Cluster-Expanded Prussian Blue Analogues

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Abstract: A method for expanding the pores in crystalline frameworks is demonstrated with the substitution of face-capped octahedral $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) clusters into the Prussian blue structure. The clusters react in aqueous solution with Ga^{3+} and Fe^{3+}, respectively, to precipitate $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ and $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$. Rietveld analysis of X-ray powder diffraction data for the former compound confirms the expanded crystal structure, which features large water-filled cavities more than twice the volume of those in Prussian blue. The new materials can be dehydrated without loss of integrity, and maintain crystallinity at temperatures up to 250 or 300 °C. Further, the increase in void volume is shown to significantly enhance their capacities as molecular sieves and enable absorption of larger alcohol molecules such as ethanol and *n*-propanol. A soluble form of the black iron-containing phase exhibits a cluster-to-metal charge-transfer band at 736 nm, slightly lower energy than the metal-to-metal charge-transfer band responsible for the color of Prussian blue.

Introduction

The demand for new porous materials that function as molecular sieves and catalysts has fueled a burgeoning interest in crystal engineering.[1] This solution-based approach to solid synthesis involves the use of molecular components with well-defined directional bonding preferences as reactants for constructing extended crystalline structures. A foremost objective in such research is to develop techniques for generating rigid zeolite-like frameworks with voluminous cavities capable of lodging (and releasing) guest molecules. The strategy commonly adopted attempts to expand a known structure by enlarging one of its framework components. However, replacement units successfully incorporated thus far have typically been enlarged in only one or two of their dimensions,[2] producing skeletal frameworks in which the void space is readily filled by one or more identical interpenetrating frameworks.[3] In cases where interpenetration is avoided, the expanded framework often is not robust, collapsing upon removal of the included guest molecules or ions.[4] We submit that the problems of interpenetration and architectural frailty may be reliably circumvented by employing components that are *isotropically enlarged in all three dimensions*.[5,6] The idea is implemented here with the

expansion of the Prussian blue structure by substituting $[Re_6Q_8]^{2+}$ (Q = Se, Te) cluster cores with a face-capped octahedral geometry for its Fe^{2+} ions.

Prussian blue has held the fascination of scientists for over two centuries.[7] The insoluble form of this brilliantly colored solid pigment, $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ ($x \approx 14$), is readily prepared by addition of ferric ions to an aqueous ferrocyanide solution.

$$4[Fe(H_2O)_6]^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3 \cdot xH_2O \quad (1)$$
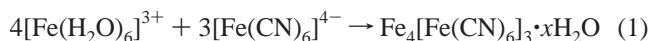
The reaction rapidly propagates with each nitrogen terminus in a ferrocyanide complex (featuring the octahedral geometry depicted at the left in Figure 1), displacing a water molecule in the coordination sphere of an Fe^{3+} ion to forge a linear $Fe^{2+}-CN-Fe^{3+}$ linkage. The true nature of the ensuing structure was not conclusively established until relatively recently.[9,10] It consists of a simple cubic lattice of alternating Fe^{2+} and Fe^{3+} ions connected through cyanide bridges (Figure 2), but with one-quarter of the $[Fe(CN)_6]^{4-}$ units missing from the framework. Typically, the arrangement of these vacancies is completely disordered; however, under slow growth conditions, a partially ordered structure with the central $[Fe(CN)_6]^{4-}$ moiety removed from the unit cell shown in Figure 2 is obtained.[9] Water molecules bind the unsaturated Fe^{3+} ions and center each cubic octant of the unit cell; they can be removed by thermolysis and are replaced upon exposure to a humid atmosphere. Reaction 1

(1) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283. (c) Moore, J. S.; Lee, S. *Chem. Ind.* **1994**, 556. (d) Ward, M. D. *Nature* **1995**, *374*, 764. (e) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (f) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13 and references therein.

(2) For example, many structures have been formed in which cyanide ligands are replaced by longer bridging ligands such as pyrazine, 4,4′-bipyridine, 4-cyanopyridine, or $[Ag(CN)_2]^-$: (a) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677. (b) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2025. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895.

(3) (a) Hirsch, K. A.; Wilson, S. C.; Moore, J. S. *Chem. Eur. J.* **1997**, *3*, 765. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1461 and references therein.

(4) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.

(5) Ideally, one might envision expanding a structure consisting of a packing of solid spheres simply by increasing the diameter of each sphere, such that the percentage of void space (and the associated structural stability) remains constant while the volume of each void increases.

