Inorganic Chemistry

Synthesis and Characterization of Prussian Blue Analogues Incorporating the Edge-Bridged Octahedral [Zr6BCl12]2+ Cluster Core

Laurance G. Beauvais and Jeffrey R. Long*

Department of Chemistry, University of California, Berkeley, California 94720-1460

In attempts to produce a microporous magnet, two approaches were explored for expanding the Prussian blue structure type via incorporation of edge-bridged octahedral $[Zr_6ZCl_{12}]^{2+}$ (Z = B, Be) cluster cores. Dissolution of $Rb_5Zr_6BCl_{18}$ and $K_5Zr_6BeCl_{15}$ in an acetonitrile solution of $Et_4N(CN)$ led to the isolation of $(Et_4N)_5[Zr_6BCl_{12}(CN)_6]$ (**1**) and $(Et_4N)_5[Zr_6BeCl_{12}(CN)_6]\cdot 2MeCN\cdot 2THF$ (**2**), respectively. The crystal structure of **1**·1.5MeCN revealed the expected cyano-terminated cluster complex with a *trans*-N···N span of 11.73(3) Å. Unfortunately, both $[Zr_6ZCl_{12}(CN)_6]^{5-}$ clusters rapidly lose their cyanide ligands in aqueous solution making them ill-suited for solid-forming reactions with hydrated metal ions. Such outer-ligand exchange, however, allows the use of $[Zr_6BCl_{18}]^{4-}$ in the synthesis of expanded Prussian blue-type solids through reactions with $[Cr(CN)_6]^{3-}$. The use of 2.2 M aqueous LiCl to stabilize the cluster during the reaction gave $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot 3H_2O$ (**3**), while the use of 1 M acetic acid yielded $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot 2H_2O\cdot CH_3CO_2H$ (**4**). A Rietveld refinement against X-ray powder diffraction data collected for **3** confirmed the presence of a cubic Prussian blue framework structure, featuring alternating $[Zr_6BCl_{12}]^{2+}$ cores and $[Cr(CN)_6]^{3-}$ anions. The temperature dependence of magnetization data obtained for **4** revealed activation of magnetic exchange interactions between the $S = \frac{1}{2}$ cluster units and the $S = \frac{3}{2}$ hexacyanochromate complexes below 10 K.

Introduction

The prospect of generating materials with tailored properties and reactivity has prompted interest in solution-based methods for solid synthesis, wherein soluble molecular components are organized into an extended framework.[1] Often the goal in such research is to design a porous solid that can act as a catalyst,[2] molecular sieve,[3] or gas storage material[3g,h,4] through the choice of appropriate molecular building units. The versatility of this approach is apparent from further demonstrations of its use in constructing ion-exchange materials,[5] chemical sensors,[6] electrical conduc-

tors,[7] and nonlinear optical materials.[8] One of the most thoroughly explored applications, however, has been in the synthesis of magnetic materials composed of exchange-coupled, paramagnetic transition metal centers.[9] An appealing challenge is to extend this work to the preparation of

* To whom correspondence should be addressed. E-mail: jlong@cchem.berkeley.edu.

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microporous magnets. Such compounds are of interest for potential applications as low-density magnetic materials and magnetic sensors, and possibly even in performing magnetic separations.[10]

The few documented examples of microporous solids exhibiting bulk magnetic ordering are typically prepared via hydrothermal methods. For example, a series of microporous Fe^{III} and V^{III} phosphate compounds that act as antiferromagnets with ordering temperatures up to 37 K and pore sizes up to 10 Å in diameter have been synthesized.[11] In addition, the pillared-layered compound $Co_4(SO_4)(OH)_6(C_6H_{12}N_2)_{0.5}\cdot$ H_2O orders ferrimagnetically at 20 K,[12] and recent work has exposed a series of formate-bridged network solids with magnetic ordering temperatures as high as 16 K.[13] The most extensive class of porous magnetic structures, however, is that exemplified by the coordination solid Prussian blue

$(Fe_4[Fe(CN)_6]_3\cdot14H_2O)$.[14] In this compound, the diamagnetic $[Fe(CN)_6]^{4-}$ complexes inhibit communication between the paramagnetic Fe^{III} ions, so the solid orders magnetically only below 5.6 K.[15] In contrast, Prussian blue analogues constructed from paramagnetic $[Cr(CN)_6]^{3-}$ complexes order at much higher temperatures.[16] Prominent among these are $V[Cr(CN)_6]_{0.86}\cdot2.8H_2O$ (T_N = 315 K) and $KV[Cr(CN)_6]\cdot$ $2H_2O$ (T_N = 376 K), prepared via reaction of $[Cr(CN)_6]^{3-}$ with a variety of V^{II} salts.[17] To date, however, the only Prussian blue analogue in which microporosity and bulk magnetic ordering have been demonstrated to coexist is $Co_3[Co(CN)_5]_2$ (T_N = 38 K).[18] Note also that access to the cavities in such compounds is likely to be limited to relatively small molecules, such as dinitrogen and methanol.[3d]

