# [Cd₂(H₂O)₄][Re₆S₈(CN)₆]·14H₂O: A Cyano-Bridged Cluster−Cluster Framework Solid with Accessible Cubelike Cavities

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Recent work has led to the synthesis of water-soluble $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te) clusters with an outer ligand topology equivalent to that displayed in hexacyanometalate ions such as $[Fe(CN)_6]^{4-}$.[1,2] The face-capped octahedral core structure common to the clusters lends them an overall span which is nearly 4 Å longer than that of any of their mononuclear counterparts. With the expectation that these larger cluster components might lead to expanded cavities (and enhanced inclusion properties) in the ensuing framework solids, we have begun to explore aqueous solid assembly reactions paralleling those employed in the synthesis of Prussian blue and its analogues:[3]

$$\frac{4}{x}[M(H_2O)_6]^{x+} + [Re_6Q_8(CN)_6]^{4-} \rightarrow$$
$$M_{4/x}[Re_6Q_8(CN)_6]\cdot yH_2O \quad (1)$$
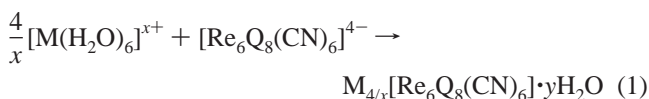
This strategy has succeeded in producing two phases that are direct structural analogues of known metal−cyanide compounds with zeolitic properties:[3] $Fe_4[Re_6Te_8(CN)_6]_3\cdot27H_2O$,[4] an expanded version of Prussian blue ($Fe_4[Fe(CN)_6]_3\cdot14H_2O$),[5] and $Na_2Zn_3[Re_6Se_8(CN)_6]_2\cdot11H_2O$,[6] an expansion of $Na_2Zn_3[Fe(CN)_6]_2\cdot9H_2O$.[7] Other variations of reaction 1 have yielded a range of unexpected new structure types, including phases marked by large spherical cavities, neutral or anionic two-dimensional sheets, and one-dimensional channels.[2,6,8] The results gathered thus far indicate that both the relative concentrations of reactants and the nature of the countercations present in solution can be used to influence the structure of the product. Herein, we report the synthesis of the porous solid $[Cd_2(H_2O)_4][Re_6S_8(CN)_6]\cdot14H_2O$ (**1**), a compound in which the association of Cd^{2+} ions into water-bridged dimers leads to still further expansion of a Prussian blue type framework.

To probe the possible templating effects of monovalent cations on the formation of framework solids via reaction 1, several salts of the $[Re_6S_8(CN)_6]^{4-}$ cluster were prepared by metathesis reactions. Addition of $(Bu_4N)I$ to an aqueous solution of $NaCs_3$-$[Re_6S_8(CN)_6]^2$ induced precipitation of $(Bu_4N)_4[Re_6S_8(CN)_6]$ as a pale yellow solid in 72% yield.[9] Dissolution in acetonitrile followed by addition of $Na(BPh_4)$ then gave $Na_4[Re_6S_8(CN)_6]$ as an orange solid in 97% yield.[10]

In accord with reaction 1 (M = Cd, Q = S, $x = 2$), a solution of $CdSO_4\cdot2.67H_2O$ (0.27 g, 1.1 mmol) in 7 mL of water was added to a solution of $Na_4[Re_6S_8(CN)_6]$ (0.28 g, 0.17 mmol) in 6 mL of water to give an immediate orange precipitate. The solid was washed with water (3 × 25 mL aliquots), collected by centrifugation, and dried in air to afford 0.25 g (0.12 mmol, 84%) of compound **1** as an orange powder.[11] In carrying out this reaction, even severe deviations of the reactant concentrations away from the product stoichiometry were found to have no effect on the structure formed. Similarly, the product obtained was unaffected by changes in the pH of the reaction solution. It is clear, however, that the choice of an innocent countercation (as Na^+ is here) for the $[Re_6S_8(CN)_6]^{4-}$ cluster reactant is critical to the formation of compound **1**. The analogous reaction between Cd^{2+} and $NaCs_3[Re_6S_8(CN)_6]$ produces a two-dimensional phase, $Cs_2[trans-Cd(H_2O)_2][Re_6S_8(CN)_6]$,[2] wherein Cs^+ cations incorporate in the structure, presumably due to a stronger interaction with the soft cyanide ligands. Furthermore, when $(Bu_4N)_4[Re_6S_8$-$(CN)_6]$ is employed in the reaction, a new and as of yet unidentified product is obtained.

