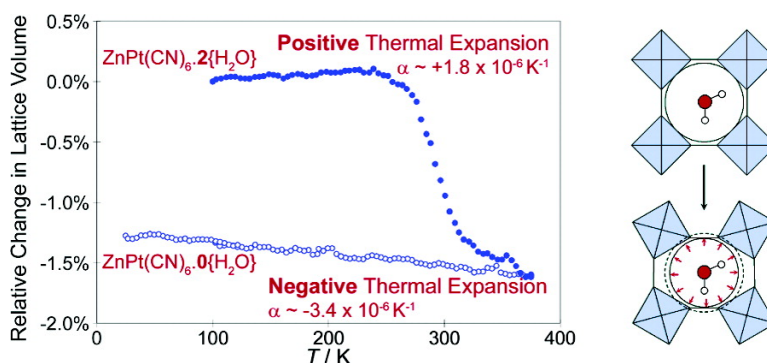


Guest-Dependent Negative Thermal Expansion in Nanoporous Prussian Blue Analogues $M\text{Pt}(\text{CN})_6 \cdot x\{\text{HO}\}$ ($0 \leq x \leq 2$; $M = \text{Zn}, \text{Cd}$)

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J. Am. Chem. Soc., **2005**, 127 (51), 17980-17981 • DOI: 10.1021/ja056460f • Publication Date (Web): 06 December 2005

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Guest-Dependent Negative Thermal Expansion in Nanoporous Prussian Blue Analogues $M^{II}Pt^{IV}(CN)_6 \cdot x\{H_2O\}$ ($0 \leq x \leq 2$; $M = Zn, Cd$)

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Materials that exhibit negative thermal expansion (NTE) behavior are of particular interest for their ability to compensate for the more usual positive thermal expansion (PTE) of other materials.¹ Applied in this way, NTE/PTE composites can be tuned to exhibit a preferred intermediate (e.g., zero) thermal expansion behavior. Once considered rare, NTE has been reported in an increasingly wide range of materials, including members of the AM_2O_8 ,² AM_2O_7 ,³ $A_2M_3O_{12}$,⁴ zeolite,⁵ $M(CN)_2$,⁶ and Prussian Blue⁷ structural families. The mechanism responsible for NTE behavior in these materials is generally well understood: on an elementary level, thermally induced transverse vibrational motion of bridging oxide or cyanide ions has the effect of drawing their metal-atom “anchors” closer together.^{2,6,8} However, the effect of guest inclusion on thermal expansion behavior within nanoporous NTE materials remains unclear. Indeed, both expansion and contraction upon sorption of guests have been observed in various zeolites.⁹ Given that NTE properties are dependent on lattice dynamic effects, which may be perturbed by the presence of guest molecules, an exploration of the guest dependence of NTE in such systems is of fundamental interest. Further, the sorption properties of nanoporous materials are strongly influenced by their pore size/geometry, and hence, this study is relevant to host–guest applications of zeolites¹⁰ and Prussian Blue analogues.¹¹

Here we report the guest-dependent thermal expansion behavior and structure of the Prussian Blue analogues $M^{II}Pt^{IV}(CN)_6 \cdot x\{H_2O\}$ ($0 \leq x \leq 2$; $M = Zn, Cd$) using variable temperature single-crystal X-ray diffraction (SCXRD). The hexacyanoplatinate framework bears no charge, and consequently its pores contain only neutral (removable) guests.¹² This is important as it allows direct comparison of the thermal expansion of the vacant and guest-loaded frameworks. Furthermore, it is possible to systematically vary the pore size by tuning the framework composition. Our results suggest that if the volume occupied by included guest molecules is commensurate with the available pore volume, the NTE effect can be reduced. We postulate that this effect arises from steric dampening of the vibrational modes responsible for NTE.

Both phases were found to crystallize with a face-centered cubic structure in which octahedrally coordinated Zn^{II}/Cd^{II} and Pt^{IV} ions are bridged in a linear fashion by cyanide anions, forming the cubic network (ReO_3 or α -Po type) common to the Prussian Blue family (Figure 1).^{12–16} The (N-bound) Zn^{II}/Cd^{II} and (C-bound) Pt^{IV} ions alternate throughout the lattice. The framework defines a three-dimensional pore system that accounts for approximately 40% of the crystal volume and consists of linked pseudo-spherical cavities. In the as-synthesized forms, both phases crystallized as air-stable dihydrates in which each cavity was occupied by a single orientationally disordered water molecule evident as a diffuse, near

