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Expansion of the Porous Solid $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$: Enhanced Ion-Exchange Capacity in $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$

Miriam V. Bennett, Matthew P. Shores, Laurance G. Beauvais, and Jeffrey R. Long*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720-1460

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Abstract: A technique for increasing the porosity in solid structures by replacing octahedral metal ions with hexanuclear cluster cores is extended with the expansion of the ion-exchange material $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$. At high relative cluster concentrations, the reaction between $[Zn(H_2O)_6]^{2+}$ and $Na_4[Re_6Se_8(CN)_6]$ produces $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (**1**), a compound exhibiting a porous three-dimensional framework isotypic with that of $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$. Its framework is characterized by hexagonal bipyramidal cages, each enclosing two Na^+ ions and 24 water molecules in a volume of 1340 $Å^3$—more than triple the volume of the cages in the original structure. The expanded cavities and framework openings in compound **1** are shown to facilitate absorption of larger cationic complexes, specifically $[M(H_2O)_6]^{n+}$ ($M = Mg^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}$) and $[Cr(en)_3]^{3+}$, via exchange for the Na^+ ions. Indeed, when the preparation of **1** is attempted using a slight excess of the zinc reactant, $[Zn(H_2O)_6]^{2+}$ incorporates instead of Na^+, leading to direct formation of the ion-exchanged compound $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (**2**). The crystal structure of **2** reveals the $[Zn(H_2O)_6]^{2+}$ complexes to reside at the exact center of the hexagonal bipyramidal cages. With prolonged exposure to air, compound **1** and its ion-exchanged variants undergo a color change from orange to green, which is attributed to the one-electron oxidation of the $[Re_6Se_8]^{2+}$ cluster cores in the solid framework. In a further parallel with ferrocyanide chemistry, the reaction between $[Zn(H_2O)_6]^{2+}$ and $Na_4[Re_6Se_8(CN)_6]$ at low relative cluster concentrations is found to yield $[Zn(H_2O)]_2[Re_6Se_8CN)_6]{\cdot}13H_2O$ (**3**), a phase exhibiting a two-dimensional framework structure isotypic with that of $[Zn(H_2O)]_2[Fe(CN)_6]{\cdot}0.5H_2O$.

Introduction

Over the past decade, increasing attention has been devoted to investigating solution-based methods of solid synthesis, wherein simple ligand substitution reactions are used to generate extended framework structures.[1] Much of this research has been prompted by the prospect of using molecular design principles for tailoring functional solid materials—particularly porous materials exhibiting zeolite-type behavior. The strategy commonly adopted for introducing porosity involves expanding the framework of a known solid structure by enlarging one or more of its components. Unfortunately, such efforts are often thwarted by interpenetration and architectural frailty, difficulties that arise from the skeletal nature of the framework obtained when the enlargement is in only one or two dimensions.[2] It has been suggested that these difficulties might be reliably avoided by utilizing multinuclear clusters as replacement components that are isotropically enlarged in all three dimensions.[3] While there now exist numerous examples of porous solids with frameworks featuring cluster components that have been assembled in situ,[4−6] only a few such materials have been formed via ligand substitution reactions employing an intact cluster precursor.[3,7,8] The latter process, however, offers a clear advantage in its potential for controlling product structure. As a demonstrative example, we recently showed that the cubic structure of Prussian blue ($Fe_4[Fe(CN)_6]_3{\cdot}14H_2O$)[9] can be expanded by replacing the $[Fe(CN)_6]^{4-}$ reactants in its aqueous assembly reaction with

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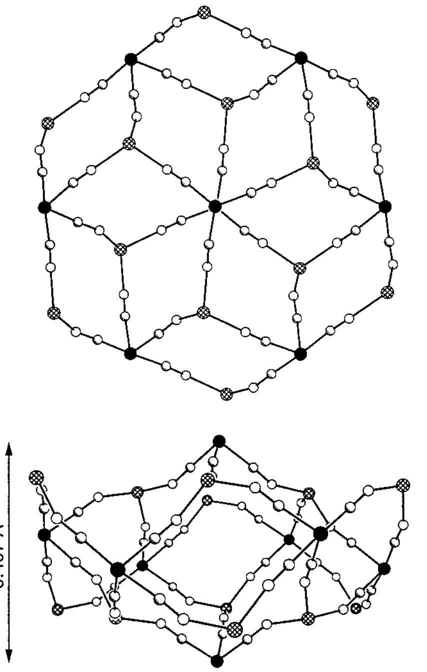