Crystals of **1**·3H₂O suitable for X-ray analysis were grown by carefully layering aqueous solutions of the reactants in a narrow-diameter tube; large orange-red block-shaped crystals formed after 1 day. A structure determination[12] revealed a three-dimensional framework of $[Re_6S_8]^{2+}$ and $[Cd_2(\mu-OH_2)_2]^{4+}$ cluster cores linked through bridging cyanide ligands. Each Cd^{2+} ion exhibits pseudo-octahedral coordination, with three nitrogen atoms from cyanide ligands and three water ligands bound in a *fac* arrangement (Figure 1). Two of these water ligands bridge to another Cd^{2+} ion, creating a rhombic $[Cd_2(\mu-OH_2)_2]^{4+}$ cluster unit. Although bridging water ligands are less commonly encountered than bridging hydroxo ligands, their presence in dinuclear cadmium species is well-established.[13] The bond lengths in the dicadmium unit as well as the infrared spectrum and elemental analysis of compound **1** are

(10) Absorption spectrum (H₂O): λ_{max} (ϵ_M) 222 (57 400), 249 (16 400), 285 (sh, 5790), 329 (4530), 358 (sh, 2540), 436 (294) nm. IR (KBr): ν_{CN} 2123 cm⁻¹. Anal. Calcd for $C_6N_6Na_4Re_6S_8$: C, 4.44; H, 0.00; N, 5.18. Found: C, 4.43; H, <0.2; N, 4.78.

(11) IR (KBr): ν_{CN} 2128 cm⁻¹. Anal. Calcd for $C_6H_{36}Cd_4N_6O_{18}Re_6S_8$: C, 3.47; H, 1.75; N 4.04; Na, 0.00. Found: C, 4.01; H, 1.73; N, 3.84; Na, <0.2. The identity and purity of this compound were confirmed by comparison of its X-ray powder diffraction (Siemens D5000, Cu Kα radiation) pattern to one simulated from the single-crystal results. Its water content was verified by thermogravimetric analysis.

(12) Crystal data: $C_6H_{42}Cd_4N_6O_{21}Re_6S_8$, $M = 2132.92$, orthorhombic *Pnnm*, $Z = 2$, $a = 13.268(3)$ Å, $b = 15.236(3)$ Å, $c = 10.963(2)$ Å, $V = 2216.2$-(8) Å³, $\mu = 17.714$ mm⁻¹. Data (2° < 2θ < 60°) were collected at 140 K using a Siemens R3m/V diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation and were corrected for Lorentz, polarization, and absorption effects. Using the SHELXTL 5.0 software package, the structure was solved by direct methods with the aid of successive difference Fourier maps and was refined against all data (3392 unique) to give final agreement factors R1 = 0.0478 and wR2 = 0.1175. Thermal parameters for lattice water oxygen atoms were refined isotropically; all other thermal parameters were refined anisotropically.

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(9) IR (KBr): ν_{CN} 2114 cm⁻¹. Anal. Calcd for $C_{70}H_{144}N_{10}Re_6S_8$: C, 33.63; H, 5.81; N, 5.60. Found: C, 33.42; H, 5.63; N, 5.45.
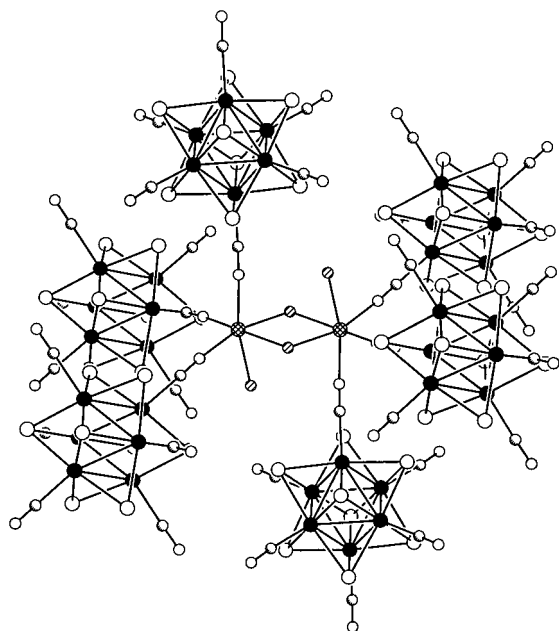
Figure 1. Local coordination environment of the dinuclear cadmium units in the structure of **1**·3H$_2$O. Solid, large open, shaded, small open, crosshatched, and hatched spheres represent Re, S, C, N, Cd, and O atoms, respectively. Selected mean interatomic distances (Å) and angles (deg): Re−Re 2.600(3), Re−S 2.404(3), Re−C 2.121(4), Cd−N 2.251(9), Cd−O(μ) (μ = bridging) 2.410(6), Cd−O(t) (t = terminal) 2.37(1), Cd···Cd 3.765, Re−C−N 177(3), Cd−N−C 177(2), N−Cd−N 101(3), N−Cd−O(μ) 89.05(7), N−Cd−O(t) 88.0(3), O(μ)−Cd−O(μ) 77.3(4), Cd−O(μ)−Cd 102.7(4), O(t)-Cd−O(μ) 81.9(2).