(6) Tetrahedral $[Ge_4S_{10}]^{4-}$ clusters which may be viewed as isotropically enlarged $[MS_4]^{4-}$ moieties have previously been used to construct porous three-dimensional frameworks; however, the structures obtained are not direct expansions of a known metal–sulfide framework. (a) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807. (b) Bowes, C. L.; Huynh, W. U.; Kirkby, S. J.; Malek, A.; Ozin, G. A.; Petrov, S.; Twardowski, M.; Young, D.; Bedard, R. L.; Broach, R. *Chem. Mater.* **1996**, *8*, 2147. (c) Cahill, C. L.; Parise, J. B. *Chem. Mater.* **1997**, *9*, 807.

(7) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283 and references therein.

(8) Pospelov, V. A.; Zhdanov, G. S. *Zhur. Fiz. Khim.* **1947**, *21*, 879.

(9) (a) Buser, H. J.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1299. (b) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. *Inorg. Chem.* **1977**, *16*, 2704.

(10) Herren, F.; Fischer, P.; Ludi, A.; Hälg, W. *Inorg. Chem.* **1980**, *19*, 956.
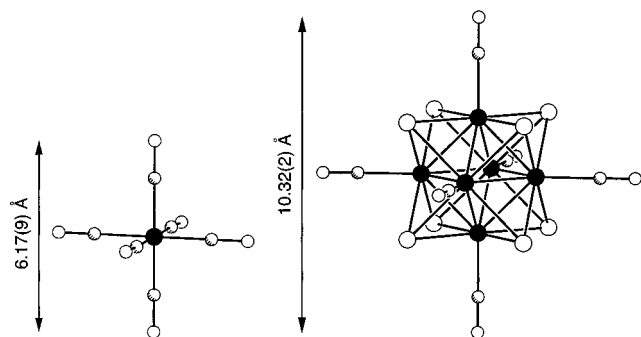
Figure 1. Left: Structure of the octahedral ferrocyanide complex, $[Fe(CN)_6]^{4-}$, as present in $K_4[Fe(CN)_6]$.[8] Black, shaded, and white spheres represent Fe^{2+}, C, and N atoms, respectively. Selected mean interatomic distances (Å) and angles (deg): Fe−C 1.92(5), C−N 1.15-(4), C−Fe−C 90(3), Fe−C−N 177(2). Right: Structure of the face-capped octahedral $[Re_6Te_8(CN)_6]^{4-}$ cluster, as present in $(Me_4N)_4[Re_6Te_8(CN)_6]$.[13] Black, white, shaded, and smaller white spheres represent Re, Te, C, and N atoms, respectively. Selected mean interatomic distances (Å) and angles (deg): Re−Re 2.681(3), Re−Te 2.694(2), Re−C 2.103(4), C−N 1.158(8), Te−Re−C 90(1), Re−C−N 178.8(1). Corresponding mean interatomic distances (Å) and angles (deg) from the structure of $NaCs_3[Re_6Se_8(CN)_6]$:[13] Re−Re 2.634(4), Re−Se 2.52(1), Re−C 2.10(2), C−N 1.173(5), *trans* N···N 10.237(1), Se−Re−C 92(4), Re−C−N 175(2).
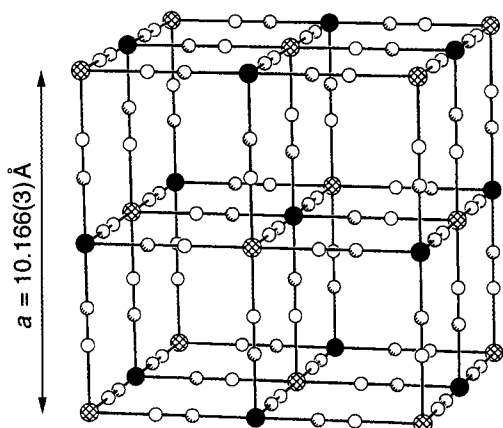

Figure 2. Unit cell for the structure of Prussian blue.[9] Cross-hatched spheres represent Fe^{3+} ions; other atom types are as designated in Figure 1 (top). Note that the $[Fe(CN)_6]^{4-}$ complex sites are only 75% occupied and water molecules have been omitted for clarity. Selected mean interatomic distances (Å): Fe−C 1.923(8), Fe−N 2.029(6), Fe−O 2.14(2), C−N 1.131(6).

may be generalized to include a variety of hexaaquo and hexacyano transition metal complexes which combine to form an extensive family of Prussian blue analogues with structures based on the same cubic framework.[7,11,12]