One strategy for preparing materials with increased porosity is to expand the frameworks of known microporous solids by isotropically enlarging a molecular component. This approach has been demonstrated, for example, with the synthesis of an expanded Prussian blue analogue, wherein the face-capped octahedral $[Re_6Se_8(CN)_6]^{4-}$ cluster is substituted for the octahedral $[Fe(CN)_6]^{4-}$ complex in the framework[19]

$$4[Fe(H_2O)_6]^{3+} + 3[Re_6Se_8(CN)_6]^{4-} \rightarrow$$
$$Fe_4[Re_6Se_8(CN)_6]_3\cdot36H_2O \quad (1)$$
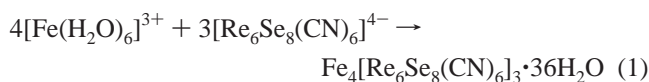
Gas sorption and solvent uptake experiments show that the enlarged pores within compounds of this type result in a higher gas-storage capacity and permit absorption of larger solvent molecules.[3d,19] This method has now been applied in the expansion of a wide range of cyano-bridged frameworks[5f,6d,19,20] and has further led to discovery of some unprecedented porous frameworks.[6d,19,21] Similar reactions employing face-capped octahedral $[W_6S_8(CN)_6]^{6-}$ and edge-bridged octahedral $[Nb_6Cl_{12}(CN)_6]^{4-}$ clusters have also been shown to produce cyano-bridged solids.[22,23]

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A reaction related to eq 1 using $[Ni(H_2O)_6]^{2+}$ and the oxidized cluster $[Re_6Se_8(CN)_6]^{3-}$ yields the highly porous Prussian blue analogue $Ni_3[Re_6Se_8(CN)_6]_2 \cdot 33H_2O$.[19] Magnetic susceptibility data, however, reveal the absence of significant magnetic exchange interactions between the $S = 1$ Ni^{II} centers and the $S = {}^1/_2$ cluster cores at temperatures down to 5 K. Consistent with this result, the calculations indicate that the spin-containing orbital for such face-capped octahedral clusters should have δ-type symmetry with respect to the terminal ligands[24] and thus will not project spin density out onto the cyanide ligands. In contrast, interstitially centered, edge-bridged octahedral clusters of the type $[Zr_6ZX_{18}]^{n-}$ (Z = main group or transition metal atom; X = Cl, Br, I) display metal-based HOMOs featuring π-type symmetry with respect to the terminal ligands,[25] which should facilitate magnetic exchange coupling through a cyanide bridge. The chemistry of these clusters has been thoroughly explored, both in condensed solids[26] and in solution,[27] and it suggests that the paramagnetic cluster cores $[Zr_6BCl_{12}]^{2+}$ and $[Zr_6BeCl_{12}]^{2+}$ (with one and two unpaired electrons, respectively) could be suitable building units for the synthesis of porous cyano-bridged magnets.

Herein, we report the synthesis and magnetic properties of the first expanded Prussian blue analogues incorporating clusters of this type.

Experimental Section

Preparation of Compounds. The compounds $Et_4N(CN)$,[28] $K_3[Cr(CN)_6]$,[29] $Rb_5Zr_6BCl_{18}$,[26c] $K_3Zr_6BeCl_{15}$,[26a] and $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$[27c] were prepared as described previously. Tetrahydrofuran was distilled over Na/benzophenone; acetonitrile was distilled over CaH_2, and water was distilled and deionized with a Milli-Q filtering system. All other reagents were used as purchased. All reactions were carried out in deoxygenated solvents under the anaerobic conditions provided by a nitrogen-filled glovebag or glovebox. Reactions utilizing $[Cr(CN)_6]^{3-}$ were carried out in the absence of light to prevent its photochemical decomposition.

$(Et_4N)_5[Zr_6BCl_{12}(CN)_6]$ (1). Solid $Rb_5Zr_6BCl_{18}$ (0.193 g, 0.119 mmol) was added to a solution of $Et_4N(CN)$ (0.334 g, 2.14 mmol) in 15 mL of acetonitrile, and the mixture was stirred for 24 h. The resulting orange-red solution was filtered to remove insoluble materials, and 20 mL of THF was added to give an orange precipitate. The solid was collected by filtration, washed with THF (3 × 5 mL), and dried under vacuum to give 0.155 g (73%) of product. IR: ν_{CN} 2103 cm^{-1}. Anal. Calcd for $C_{46}H_{100}BCl_{12}N_{11}Zr_6$: C, 30.85; H, 5.63; N, 8.60. Found: C, 30.84; H, 5.60; N, 9.04. Orange rod-shaped single-crystals of $1 \cdot 1.5MeCN$ suitable for X-ray analysis were grown by diffusing diethyl ether vapor into an acetonitrile solution containing 1 and excess $Et_4N(CN)$.

$(Et_4N)_5[Zr_6BeCl_{12}(CN)_6] \cdot 2MeCN \cdot 2THF$ (2). Solid $K_3Zr_6BeCl_{15}$ (0.125 g, 0.104 mmol) was added to a solution of $Et_4N(CN)$ (0.292 g, 1.87 mmol) in 15 mL of acetonitrile, and the mixture was stirred for 24 h. The ensuing wine red solution was filtered to remove insoluble materials, and 20 mL of THF was added to produce a maroon precipitate. The solid was collected by filtration, washed with THF (3 × 5 mL), and dried under vacuum to give 0.111 g (65%) of product. IR: ν_{CN} 2082 (vs), 2098 (m) cm^{-1}. $\mu_{eff} = 2.23$ μ_B at 298 K. Anal. Calcd for $C_{58}H_{122}BeCl_{12}N_{13}O_2Zr_6$: C, 34.56; H, 6.10; N, 9.03. Found: C, 33.98; H, 6.53; N, 9.03.