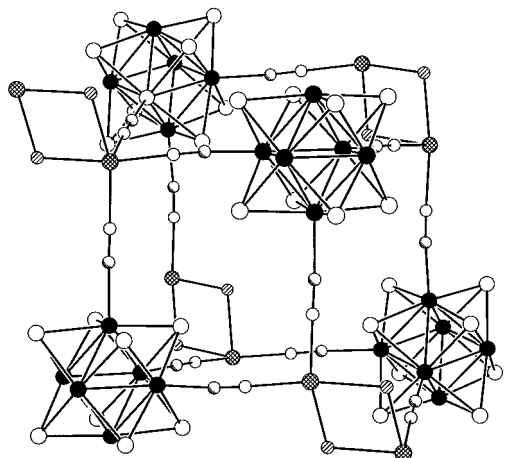**Figure 2.** Cage unit defining the cubelike cavities in the structure of **1**·3H$_2$O. Atom types are as designated in the caption of Figure 1. This unit corresponds to one octant of the face-centered cubic unit cell of Prussian blue. Crystallographic mirror planes lie along the diagonals of the smallest (front) and largest (rear) faces of the cage, bisecting both types of clusters.

all consistent with the assignment of bridging water ligands. Each Cd$_2$ cluster is bound to six neighboring Re$_6$ clusters in a distorted octahedral arrangement, as shown in Figure 1. In turn, each Re$_6$ cluster is linked to six Cd$_2$ clusters to give a fully occupied Prussian blue type lattice with the cluster cores positioned on alternate metal ion sites.

Incorporation of the larger cluster units results in an overall expansion of the Prussian blue structure, including its cavities, which are defined by the large cubelike cage unit depicted in Figure 2. On the basis of the estimated van der Waals radii of the framework atoms, the volume of each water-filled cavity is 345 Å^3.[14] These cavities, which represent 62% of the total volume in the structure, are accessible through three distinct types of openings. The smallest and largest openings consist of the front and rear faces of the cubelike cage (Figure 2), with square edge dimensions of approximately 7.3 and 9.6 Å, respectively. Exhibiting intermediate dimensions, the four remaining cage faces are all less regularly shaped and equivalent by symmetry. Significantly, the smallest and largest faces alternate in orientation between neighboring cages, such that the entire structure could be penetrated by molecules that are capable of passing through only the large- and medium-sized openings. A closely related network of pores with a considerably smaller 130 Å^3 volume[14] is present in [Mn$_2$(H$_2$O)$_4$][Ru(CN)$_6$]·5H$_2$O.[15] Indeed, compound **1** represents a direct expansion of this solid, with Cd^{2+} ions and [Re$_6$S$_8$]$^{2+}$ cores replacing the Mn^{2+} and Ru^{2+} ions in its structure, respectively.

The thermal properties of compound **1** were investigated to assess the importance of water in stabilizing its framework. Thermogravimetric analysis revealed complete dehydration of the solid by 150 °C, with no further significant weight loss below 400 °C. X-ray powder diffraction data show that **1** undergoes a structure change when dehydrated. However, subsequent exposure to water re-forms the original structure, suggesting that only minor perturbations occur in the arrangement of its framework components upon dehydration. The infrared spectrum confirms that no bridging water ligands are retained, but the exact nature of the interaction between Cd^{2+} ions is not known.

Experiments measuring the uptake of selected alcohols by this dehydrated form of compound **1** were carried out using a previously reported technique.[4,16] Samples of the dehydrated material, each weighing at least 30 mg, were exposed to a ca. 1% (w/w) solution of the alcohol in toluene for 10 min. Changes in alcohol concentration due to uptake by the solid were then measured by gas chromatography. The results[17] show that the material absorbs significant amounts of methanol and ethanol, some *n*- and *i*-propanol, but no higher alcohols or toluene. Thus, dehydrated compound **1** should be capable of sieving water, methanol, ethanol, and trace quantities of *n*- and *i*-propanol from mixtures with more sterically hindered solvents. As might be expected, the inclusion capacities for the expanded framework surpass those of dehydrated Prussian blue, which absorbs relatively small amounts of methanol and ethanol, but no *n*- or *i*-propanol.[4] It should be noted, however, that, due to the partial occupancy of the [Fe(CN)$_6$]$^{4-}$ sites in Prussian blue, the effectual difference between these two materials lies in the dimensions of their cage openings, rather than in the volumes of their cavities. Investigations further probing the inclusion properties of **1** and related solids are in progress.

Supporting Information Available: Thermogravimetric analysis and X-ray powder diffraction patterns (before and after dehydration) for **1**. X-ray structural information for **1**·3H$_2$O, including tables of crystal and collection data, positional and thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) This volume was determined using a Monte Carlo integration procedure described previously.[4]
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(17) Inclusion capacities for **1** listed as the number of guest molecules taken up per cubelike cavity (=per one-half formula unit): water, 9; methanol, 2.3(4); ethanol, 0.4(1); *n*-propanol, 0.08(1); *i*-propanol, 0.12(6); *n*-butanol, 0.02; *t*-butanol, 0.03; toluene (measured as a 1% w/w solution in mesitylene), 0.007. Numbers in parentheses represent standard deviations in the final digit. To make comparisons with the face-centered cubic unit cell of a Prussian blue analogue, these values should each be multiplied by 8.