Recent work has led to the preparation of a set of molecular clusters, $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te), bearing a resemblance to cyanometalate complexes such as ferrocyanide.[13,14] The geometry assumed by these clusters (Figure 1, right) consists of a central Re_6 octahedron with a Q atom capping each triangular face and a cyanide ligand projecting radially from each apex.[15] For our present purposes, they may be regarded as cyanometalates with large, isotropically expanded central metal "atoms" that serve to extend their overall span by more than 4 Å (Figure 1). In view of their overall charge and the

disposition of their cyanide ligands, one might expect the clusters to exhibit a similar reaction chemistry to $[Fe(CN)_6]^{4-}$. Indeed, the sulfur- and selenium-containing variants have been shown to react with divalent metal ions in aqueous solution to precipitate a range of framework solids with unprecedented structures.[14,16] We have discovered that the tellurium-containing cluster mimics ferrocyanide even more closely, undergoing a reaction with Fe^{3+} ions that parallels the formation of Prussian blue (see reaction 1, above).

$$4[Fe(H_2O)_6]^{3+} + 3[Re_6Te_8(CN)_6]^{4-} \rightarrow$$
$$Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O \quad (2)$$
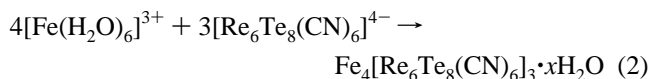
Experimental Section

Preparation of Compounds. The compounds $Na_4[Re_6Q_8(CN)_6]$ (Q = Se, Te) and Prussian blue were prepared as described previously.[13,17] Other reagents were of commercial origin, and were used as received. Water was distilled and deionized with a Milli-Q filtering system.

$Na_4[Re_6Se_8(CN)_6]$. A typical preparation produced 0.56 g (86%) of yellow-orange solid. IR (KBr): ν_{CN} 2110 cm^{-1}. Absorption spectrum (H_2O): λ_{max} (ϵ_M) 230 (48700), 265 (15900), 290 (7310), 337 (5120), 360 (sh, 4280), 387 (sh, 2950), 458 (486) nm. Anal. Calcd for C_6N_6-$Na_4Re_6Se_8$: C, 3.61; H, 0.00; N, 4.21. Found: C, 4.05; H, <0.2, N, 3.83.

$Na_4[Re_6Te_8(CN)_6]$. A typical preparation produced 1.55 g (61%) of orange-red solid. IR (KBr): ν_{CN} 2079 cm^{-1}. Absorption spectrum (H_2O): λ_{max} (ϵ_M) 209 (74400), 242 (51400), 260 (44800), 315 (17200), 340 (10700), 416 (4800), 505 (sh, 915) nm. Anal. Calcd for $C_6N_6Na_4$-Re_6Te_8: C, 3.02; H, 0.00; N, 3.52. Found: C, 3.29; H, <0.2; N, 3.52.

$Fe_4[Re_6Te_8(CN)_6]_3 \cdot 27H_2O$. A 50 mL aqueous solution of 0.155 g of $FeSO_4 \cdot 7H_2O$ (0.16 g, 0.56 mmol) was slowly added to a 70 mL aqueous solution of $Na_4[Re_6Te_8(CN)_6]$ (0.22 g, 0.091 mmol). After allowing it to stand for 30 min, the mixture was centrifuged and the supernatant solution was decanted. The remaining black solid was washed with successive aliquots of water (3 × 25 mL) and dried in air to give 0.20 g (92%) of product. The X-ray powder diffraction pattern of this compound exhibits broad peaks corresponding to an *F*-centered cubic lattice with $a = 13.850(2)$ Å. $\mu_{eff} = 13.5(1)$ μ_B at 295 K. Fit of Mössbauer data (δ, ΔE_q, Γ (mm/s, 78 K)): 0.47, 0.77, 0.48. IR (KBr): ν_{CN} 2099 cm^{-1} (broad). Anal. Calcd for $C_{18}H_{54}N_{18}O_{27}Fe_4Re_{18}Te_{24}$ plus 4% amorphous Fe_2O_3:[18] C, 2.73; H, 0.69; Fe, 5.65; N, 3.19; Na, 0.00. Found: C, 2.51; H, 0.70; Fe, 5.83; N, 2.89; Na, <73 ppm.

This compound can also be prepared from $Fe_2(SO_4)_3 \cdot xH_2O$ by analogous means; a typical yield was 0.041 g (74%).

(11) (a) Weiser, H. B.; Milligan, W. O.; Bates, J. B. *J. Phys. Chem.* **1942**, *46*, 99. (b) Shriver, D. F.; Shriver, S. A.; Anderson, S. E. *Inorg. Chem.* **1965**, *4*, 725. (c) Ludi, A.; Güdel, H.-U.; Rüegg, M. *Inorg. Chem.* **1970**, *9*, 2224. (d) Griebler, W.-D.; Babel, D. *Z. Naturforsch. B* **1982**, *37*, 832.