$(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl \cdot 3H_2O$ (3). A 15 mL aqueous solution of $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$ (0.15 g, 0.084 mmol) and LiCl (1.2 g, 45 mmol) was combined with a 5 mL aqueous solution of $K_3[Cr(CN)_6]$ (0.021 g, 0.065 mmol). Upon standing for 5 h, a dark green microcrystalline solid had precipitated. The solid was collected by centrifugation, washed with successive aliquots of water (20 mL), methanol (2 × 20 mL), and diethyl ether (20 mL), and dried under a dinitrogen purge to give 0.051 g (51%) of product. Product identity and purity were verified by comparison of the observed powder X-ray diffraction pattern with a simulated pattern. The water content was determined by combining results from thermogravimetric and elemental analyses. IR: ν_{CN} 2149 (broad) cm^{-1}. Anal. Calcd for $C_{22}H_{46}BCl_{13}CrN_8O_3Zr_6$: C, 17.14; H, 3.01; N, 7.27. Found: C, 17.70; H, 3.17; N, 7.49.

$(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl \cdot 2H_2O \cdot CH_3CO_2H$ (4). A solution of $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$ (0.20 g, 0.11 mmol) in 15 mL of 1 M aqueous acetic acid was combined with a solution of $K_3[Cr(CN)_6]$ (0.039 g, 0.12 mmol) in 2 mL of 1 M aqueous acetic acid to yield a dark green precipitate. After the mixture stood for 1 h, the solid was collected by centrifugation, washed with three successive 20 mL aliquots of water, and dried under a purge of dinitrogen to give 0.15 g (81%) of product. Product identity and purity were verified by comparison of the observed powder X-ray diffraction pattern with a simulated pattern. The water content was determined by combining results from thermogravimetric and elemental analyses. Diffuse reflectance spectrum (powder): λ_{max} 293 (sh), 312, 455, 494 (sh), 540 (sh), 672, 792 nm. IR: ν_{CN} 2132 (broad), ν_{CO} 1458 cm^{-1}. $\mu_{eff} = 6.94$ μ_B at 298 K. Anal. Calcd for $C_{24}H_{48}BCl_{13}CrN_8O_4Zr_6$ plus 2.4% amorphous $Cr(CH_3CO_2)_3$: C, 18.57; H, 3.08; Cl, 28.28; Cr, 3.83; N, 6.88; Zr, 33.59. Found: C, 18.73; H, 3.32; Cl, 27.46; Cr, 3.80; N, 7.08; Zr, 33.10.

X-ray Structure Determinations. A single crystal of $1 \cdot 1.5MeCN$ was coated in Paratone-N oil, attached to a quartz fiber, transferred to a Bruker SMART diffractometer, and cooled in a dinitrogen stream. Lattice parameters were initially determined from a least-squares refinement of 175 carefully centered reflections. The raw intensity data were converted (including corrections for background and Lorentz and polarization effects) to structure factor amplitudes and their esd's using the SAINT 5.00 program. An

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Table 1. Crystallographic Data and Structural Refinement Parameters for $(Et_4N)_5[Zr_6BCl_{12}(CN)_6] \cdot 1.5MeCN$ ($\mathbf{1} \cdot 1.5MeCN$), $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl \cdot 3H_2O$ ($\mathbf{3}$), and $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl \cdot 3H_2O \cdot CH_3COOH$ ($\mathbf{4}$)

	$\mathbf{1} \cdot 1.5MeCN^a$	$\mathbf{3}^b$	$\mathbf{4}^b$
formula	$C_{49}H_{104.5}BCl_{12}N_{12.5}Zr_6$	$C_{22}H_{46}BCl_{13}CrN_8O_3Zr_6$	$C_{25}H_{54}BCl_{13}CrN_8O_7Zr_6$
fw	1852.48	1541.7	1649.8
T (K)	159	295	295
space group	$P\bar{4}$	$Fm\bar{3}m$	$Fm\bar{3}m$
Z	4	4	4
a (Å)	23.702(1)	16.182(3)	16.06(1)
c (Å)	13.7979(9)		
V (Å^3)	7751.6(7)	4237(2)	4145(9)
d_{calcd} (g/cm^3)	1.587	2.416	2.643
R_1, R_2^c (%)	5.56, 10.00		
R_p, wR_p, R_{F2}^d (%)		5.37, 8.13, 6.82	

^{a} Obtained using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. ^{b} Obtained using synchrotron radiation of wavelength $\lambda = 1.278041(5)$ Å. ^{c} $R_1 = \sum ||F_o| - |F_c||/\sum|F_c|$; $R_2 = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w(|F_o|^2)]\}^{1/2}$. ^{d} $R_p = \sum|y_i(obsd) - y_i(calcd)|/\sum y_i(obsd)$; $wR_p = \{\sum[w_i(y_i(obsd) - y_i(calcd))^2]/\sum[w_i(y_i(obsd))^2]\}^{1/2}$; $R_{F2} = \sum|F_o^2 - F_c^2|/\sum F_o^2$.

