intra-framework correlations, confirm the high degree of guest disorder. The systematic errors which dominate at unphysical distances ( $<1$  \AA) cancel in the low  $r$  region of the differential PDF, allowing the accurate recovery of short correlations, including the sharp peak at  $1.0951(3)$  \AA, corresponding to the  $\text{N}_2$  triple bond (lit.<sup>17</sup>  $1.098$  \AA) consistent with ca. 35% pore loading. Features related to the peak shift in the PDF at  $\sim 2.2$  \AA (and  $\sim 5.2$  \AA) reflect expansion of the Mn-N bond from  $2.1908(3)$  \AA to  $2.1957(2)$  \AA, a statistically significant change relative to the resolution of the PDF.<sup>5,18</sup>

The differential PDF was initially fit using a simple model based on the Rietveld refined framework model with a Gaussian distribution of electron density<sup>19</sup> to represent the assembly of dynamic guests about the pore center at  $(1/4, 1/4, 1/4)$ . This model reproduces the approximate peak positions and intensities observed in the differential PDF (Figure 3). Inclusion of general lattice expansion effects using a “difference modeling” strategy,<sup>16</sup> refining the difference between the model  $G(r)$  and a reference PDF generated for the framework with the smaller lattice, against the measured differential yielded an improved the fit, particularly at high  $r$ . The remaining deviation in the fit occurs in the region  $5$ – $12$  \AA corresponding to  $\text{N}_{\text{guest}}-\text{Mn}$  and  $\text{N}_{\text{guest}}-\text{Co}$  correlations in the immediately surrounding unit cells. This is due to inadequate complexity of the framework model obtained from Rietveld analysis, which does not account for disorder of the vacancies or distortions about the Mn<sup>II</sup> ions. We are currently exploring reverse Monte Carlo methods to generate a more realistic configuration for disordered empty frameworks and to subsequently refine the structure of the guest.

Thus, modeling of the differential PDF indicates that the  $\text{N}_2$  guests are confined to positions around  $(1/4, 1/4, 1/4)$  with the wide

$Q$ -range used allowing a more accurate refinement of occupational and thermal parameters. This work clearly demonstrates the value of differential PDF methods in probing host-guest interactions in nanoporous materials. This approach does not rely on the assumption of translational symmetry, which is fundamental to conventional Bragg analysis, and may therefore prove advantageous in disordered systems. Application of this approach can be readily envisaged to the structural studies of a variety of other systems including catalysts,  $\text{O}_2/\text{N}_2$  separation materials, sequestration of environmental pollutants, and gas storage.

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**Supporting Information Available:** Details of PDF and Rietveld analysis, synthesis, thermogravimetry, and nitrogen sorption isotherms (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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