(12) Prussian blue analogues have drawn a great deal of attention lately for their unusual physical (particularly magnetic) properties: (a) Mallah, T.; Thiébault, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554. (b) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397. (c) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701. (d) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49. (e) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (f) Brousseau, L. C.; Williams, D.; Kouvetakis, J.; O'Keefe, M. *J. Am. Chem. Soc.* **1997**, *119*, 6292. (g) Ohkoshi, S.; Fujishima, A.; Hashimoto, K. *J. Am. Chem. Soc.* **1998**, *120*, 5349.

(13) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.

(14) Beauvais, L. G.; Shores, M. P.; Long, J. R. *Chem. Mater.* **1998**, *10*, 3783.

(15) This M_6Q_8 core geometry is common to a variety of transition metal clusters: Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840 and references therein.

(16) Naumov, N. G.; Virovets, A. V.; Sokolov, M. N.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1943.

(17) Cosgrove, J. G.; Collins, R. L.; Murty, D. S. *J. Am. Chem. Soc.* **1973**, *95*, 1083.

(18) Small amounts of metal oxides are common impurities in Prussian blue and its analogues.[19] Their coprecipitation can sometimes be prevented by carrying out the reaction in acidic solution; however, this was generally found to have an adverse effect on the purity and/or crystallinity of the cluster-expanded phases.

$Ga_4[Re_6Se_8(CN)_6]_3 \cdot 38H_2O$. An orange solution of $Ga(NO_3)_3 \cdot H_2O$ (0.95 g, 3.5 mmol) and $Na_4[Re_6Se_8(CN)_6]$ (0.92 g, 0.46 mmol) in 100 mL of water was stirred and heated at reflux for 30 min, inducing formation of a pale orange precipitate. Upon cooling, the mixture was centrifuged and the supernatant solution was decanted. The remaining solid was washed with successive aliquots of water (3 × 25 mL) and dried in air to give 0.74 g (81%) of product. IR (KBr): ν_{CN} 2167 cm^{-1}. Anal. Calcd for $C_{18}H_{76}N_{18}O_{38}Ga_4Re_{18}Se_{24}$: C, 3.24; H, 1.15; Ga, 4.18; N, 3.78; Na, 0.00. Found: C, 3.25; H, 1.33; Ga, 4.89; N, 3.79; Na, <0.3. Overall, these values improve slightly if the presence of ca. 1% amorphous Ga_2O_3 is assumed.[18] The assumed 4:3 ratio of Ga^{3+} ions to $[Re_6Se_8(CN)_6]^{4-}$ cluster units is consistent with charge balance, as well as the measured C, H, and N content. Water content was independently verified by thermogravimetric analysis. This compound was structurally characterized by analysis of X-ray powder diffraction data (see below).

Colloidal "$Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$". Iron powder (2.1 mg, 0.038 mmol) and $Na_4[Re_6Te_8(CN)_6]$ (0.090 g, 0.038 mmol) were added to 10 mL of 0.33 M HCl. The color of the solution changed gradually from orange to brown. After 10 min, the mixture was centrifuged, and the dark brown supernatant solution was decanted from a small amount of black solid. The product used for measuring the absorption spectrum presented below was obtained by concentrating this solution to a volume of 7 mL.

Solvent Uptake Measurements. The method used was based on a previously reported technique.[20] Solid samples were dehydrated by heating at 125 °C under vacuum for several hours. An approximately 1% (w/w) solution of alcohol in a precisely determined volume (ca. 1 mL) of toluene was added to the dehydrated solid under a dinitrogen atmosphere. The mixture was allowed to stand in a capped vial for 10 min. The alcohol concentrations before and after exposure to the solid were measured by comparing integrated peak areas in gas chromatographs with a linear calibration plot obtained from standards prepared with a range of concentrations. These measurements were performed on a Hewlett-Packard 5890 Series II gas chromatography instrument equipped with an FID detector, and employing a J&W Scientific DB-1 column. Toluene uptake was determined by an analogous procedure with a ca. 1% (w/w) solution in mesitylene.

X-ray Structure Determination. X-ray powder diffraction data were collected for $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ on a Siemens D500 diffractometer with Ge monochromated Cu $K\alpha_1$ radiation. Two overlapping sets of data, $8° \leq 2\theta \leq 75°$ and $28° \leq 2\theta \leq 140°$, were collected at different slit settings in 0.02° steps. Diffractometer constants were determined from data collected for NIST standard SRM660 (LaB_6) under identical conditions. An initial model for the structural refinement was created in space group $Fm\bar{3}m$ by replacing the Fe^{2+} ions in the Prussian blue structure[9] with an idealized $[Re_6Se_8]^{2+}$ cluster core. The correctness of this model was confirmed with an independent direct methods solution of the structure. Crystallographic parameters were refined against both data sets simultaneously with *GSAS*.[21] Pseudo-Voight peak shapes were employed. Thermal parameters for heavier atoms were refined anisotropically, while those of C, N, and O atoms were fixed with an isotropic value. Only eight of the total thirty-eight water molecules per unit cell could be located with confidence. The fit of the fully refined structure to the low angle data is shown in Figure 3; crystallographic data are listed in Table 1. Further details of the structural refinement have been deposited as Supporting Information.