empirical absorption correction was applied to the data set using SADABS. The space group assignment was based on systematic absences, E statistics, and successful refinement of the structure. Initially, the data indicated $4/mmm$ symmetry, and the space group $P4_2/ncm$ was chosen. In this space group, it was possible to locate the cluster and almost all of the tetraethylammonium cations. However, it was not possible to obtain a value for R_2 below 30%, and the light atoms would have unreasonably large thermal parameters. At this point, we attempted to solve the structure in lower-symmetry space groups employing several twin laws to account for the higher apparent symmetry. Numerous space groups were tested, and we determined the true space group of the crystal to be $P\bar{4}$ twinned by a 2-fold rotation along 110 (twin law = 0 1 0 1 0 0 0 0 −1). The structure was solved by direct methods, with the aid of difference Fourier maps, and was refined with successive full-matrix least-squares cycles. The final refinements reveal that each twin occupies approximately the same volume (scale factor = 50.3%). Light atoms ($Z < 8$) were refined isotropically, while all other atoms were refined anisotropically. The bond distances for two of the cyanide ligands (Zr(3)−C(3)−N(3) and Zr(6)−C(6)−N(6)) had to be restrained to maintain reasonable values during refinement. This was accomplished by restraining the Zr−C, C−N, and Zr−N bond distances to 2.4(1), 1.14(1), and 3.54(2) Å, respectively. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Crystallographic parameters are listed in Table 1.

High-resolution X-ray powder diffraction data were collected for compounds **3** and **4** at beamline 2-1 of the Stanford Synchrotron Radiation Laboratory. Finely ground powders of the samples were loaded into 0.5 mm quartz capillaries under anaerobic conditions, and the capillaries were sealed. Radiation of wavelength 1.278041(5) Å was selected using a Si(111) monochromator. Diffraction data for compounds **3** and **4** were collected in Q space ($Q = 2\pi/d$) over the ranges of 0.600−6.00 Å^{-1} ($2\theta = 7-75°$) with 0.003 Å^{-1} steps and 0.500−8.00 Å^{-1} ($2\theta = 6-100°$) with 0.006 Å^{-1} steps, respectively. The wavelength, zero point, and profile parameters were refined using a Si standard (NIST 640b). A model structure was generated using the geometries taken from the structures of $K_3[Cr(CN)_6]$[30] and $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$[27c] and employed as a starting point for Rietveld refinements against the diffraction data using the program GSAS.[31] A tetraethylammonium cation disordered over an inversion center was fixed at the center of each octant

of the Prussian blue-type unit cell. A cosine Fourier series background and a pseudo-Voigt peak shape[32] (corrected[33] for asymmetry) were also refined. The molecular geometries of the $[Zr_6BCl_{12}]^{2+}$ cluster core and $[Cr(CN)_6]^{3-}$ complex were maintained by imposing the following restraints: Zr−Zr = 3.35(2) Å, Zr−Cl = 2.57(2) Å, Zr−B = 2.36(1) Å, Cr−C = 2.08(2) Å, and C−N = 1.15(1) Å. The N−C and C−C bond distances were maintained by soft constraints by imposing reasonable values for the N−C and C−C bonds. The weighting factor for the soft constraints was fixed at 1000 during the initial stages of the refinement and reduced to 10 during the course of the refinement. Because of the limited amount of data, isotropic thermal parameters for Zr, B, and Cl atoms were fixed at a value of 0.055 Å^2, Cr, C and N atoms were fixed at a value of 0.08 Å^2, and the thermal parameters for tetraethylammonium cations were fixed at 0.2 Å^2. Crystallographic parameters are listed in Table 1.

Other Physical Measurements. Routine X-ray powder diffraction data were collected using Co Kα ($\lambda = 1.79026$ Å) radiation on a Bruker-AXS D8 general area detector diffractometer system. Diffuse reflectance spectra were acquired on a Perkin-Elmer Lambda 9 spectrophotometer equipped with a 60 mm integrating sphere. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with a horizontal attenuated total reflectance accessory. Elemental analyses for C, H, and N were carried out in the microanalytical facility at UC Berkeley, and analyses for Zr, Cr, and Cl were performed by Galbraith Laboratories. Thermogravimetric analyses were carried out at a ramp rate of 1 °C/min under a dinitrogen atmosphere, using a TA Instruments TGA 2950. Magnetic susceptibility measurements were performed on a Quantum Design MPMS2 SQUID magnetometer using at least 30 mg of sample.

Results and Discussion

The synthesis of expanded Prussian blue-type compounds has previously been achieved by adding transition metal ions to an aqueous solution containing octahedral cyano-terminated clusters, as in reaction 1 above.[3d,19] Accordingly, reactions employing the edge-bridged octahedral clusters

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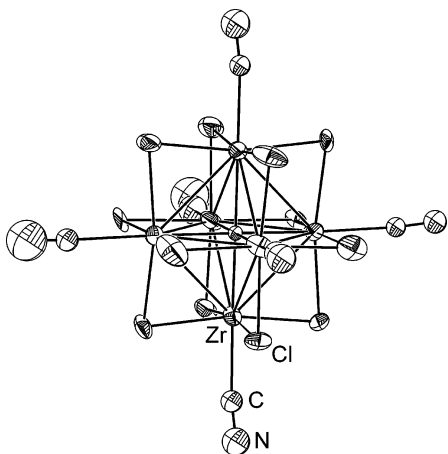
Figure 1. Structure of the $[Zr_6BCl_{12}(CN)_6]^{4-}$ cluster, as observed in **1**·1.5MeCN. Ellipsoids are drawn at the 50% probability level. Note that the cluster sits on a general position and possesses no crystallographically imposed symmetry. Selected mean interatomic distances (Å): Zr–Zr, 3.26(1); Zr–B, 2.31(2); Zr–Cl, 2.56(3); Zr–C, 2.39(4); C–N, 1.19(9).