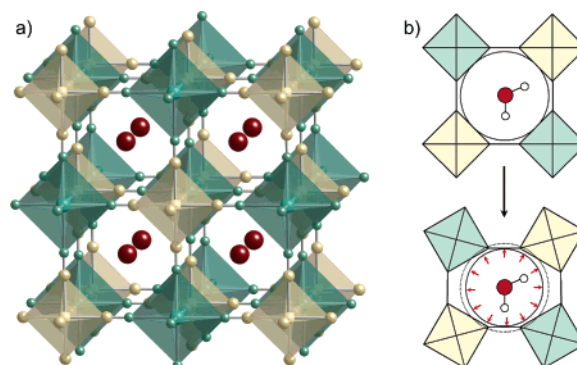


Figure 1. Representations of the crystal structure of the $M^{II}Pt^{IV}(CN)_6$ Prussian Blue framework (a) and the proposed dampening effect of guests on the vibrational modes underlying NTE behavior (b). Alternating Pt^{IV} (beige) and M^{II} (green) octahedra and water guests (red) are indicated.

spherical electron density distribution with no apparent directional guest–framework interactions.

The thermal expansion behavior of each phase was measured using SCXRD to monitor the lattice parameters as a function of temperature. The as-synthesized phases were first heated from 100 to 375 K and subsequently cooled to 25 K (Figure 2).¹⁷ For each phase, two distinct processes are evident: first, there is the approximately linear thermal expansion behavior of the vacant and guest-loaded frameworks themselves; second, the in situ desorption of guest molecules from within the host framework results in a marked contraction of the lattice volume at higher temperatures. The data collected upon cooling relate to the vacant framework and confirm NTE behavior in this family of Prussian Blue analogues.

Structural refinement of data collected at 25, 50, 100, 150, 225, 300, and 375 K reveals that the most strongly temperature-dependent of the atomic displacement parameters correspond to motion of the C and N atoms perpendicular to the $Pt-CN-M$ axis (Figure 2b). Such motion is consistent with thermal population of the low-energy transverse vibrational modes of the cyanide bridges implicated in NTE behavior for this family.^{6,7} The different vibrational amplitudes of the C and N atoms can be attributed to the greater relative strength of the $Pt^{IV}-C$ bond compared to the $M^{II}-N$ bond.

While the coefficient of thermal expansion of $CdPt(CN)_6 \cdot x\{H_2O\}$ is essentially independent of guest inclusion, pronounced guest-dependent behavior is observed for the Zn^{II} analogue (Table 1): in this case, the hydrated framework exhibits PTE behavior that reverts to NTE upon guest desorption. Taken together, these results can be rationalized in terms of the void volumes accessible to included water molecules in each phase, calculated to be ca. 45 \AA^3 and 65 \AA^3 for the Zn^{II} and Cd^{II} analogues, respectively.¹⁸ Individual water molecules typically occupy a volume of ca. 40 \AA^3 in

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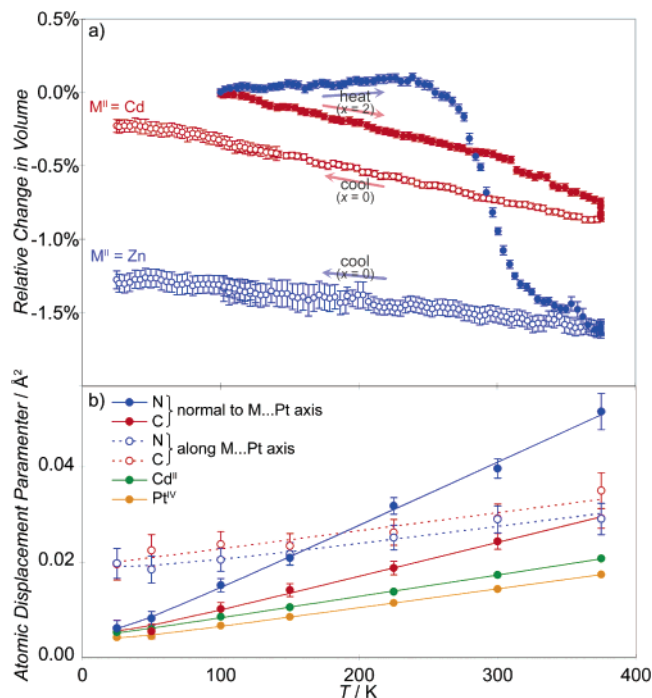


Figure 2. Temperature-dependent structural parameters of the $M^{II}Pt^{IV}(CN)_6 \cdot x\{H_2O\}$ family from single-crystal X-ray diffraction data. (a) The unit cell volume change (relative to the initial value at 100 K) for the guest-loaded (●) and vacant (○) frameworks. (b) Atomic displacement parameters for $CdPt(CN)_6$. The lines correspond to Debye-model fits to the data.