Other Physical Measurements. Other X-ray powder diffraction data were collected on a Siemens D5000 diffractometer with Cu $K\alpha$ radiation. Infrared spectra were recorded on a Mattson Infinity System FTIR spectrometer. Absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer. Magnetic susceptibility data were obtained with a Quantum Design MPMS2 SQUID magnetometer. Mössbauer spectra were collected with a constant-acceleration spectrometer that employed a rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. Cyclic voltammetry
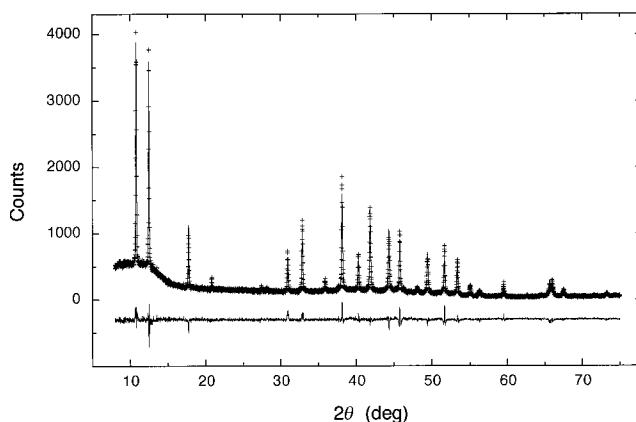
Figure 3. A portion of the X-ray powder diffraction data for $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ (crosses) along with the final fit from the crystallographic analysis (upper solid line). The lower line plots the difference between the observed and simulated patterns. Figure 4 depicts the final unit cell contents.

Table 1. Crystallographic Data^a for $Ga_4[Re_6Se_8(CN)_6]_3 \cdot 38H_2O$

formula	$C_{18}H_{76}Ga_4N_{18}O_{38}Re_{18}Se_{24}$
formula wt	6678.41
space group	$Fm\bar{3}m$
a, Å	14.1285(2)
V, Å^3	2820.27(6)
d_{calc}, g/cm^3	3.932
R_p (R_{wp}),^{b} %	7.21 (9.25)

^{a} Obtained at 295 K with Ge monochromated Cu $K\alpha_1$ ($\lambda = 1.5406$ Å) radiation. ^{b} $R_p = \sum|I_o - I_c|/\sum I_o$; $R_{wp} = [\sum w(I_o - I_c)^2/\sum wI_o^2]^{1/2}$.

was performed with a Bioanalytical Systems CV-50W voltammagraph, 0.1 M KNO_3 supporting electrolyte, and a glassy carbon working electrode. Potentials were determined vs an SCE reference electrode. Thermogravimetric analyses were carried out in a dinitrogen atmosphere with a TA Instruments TGA 2950.

Void Volume Calculations. Void volumes were calculated from crystal structures with a simple Monte Carlo type integration procedure. Any point in the unit cell that did not lie within the estimated van der Waals radius[22] of a framework atom (water molecules were excluded from the calculations) was considered to be part of the void space. Statistics were gathered until the percentage of void space converged to a value with a precision of 0.0001%. The crystal structure employed for $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ was based on the measured unit cell parameter and idealized atom positions derived from the structure of the $[Re_6Te_8(CN)_6]^{4-}$ cluster.

Results and Discussion

Addition of ferric sulfate to an aqueous solution of $Na_4[Re_6Te_8(CN)_6]$ results in the immediate precipitation of $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ ($x \approx 27$) as a fine black solid. Both reaction 1 and reaction 2 can be carried out with $[Fe(H_2O)_6]^{2+}$ (or a selection of other iron sources) in place of $[Fe(H_2O)_6]^{3+}$ to give the same product via autoxidation. The X-ray powder diffraction pattern of the new material indexes to a face-centered cubic lattice with a unit cell parameter of $a = 13.850(2)$ Å. The relative peak intensities match those in a simulated pattern based on the anticipated cluster-expanded Prussian blue structure shown in Figure 4. A full Rietveld refinement of the structure with the diffraction data was not possible, however, owing to the broad peak widths and lack of well-resolved peaks beyond a diffraction angle of $2\theta = 45°$ (using Cu $K\alpha$ radiation) which presumably arise from the small crystallite size. The magnetic susceptibility data and the Mössbauer spectrum are consistent

(19) Wilde, R. E.; Ghosh, S. N.; Marshall, B. J. *Inorg. Chem.* **1970**, *9*, 2512.