$[Zr_6ZCl_{12}(CN)_6]^{4-}$ (Z = B, Be) might be expected to proceed as follows

$$4[M(H_2O)_6]^{3+} + 3[Zr_6ZCl_{12}(CN)_6]^{4-} \rightarrow$$
$$M_4[Zr_6ZCl_{12}(CN)_6]_3 \cdot xH_2O \quad (2)$$
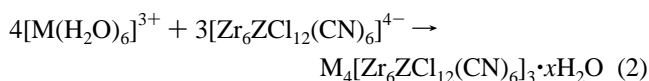
The success of this reaction depends, however, on the $[Zr_6ZCl_{12}(CN)_6]^{4-}$ cluster being substitutionally inert. If it is not, then the terminal cyanide ligands may be quickly exchanged for water, and the anticipated cyano-bridged solid will not ensue. Under such circumstances, an alternative strategy could be adopted, in which the chloro-terminated cluster is employed in combination with a substitutionally inert hexacyanometalate complex

$$3[Zr_6ZCl_{18}]^{4-} + 2[M(CN)_6]^{3-} \rightarrow$$
$$[Zr_6ZCl_{12}]_3[M(CN)_6]_2 \cdot xH_2O \quad (3)$$
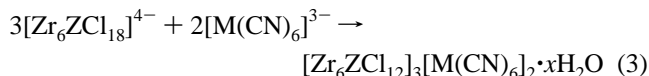
Both of these approaches were pursued in our efforts to produce magnetic Prussian blue analogues incorporating $[Zr_6ZCl_{12}]^{2+}$ (Z = B, Be) cluster cores.

Cyano-Terminated Clusters. The molecular salts $(Et_4N)_5$-$[Zr_6BCl_{12}(CN)_6]$ (**1**) and $(Et_4N)_5[Zr_6BeCl_{12}(CN)_6] \cdot 2MeCN \cdot$ 2THF (**2**) were synthesized by adding cyanide to reactions performed under conditions similar to those employed in the preparations of $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$ and $(Et_4N)_5$-$[Zr_6BeCl_{18}] \cdot 3MeCN$.[27cd] Dissolving $Rb_5Zr_6BCl_{18}$ in acetonitrile in the presence of an excess of anhydrous $Et_4N(CN)$ produced the 14-electron[34] cluster $[Zr_6BCl_{12}(CN)_6]^{5-}$. When $K_3Zr_6BeCl_{15}$ is dissolved under the same conditions, the 13-electron cluster $[Zr_6BeCl_{12}(CN)_6]^{5-}$ results. Note that the reaction involves spontaneous oxidation of the 14-electron

parent cluster, which is also observed in the preparation of $(Et_4N)_5[Zr_6BeCl_{18}] \cdot 3MeCN$.[27d]

X-ray analysis of a single crystal of **1**·1.5MeCN revealed the expected molecular geometry (Figure 1). Here, a central boron atom is surrounded by a regular octahedron of six zirconium atoms, with each edge bridged by a μ_2-Cl atom and each apex coordinated by a terminal cyanide ligand. The mean Zr–B and Zr–Zr distances of 2.31(2) and 3.26(1) Å, respectively, agree well with those previously observed for the 14-electron clusters in $Rb_5Zr_6BCl_{18}$[26c] and $(Im)_5[Zr_6$-$BCl_{18}] \cdot C_6H_5CH_3 \cdot 2MeCN$ (Im = 1-ethyl-3-methylimidazolium).[27c] In addition, the mean Zr–C distance of 2.39(4) Å is comparable to the 2.36 Å Zr–C bond observed for the 14-electron cluster $[Zr_6BeCl_{12}(CNXyl)_6]$ (CNXyl = 2,6-dimethylphenyl isocyanide).[27h] The mean *trans*-N···N distance within the hexacyanide cluster is 11.73(3) Å. This is 5.5 Å longer that the overall span of $[Fe(CN)_6]^{4-}$[35] and 1.4 Å longer than the span of $[Re_6Te_8(CN)_6]^{4-}$.[36] Thus, the incorporation of such Zr_6 cluster units can be anticipated to result in an even greater expansion of the Prussian blue framework structure.

Typically, the synthesis of expanded Prussian blue analogues must be carried out in aqueous solution to obtain crystalline materials. Unfortunately, experiments probing the solubility of **1** and **2** revealed that the $[Zr_6ZCl_{12}(CN)_6]^{5-}$ (Z = B, Be) clusters rapidly decompose in water. Compound **1** dissolves in degassed water to give an orange solution, from which an amorphous orange solid begins to precipitate after approximately five minutes. Over the course of several hours, this solid gradually turns white and evolves gas, resulting in a highly acidic supernatant solution. Compound **2** behaves similarly, except that only a small amount of solid precipitates, and the solution bleaches completely within fifteen minutes. Other than formation of a precipitate, which may be the result of the assembly of insoluble of cyano-bridged cluster oligomers, very similar behavior has been observed for the $[Zr_6ZCl_{18}]^{5-}$ (Z = B, Be) clusters in aqueous solution.[27m] Upon dissolution, the six labile chloride ligands are exchanged for water molecules to give $[Zr_6BeCl_{12}$-$(H_2O)_6]^+$. A bound water ligand can then hydrolyze to give $H^+_{(aq)}$ and $[Zr_6BeCl_{12}(H_2O)_5(OH)]$. Further decomposition of the cluster occurs with the evolution of H_2 by an unknown pathway. It is possible to inhibit decomposition of the chloro-terminated clusters, however, by dissolving them in the presence of excess chloride ions (to compete with water ligands for complexation) or in acidic solution (to prevent hydrolysis).[27jm] Regardless, the lability of the cluster-cyanide complexes in **1** and **2** renders them unsuitable for the preparation of expanded Prussian blue solids as shown in reaction 2.