Table 1. Coefficients of Thermal Expansion ($\alpha = dl/dT$) and Cubic Lattice Parameters (a) of the $M^{II}Pt^{IV}(CN)_6$ Family as Determined by Single-Crystal X-ray Diffraction

compound	a(100 K)/Å	$\alpha^a/10^{-6} K^{-1}$	T/K
$ZnPt(CN)_6 \cdot 2\{H_2O\}$	10.5467(4)	+1.82(15)	100 → 250
$ZnPt(CN)_6 \cdot 0\{H_2O\}$	10.5234(3)	-3.38(9)	375 → 25
$CdPt(CN)_6 \cdot 2\{H_2O\}$	10.9530(2)	-7.31(5)	100 → 320
$CdPt(CN)_6 \cdot 0\{H_2O\}$	10.94610(10)	-6.69(5)	375 → 25

^a The errors in the values of α given are from the least-squares linear fits to the data over the specified temperature range; these errors neglect any systematic experimental effects and subtle nonlinearities of behavior.

nanoporous structures,¹⁸ commensurate with the cavity size found in $ZnPt(CN)_6$, but smaller than that found in $CdPt(CN)_6$. It is postulated that the presence of guests within the pores of $ZnPt(CN)_6 \cdot x\{H_2O\}$ impedes the vibrational motion of the cyanide linkages responsible for NTE behavior in these systems (Figure 1b). This effect is absent in the larger-pore framework, $CdPt(CN)_6 \cdot x\{H_2O\}$. A similar dampening of NTE behavior has been suggested to occur in $Zn(CN)_2$, where the relevant steric interactions arise from framework interpenetration rather than guest inclusion.⁸ The repulsive steric effect of the included water molecules is also evident here from the larger volume of the guest-loaded framework relative to the vacant framework, an effect that is most pronounced for the Zn^{II} analogue. The increased thermal volume of the guests at higher temperatures may also contribute to the observed reduction in NTE behavior.

Finally, we note that the magnitude of NTE observed for $M^{II}Pt^{IV}(CN)_6$ ($M = Zn/Cd$) is significantly less than that for the related $Zn_xCd_{1-x}(CN)_2$ family;⁶ this is attributed to the presence of strong $Pt^{IV}-CN$ bonds, which are expected to raise the energy of NTE vibrational modes that involve bending about the C atom.

This work has shown that guest inclusion can influence the thermal expansion behavior of nanoporous NTE materials via steric

dampening of the transverse vibrational modes responsible for NTE itself. Such an effect is of interest in offering new insight into the vibrational mechanism of NTE. The particular systems studied here illustrate how NTE can be perturbed by guest molecules to moderate and tune thermal expansion behavior, one of the principal goals in the practical application of NTE materials.

Acknowledgment. A.L.G. thanks Trinity College, Cambridge for a Junior Research Fellowship.

Supporting Information Available: Details of SCXRD structural parameters (PDF) and crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) $ZnPt(CN)_6 \cdot 2\{H_2O\}$ and $CdPt(CN)_6 \cdot 2\{H_2O\}$ were prepared as pale yellow single crystals by reaction of aqueous solutions of $K_2Pt(CN)_6$ (0.1 M, Aldrich) and either $Zn(NO_3)_2 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 M), followed by slow evaporation of the solvent.
- (14) Crystals of the hydrated compounds could be exposed to the atmosphere for a number of days without any detectable guest loss; moreover, the crystals retained their structural integrity over such periods.
- (15) Low thermal expansion behavior is known for ReO_3 -type materials, e.g., TaO_2F ; Tao, J. Z.; Sleight, A. W. *J. Solid State Chem.* **2003**, 173, 45–48.
- (16) Variable temperature SCXRD data were collected on a Bruker-AXS SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo K α radiation, an Oxford Cryostreams nitrogen cryostream, and an Oxford Instruments helium cryostream. The samples were mounted with a thin film of grease to the interior of a 0.3 mm glass capillary inserted in a copper mounting pin. Data collection, integration of frame data, and conversion to intensities corrected for Lorenz, polarization, and absorption effects were performed using the programs SMART and SAINT+ (BrukerAXS, SMART, SAINT, and XPREP. Area detector control and data integration and reduction software. Bruker Analytical X-ray Instruments Inc.: Madison, Wisconsin, U.S.A., 1995) and SADABS (Sheldrick, G. M. SADABS. Empirical absorption correction program for area detector data. University of Göttingen, Germany, 1996). Structure solutions and refinement were carried out using the programs SHELXS-97 (Sheldrick, G. M. SHELXS-97. Program for crystal structure solution. University of Göttingen, Germany, 1997) and SHELXL-97 (Sheldrick, G. M. SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany, 1997).
- (17) Samples were held at 375 K for ca. 2 h to ensure complete dehydration. The absence of water was confirmed by the lack of residual electron density in the pores in SCXRD refinements of the dehydrated phases and thermogravimetric analysis of bulk samples treated in an identical manner. For the measurements over the temperature range 25 K to 100 K, separate capillary mounted samples were prepared by ex situ dehydration at ca. 425 K under dynamic vacuum for 16 h. The capillaries were flame-sealed to prevent rehydration.
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JA056460F