(20) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.

(21) Larson, A. C.; von Dreele, R. B. *GSAS: Generalized Structural Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1990.

(22) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Batsanov, S. S. *Russ. Chem. Bull.* **1995**, *44*, 18.
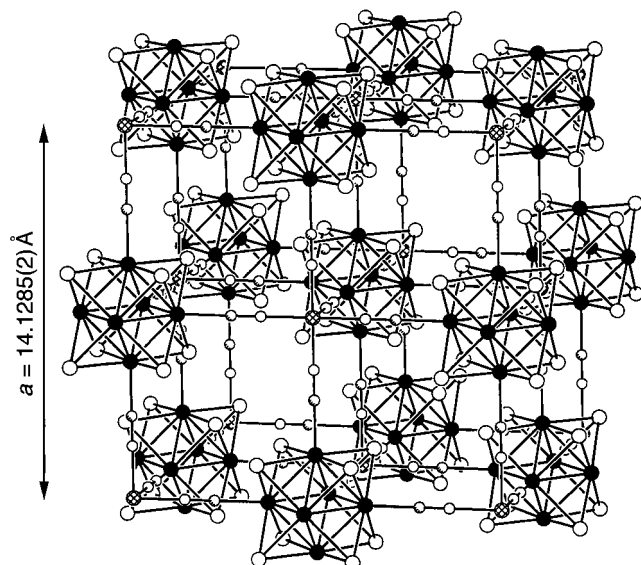
Figure 4. Unit cell for the structures of the cluster-expanded Prussian blue analogues $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ and $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$. Cross-hatched and white spheres represent Fe^{3+} or Ga^{3+} ions and Se or Te atoms, respectively; other atom types are as designated in Figure 1 (bottom). The $[Re_6Q_8(CN)_6]^{4-}$ cluster sites are only 75% occupied; water molecules have been omitted for clarity. Atom positions and the unit cell parameter shown are those obtained from the structural refinement of $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$. Selected mean interatomic distances (Å): Re−Re 2.631(1), Re−Se 2.533(1), Re−C 2.092(4), Ga−N 1.957(6), Ga−O 2.001, C−N 1.154(4).

with the presence of four isolated (and roughly equivalent) high-spin Fe^{3+} ions per formula unit. Further magnetic measurements at temperatures down to 1.7 K are planned to probe the possible existence of a long-range ferromagnetic ordering of the paramagnetic Fe^{3+} centers through the intervening diamagnetic clusters (analogous to the ordering observed in Prussian blue below 5.6 K).[10,23]

Variations of reaction 2 were explored in an effort to produce a more crystalline sample with which to prove the cluster-expanded Prussian blue structure. Experiments utilizing the slightly more labile but similarly sized Ga^{3+} ions in place of Fe^{3+} ions ultimately succeeded with the synthesis of $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ ($x \approx 38$) as a pale orange solid. The X-ray powder diffraction data for this compound exhibit discernible peaks out to $2\theta = 140°$, and were subjected to a Rietveld analysis (Figure 3). The resulting structure is presented in Figure 4, and indeed consists of a direct expansion of Prussian blue with $[Re_6Se_8]^{2+}$ cluster cores and Ga^{3+} ions occupying the Fe^{2+} and Fe^{3+} sites, respectively. It is important to emphasize that, analogous to the situation in Prussian blue, one out of every four $[Re_6Se_8(CN)_6]^{4-}$ units is missing from the structure depicted, with water molecules coordinating Ga^{3+} ions in place of absent cyanide nitrogen atoms. These vacancies create large water-filled cavities (best envisioned by excising the central cluster from the unit cell in Figure 4) with a *minimum* dimension of 10.0 Å, based on the separation between Fe^{3+} ions minus their estimated van der Waals radii;[22b] the related dimension in Prussian blue is only 6.2 Å. The accessible volumes associated with the cavities in the cluster-expanded structures are calculated to be more than double those in Prussian blue (see Table 1).[24] No long-range ordering of the vacancies is apparent in the X-ray

(23) Mayoh, B.; Day, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1483.