Cluster-Expanded Prussian Blue Analogues. The lability of the terminal ligands renders such Zr_6 clusters of potential utility in solid assembly reactions of the type exemplified above with reaction 3. Indeed, emulating the synthesis of $KV[Cr(CN)_6] \cdot 2H_2O$,[17c] $(Et_4N)_4[Zr_6BCl_{18}] \cdot 2MeCN$

(34) Edge-bridged octahedral $[M_6X_{18}]^{n-}$ clusters prefer a count of 16 metal-based valence electrons, which can be thought of as forming eight three-center, two-electron bonds (one for each face of the octahedron). Electronic structure calculations show, however, that the introduction of a centering main group atom Z results instead in a preference for 14 M_6Z-based valence electrons.[25]

(35) Pospelov, V. A.; Zhdanov, G. S. *Zh. Fiz. Khim.* **1947**, *21*, 879.
(36) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.

was found to react with $[Cr(CN)_6]^{3-}$ in aqueous solution to precipitate the dark green Prussian blue analogue $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot3H_2O$ (**3**):

$$2Et_4N^+ + [Zr_6BCl_{18}]^{4-} + [Cr(CN)_6]^{3-} \rightarrow$$
$$(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot3H_2O + 5Cl^- \quad (4)$$
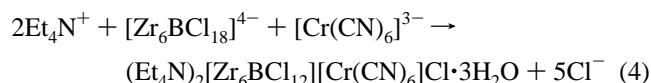
The reaction was carried out in 2.2 M aqueous LiCl to prevent the decomposition of the cluster. Unfortunately, characterization of the product by infrared spectroscopy and powder X-ray diffraction revealed the presence of a small amount of $Cr_3[Cr(CN)_6]_2\cdot xH_2O$ impurity.[9e] Presumably, this impurity develops when some $[Cr(CN)_6]^{3-}$ complexes are photoreduced,[37] permitting the labile Cr^{2+} ion to shed its cyanide ligands and react with residual $[Cr(CN)_6]^{3-}$ species. To prevent the reaction between the Cr^{2+} ions and $[Cr(CN)_6]^{3-}$, acetic acid was employed to chelate any free Cr^{2+} ions in solution, as well as to hinder the hydrolysis of the Zr_6 cluster.[27jm] The use of 1 M acetic acid as the reaction medium allowed the isolation of $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]\cdot2H_2O$ $\cdot CH_3CO_2H$ (**4**) as a green powder, which infrared spectroscopy and X-ray powder diffraction showed to be free of any $Cr_3[Cr(CN)_6]_2\cdot xH_2O$ impurity. The slightly elevated chromium content of the sample found by elemental analysis is consistent, however, with the presence of a small amount of $Cr(O_2CCH_3)_3$ impurity, the most likely impurity given the reaction conditions. Unfortunately, analogous reactions did not lead to incorporation of the $[Zr_6BeCl_{12}]^{2+}$ cluster core in a Prussian blue framework because of its rapid decomposition under the synthesis conditions.

As is frequently the case for Prussian blue analogues, sizable crystals of **3** and **4** were not readily obtained. The X-ray powder diffraction patterns for the compounds, however, index to face-centered cubic lattices with unit cell parameters of $a = 16.182(3)$ and $16.06(1)$ Å, respectively. These unit cells are consistent with a Prussian blue lattice that has been expanded by 5−6 Å, approximately the amount anticipated from inspection of the structure of **1**. Unfortunately, in each case the diffraction peaks were only well-resolved out to $2\theta \approx 50°$, and attempts to prepare more crystalline solids by heating the reactions only resulted in the decomposition of the products. Rietveld refinement of the structure was only possible against the data for compound **3** (Figure 3) because the peaks in the data from compound **4** were too broad. The positions of the framework atoms in **3** were refined using soft constraints for the bond distances. Although it was not possible to locate the extraframework species using difference Fourier maps, a reasonable fit was obtained by placing a Et_4N^+ cation at the center of each octant of the unit cell. The positions of the remaining chloride counteranions and water molecules could not be specifically resolved.

The resulting framework structure of **3** is presented in Figure 2, and it consists of the usual Prussian blue arrangement, albeit with $[Zr_6BCl_{12}]^{2+}$ cluster cores situated at alternating metal ion positions. Note that the interatomic

(37) Sieklucka, B. *Prog. React. Kinet.* **1989**, *15*, 175.
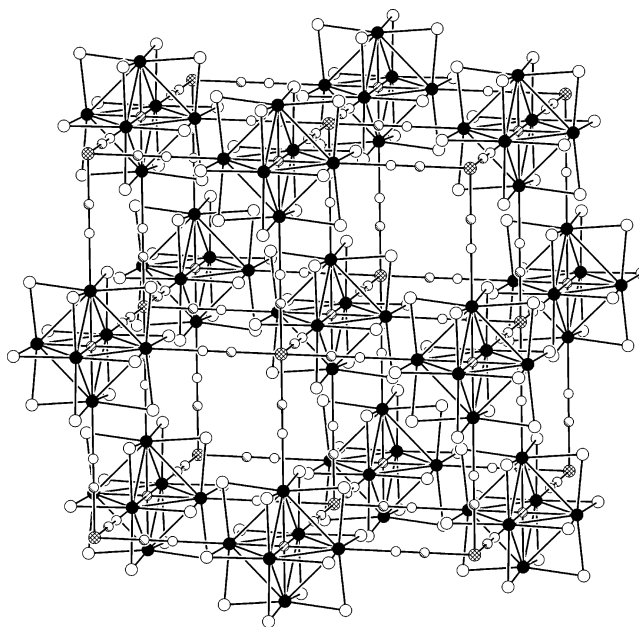
Figure 2. Unit cell for the structures of $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot 3H_2O$ (**3**) and $(Et_4N)_2[Zr_6BCl_{12}][Cr(CN)_6]Cl\cdot2H_2O\cdot CH_3COOH$ (**4**). Black, crosshatched, large white, small white, shaded, and hatched spheres represent Zr, Cr, Cl, N, C, and B atoms, respectively; Et_4N^+ cations, Cl^- anions, and solvent molecules are omitted for clarity. Atomic positions are those obtained from the structural refinement of compound **3**. Selected interatomic distances (Å): Zr−Zr, 3.330(4); Zr−B, 2.355(3); Zr−Cl, 2.552(4); Zr−N, 2.488(7); Cr−C, 2.096(6); C−N, 1.152(3).
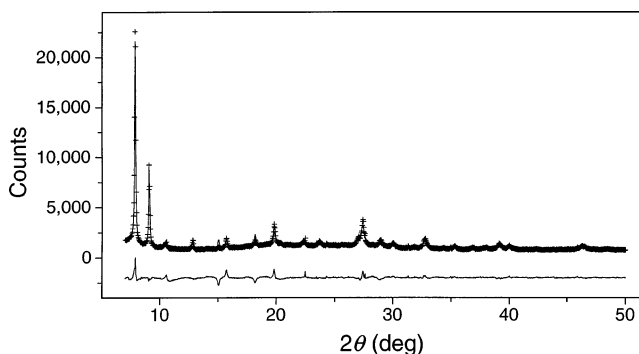

Figure 3. Portion of the powder X-ray diffraction data for compound **3** (crosses) along with the final fit from the crystallographic analysis (upper solid line). The lower line plots the difference between observed and simulated patterns. Note the broad peak at ca. 10.6°, which results from a small amount of $Cr_3[Cr(CN)_6]_2\cdot xH_2O$ impurity.

distances obtained from the refined cluster core geometry are in reasonable agreement with those observed within $(H_3O)_4[Zr_6BCl_{18}]\cdot13H_2O$.[27m] In all, the structure is quite analogous to that of the expanded Prussian blue analogue $(Me_4N)_2Mn[Nb_6Cl_{12}(CN)_6]$, which exhibits a slightly smaller unit cell dimension of $a = 15.513(4)$ Å, consistent with its noncentered edge-bridged octahedral cluster units.[23a] The atoms in the expanded framework of **3** occupy only 51% of the structure, so that each unit cell contains 2078 Å³ of extraframework space, in which the Et_4N^+ cations, Cl^- anions, and water molecules reside.[38] The geometry of one of the pore openings through which this space might be accessed is shown in Figure 4. Obviously, the protruding Cl

(38) This volume is based on the estimated van der Waals radii of the framework atoms and was calculated from the crystal structures using a Monte Carlo integration procedure described previously.[3d]
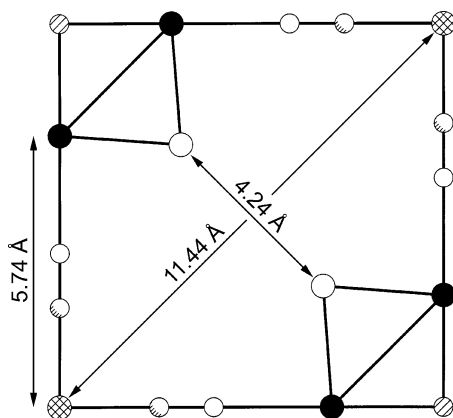
Figure 4. Geometry of the pore openings within the framework structure of **3**. Atom types are as designated in the legend of Figure 2. Accounting for the van der Waals radii leaves a gap of only ca. 0.8 Å between the two central Cl atoms.
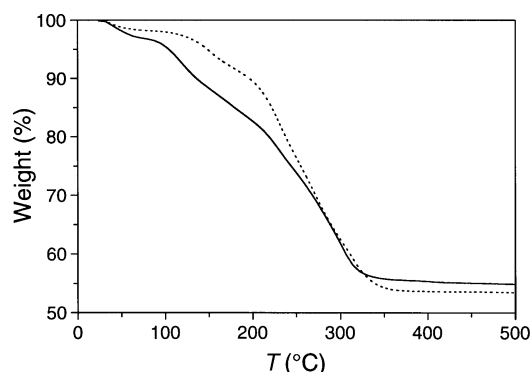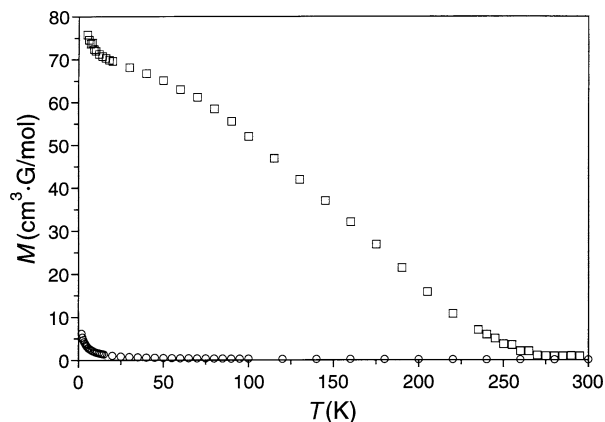