(24) For comparison, the calculated void volumes per formula unit of zeolite A ($Na_{12}[Al_{12}Si_{12}O_{48}]$) and zeolite ZSM-5 ($H_2[Al_2Si_{94}O_{192}] \cdot 24H_2O$) are 557 Å^3 (30%) and 2365 Å^3 (44%), respectively.
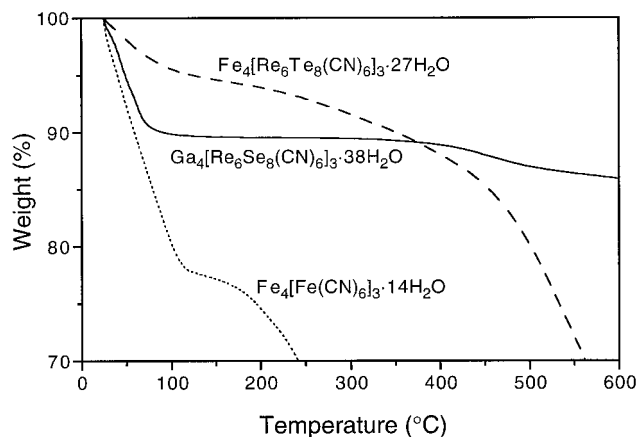
Figure 5. Thermogravimetric analyses showing the weight loss in Prussian blue (dotted line), $Fe_4[Re_6Te_8(CN)_6]_3 \cdot 27H_2O$ (dashed line), and $Ga_4[Re_6Se_8(CN)_6]_3 \cdot 38H_2O$ (solid line) with temperature increasing at a rate of 0.5 °C/min.

Table 2. Inclusion Properties of Prussian Blue and Its Cluster-Expanded Analogues[a]

	$Fe_4[Fe(CN)_6]_3$	$Fe_4[Re_6Te_8(CN)_6]_3$	$Ga_4[Re_6Se_8(CN)_6]_3$
void volume (Å^3)	557 (53%)	1275 (48%)	1579 (56%)
water	14	27	38
methanol	1.7	8.3	19
ethanol	0.2	3.2	8.6
n-propanol	0.1	1.4	2.1
i-propanol	0.1	0.9	0.7
t-butanol	0.1	1.0	0.5
toluene	0.02	0.1	0.07

[a] Entries correspond to the void volume or number of solvent molecules taken up per unit cell (= per formula unit).

diffraction data. The slightly contracted unit cell obtained for $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ is most likely due to a greater deviation of its cyanide ligands away from a strictly linear bridging geometry. A buckling effect of this type has been observed in dehydrated samples of Prussian blue.[10]

Initial experiments indicate that the cluster-expanded frameworks are at least as robust as the parent framework in Prussian blue. Thermogravimetric analyses (Figure 5) performed on $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$ and $Fe_4[Re_6Te_8(CN)_6]_3 \cdot 27H_2O$ gave remarkably similar results: as the temperature increases, both materials fully dehydrate by 125 °C and then exhibit a steady loss of mass up to 400 °C. In the former compound, this mass loss has been attributed to a gradual evolution of cyanogen.[25] The results for $Ga_4[Re_6Se_8(CN)_6]_3 \cdot 38H_2O$ differ significantly, showing complete dehydration by 100 °C, but no subsequent loss of framework mass below 400 °C. The X-ray diffraction patterns of samples heated at constant temperature for 6 h establish that the iron- and gallium-containing cluster phases retain their crystallinity unless heated above ca. 250 and 300 °C, respectively. Investigations carried out on Prussian blue place this transition temperature at approximately 240 °C.[25]

Consistent with their expanded structures, the dehydrated cluster phases exhibit an enhanced inclusion capacity relative to Prussian blue. Experiments probing the uptake of a range of alcohols and toluene are summarized in Table 2. Whereas Prussian blue absorbs some methanol but very little of any of the larger alcohols, the cluster-expanded materials absorb significant quantities of both methanol and ethanol, and some *n*-propanol. Bulkier alcohols, such as *t*-butanol, are not absorbed by any of the phases; the results obtained for these solvents are

(25) Seifer, G. B. *Russ. J. Inorg. Chem.* **1960**, *5*, 33.