Figure 5. Thermogravimetric analyses for compounds **3** (solid line) and **4** (dotted line) with temperature increasing at a rate of 1 °C/min.

Figure 6. Temperature dependence of the magnetization of compounds **3** (□) and **4** (○) in applied fields of 50 and 10 G, respectively. Note that the rise in the magnetization data for compound **3** beginning at ca. 270 K is the result of magnetic ordering in the $Cr_3[Cr(CN)_6]_2 \cdot xH_2O$ impurity.

atoms of opposing clusters severely constrict the central portion of the openings. The result is essentially two smaller square openings with dimensions defined by the Zr···Cr span of 5.74 Å.

Thermogravimetric analyses were performed to probe the thermal stability of compounds **3** and **4** (Figure 5). The results for **3** indicate that the water molecules are released by 100 °C. In contrast, the data for **4** reveals loss of water by 100 °C and then acetic acid by 160 °C. Between 200 and 400 °C, the Et_4N^+ cations and cyanide ligands decompose, the latter presumably via evolution of cyanogen, as previously observed for Prussian blue[39] and $K_2Zn_3[Fe(CN)_6]_2 \cdot 8.5H_2O$.[40] When heated at 100 °C for 2 h, a sample of compound **4** retained its intense green color but lost crystallinity, as probed via X-ray powder diffraction. The heating of a sample to 150 °C induced a change in color to light tan.

As discussed above, the 13-electron $[Zr_6BCl_{12}]^{2+}$ cluster core should possess a spin orbital of appropriate π-type symmetry to enable magnetic superexchange though the cyanide bridges. Accordingly, magnetic susceptibility measurements were performed to ascertain whether these materials exhibit magnetic ordering. At room temperature, compound **4** displays an effective magnetic moment of 6.43 μ_B, in reasonable agreement with the presence of uncoupled S

$= \frac{1}{2}$ $[Zr_6BCl_{12}]^{2+}$ cluster cores and $S = \frac{3}{2}$ $[Cr(CN)_6]^{3-}$ complexes, after the 2.4 wt. % of $Cr(O_2CCH_3)_3$ ($S = \frac{3}{2}$) impurity was taken into account. A plot of magnetization versus temperature for compound **3** reveals a sudden increase at 270 K, which is the result of the onset of magnetic ordering in the $Cr_3[Cr(CN)_6]_2 \cdot xH_2O$[9e] impurity (Figure 6). In addition, below 10 K, the data display an upturn in the magnetization that may signal the activaton of the anticipated antiferromagnetic[41] exchange interactions within the cluster-expanded material. The data for compound **4** confirm the absence of any $Cr_3[Cr(CN)_6]_2 \cdot xH_2O$ impurity and exhibit the same upturn in the magnetization below 10 K. Thus, although the spin orbital of the Zr_6 cluster is of appropriate symmetry, it appears that the amount of spin density projected onto the bridging cyanide ligands is insufficient to instill magnetic ordering at temperatures above ca. 2 K. This is most likely a consequence of the combined effects of too little orbital overlap between the Zr and N atoms (at a separation of 2.488(7) Å) and delocalization of just one unpaired electron over the six zirconium atoms of the cluster.

Outlook

These results demonstrate the feasibility of incorporating edge-bridged octahedral $[Zr_6ZX_{12}]^{n+}$ cluster cores into highly expanded Prussian blue-type frameworks. Although the use of the $S = \frac{1}{2}$ $[Zr_6BCl_{12}]^{2+}$ core did not lead to solids exhibiting magnetic ordering at high temperatures, it may be possible to increase the ordering temperature by incorporating higher-spin clusters of this type, such as $[Zr_6BeX_{12}]^{2+}$ or even transition metal-centered species.[27] The degree of spin projection onto the bridging cyanide ligands could also likely be enhanced by somehow maintaining coordination of the carbon atoms at the zirconium centers if, for example, the oxidized species $[Zr_6ZCl_{12}(CN)_6]^{4-}$ (Z = B, Be) should prove to be inert. Other potential building units under consideration for such purposes are the as-yet hypothetical clusters $[B_6(CN)_6]^-$ and $[M_6S_8(CN)_6]^{n-}$ (M = Cr, Mn, Fe, Co).[42] Ultimately, it is hoped that cyano-bridged

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materials of this type may achieve the combined characteristics of sustainable porosity and high-temperature magnetic ordering.

Supporting Information Available: An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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