indicative of the degree of uptake due to surface adsorption, and provide additional evidence for a small particle size in $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$. The findings suggest that $Ga_4[Re_6Se_8(CN)_6]_3$ should be effective in sieving water, methanol, ethanol, and trace quantities of *n*-propanol from mixtures with other more sterically hindered solvents. Although there is ample room for larger molecules to fit inside the cavities of the $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ structure, in order to penetrate deep into the framework, a molecule must be of an appropriate size to squeeze through the ca. 2.4×5.9 Å openings defined by one quadrant of a unit cell face (Figure 4). In contrast to a prior report concerning Prussian blue analogues,[26] toluene was not taken up by the solids. The lower levels of solvents absorbed by $Fe_4[Re_6Te_8(CN)_6]_3$ compared to those of its Ga-containing counterpart are likely due to a combination of the following factors: (i) a slightly smaller unit cell, (ii) the larger size of the Te atoms which project further into the cavities and cage openings, and (iii) the smaller particle size and accompanying decrease in the number of internal cavities capable of trapping noncoordinated solvent molecules.
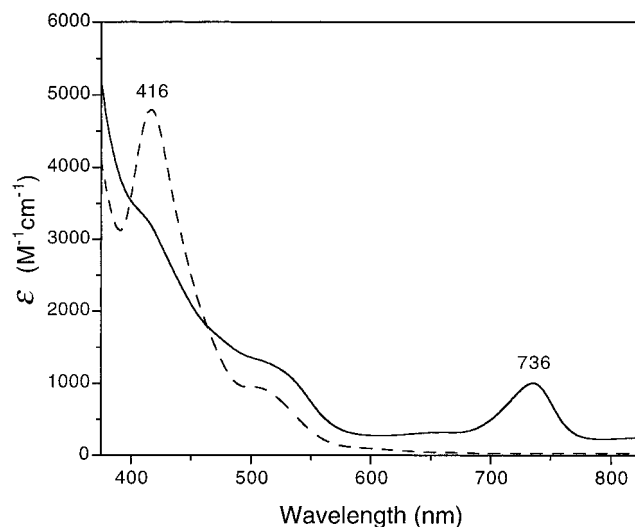
Unlike the Ga-containing phase, $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ does not retain the color of its molecular components. Rather, it assumes a deep black sheen reminiscent of the intense blue color that suddenly emerges when essentially colorless reactants are combined to form Prussian blue. The unexpected color of Prussian blue inspired much of the early interest in mixed valence compounds,[27] and has since been shown to arise from an intervalence (metal-to-metal charge transfer) transition wherein an electron transfers across a cyanide bridge from a carbon-bound Fe^{2+} site to a nitrogen-bound Fe^{3+} site in the crystal.[28] This transition is responsible for a broad band centered at 709 nm in the absorption spectrum of a soluble (colloidal) form of Prussian blue,[29] prepared by carrying out reaction 1 in acidic solution at very dilute concentrations. A soluble form of $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ was prepared by analogous means. The absorption spectrum of the resulting dark brown solution is shown in Figure 6, along with that of an orange solution of the $[Re_6Te_8(CN)_6]^{4-}$ cluster reactant. As the reaction progresses, the peak at 416 nm, presumably associated with a cluster-to-ligand charge transfer, diminishes while a new peak centered at 736 nm grows in. We assign the latter feature to a cluster-to-metal charge-transfer transition wherein an electron transfers across a cyanide bridge from an $[Re_6Te_8]^{2+}$ cluster to an Fe^{3+} ion. The band occurs at a slightly lower energy than the corresponding band in Prussian blue, an observation that is in line with the slightly lower oxidation potential of $[Re_6Te_8(CN)_6]^{4-}$ versus that of $[Fe(CN)_6]^{4-}$ in aqueous solution (as measured by cyclic voltammetry). While metal-to-cluster charge-transfer bands have been reported recently for several molecular species,[30] this, to our knowledge, represents the first observation of a cluster-to-metal charge-transfer band.

Figure 6. Electronic absorption spectra of orange $Na_4[Re_6Te_8(CN)_6]$ (dashed line) and the dark brown colloidal analogue of $Fe_4[Re_6Te_8(CN)_6]_3 \cdot xH_2O$ (solid line) in water. The peak at 736 nm is assigned to a cluster-to-metal charge-transfer transition, and did not appear in control experiments with either the Fe metal or the cluster compound omitted from the reaction. A broad, low-intensity peak (not shown) centered at ca. 970 nm was also observed.

The foregoing results clearly demonstrate the feasibility of expanding the pores in solid frameworks by substituting isotropically enlarged cluster cores for metal centers. The extent to which this method can be applied to other structures, however, remains to be tested. As a second, closely related example, we have found that the discus-shaped cavities in the three-dimensional anionic framework of $Na_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$[31] can be expanded with substitution of $[Re_6Se_8]^{2+}$ cluster cores for the Fe^{2+} ions.[32] By applying the strategy to other parent structures with even more open frameworks, including oxide- and chalcogenide-bridged structures, it is hoped that materials possessing still larger cavities may eventually be achieved.

Supporting Information Available: Full details of data collection and Rietveld refinement procedures employed in determining the structure of $Ga_4[Re_6Se_8(CN)_6]_3 \cdot xH_2O$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) "Soluble" Prussian blue has the chemical formula $KFe[Fe(CN)_6] \cdot xH_2O$ and a structure based on the same cubic framework (Figure 2) as "insoluble" Prussian blue, but with no vacancies and K^+ ions lodged in half of the unit cell octants.[19]

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