Figure 1. Top and side views of a hexagonal bipyramidal cage unit in the structure of $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$.[10] Black, shaded, white, and crosshatched spheres represent Fe, C, N, and Zn, respectively. The cage is situated on a $\bar{3}$ symmetry site. Selected mean interatomic distances (Å) and angles (deg): Fe−C 1.881(3), C−N 1.16(1), Zn−N 1.9685(7), Fe−C−N 178.8(7), Zn−N−C 159.7(6), and N−Zn−N 110(4).

face-capped octahedral $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) clusters.[3b] The ensuing cluster-expanded materials $Fe_4[Re_6Te_8(CN)_6]_3{\cdot}27H_2O$ and $Ga_4[Re_6Se_8(CN)_6]_3{\cdot}38H_2O$ were found to be at least as thermally robust as Prussian blue, and to exhibit enhanced inclusion properties commensurate with their increased pore size.[3b] Herein, we extend this approach by applying it in the expansion of a second important metal−cyanide structure: the anionic framework of the porous ion-exchange solid $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$.[10]

This compound belongs to a family of isostructural phases with formulas $A_2Zn_3[Fe(CN)_6]_2{\cdot}xH_2O$ (A = H, Na, K, Cs), and is readily prepared from aqueous solution as follows.[10,11]

$$3[Zn(H_2O)_6]^{2+} + 2Na_4[Fe(CN)_6] \rightarrow Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O + 6Na^+ \quad (1)$$

Its structure consists of octahedral $[Fe(CN)_6]^{4-}$ units linked through tetrahedral Zn^{2+} ions to form a three-dimensional framework characterized by large hexagonal bipyramidal cages (see Figure 1) encapsulating the Na^+ ions and water molecules.[10] The solid can be dehydrated without loss of crystallinity, and the potassium-containing analogue has been shown to display type I adsorption isotherms typical of microporous zeolites.[12] Due to the tetrahedral Zn^{2+} ion coordination, the cavities defined by the $\{Zn_3[Fe(CN)_6]_2\}^{2-}$ framework are significantly more accessible than those present in Prussian blue. Alkali metal cations can easily move through the structure, and consequently, these compounds have been widely studied for their ion-exchange properties.[11b,13] In particular, much research has focused on their ability to selectively absorb radioactive Cs^+ cations from nuclear waste and other contaminated solutions.[14,15]

Experimental Section

Preparation of Compounds. $Na_4[Re_6Se_8(CN)_6]$ was prepared as described previously,[3b,16] as was $[Cr(en)_3](SCN)_3$.[17] $Na_3[Re_6Se_8(CN)_6]$ was prepared by oxidizing the $[Re_6Se_8(CN)_6]^{4-}$ cluster with iodine in methanol. Water was distilled and deionized with a Milli-Q filtering system. All other reagents were used as purchased. Product identity and purity were verified by comparison of the observed X-ray powder diffraction pattern with a calculated pattern generated from the single-crystal results. The solvent content of each compound was determined by thermogravimetric analysis. Once prepared, all products were stored under dinitrogen to prevent oxidation.

$Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (1). Single crystals of this compound were obtained directly by layering reactant solutions in a narrow diameter tube; however, the material was best isolated in pure form as follows. A solution of $[Zn(H_2O)_6](ClO_4)_2$ (0.067 g, 0.25 mmol) in 5 mL of 3.5 M aqueous $NaClO_4$ was added to a solution of $Na_4[Re_6Se_8(CN)_6]$ (2.0 g, 1.0 mmol) in 10 mL of 3.5 M aqueous $NaClO_4$. After the solution was left standing for 30 min, the resulting orange precipitate was collected by centrifugation, washed with methanol, and quickly dried in air to give 0.23 g (63%) of $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}12H_2O{\cdot}4MeOH$. IR (KBr): ν_{CN} 2149 cm^{-1}. Anal. Calcd for $C_{16}H_{40}N_{12}Na_2O_{12}Re_{12}Se_{16}Zn_3$: C, 4.37; H, 0.92; N, 3.82; Na, 1.05; Zn, 4.46. Found: C, 4.37; H, 1.04; N, 3.95; Na, 0.92; Zn, 4.33.

$[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (2). Single crystals of this compound were obtained by layering a 0.075 M aqueous solution of $[Zn(H_2O)_6](ClO_4)_2$ over a 0.015 M aqueous solution of $Na_4[Re_6Se_8(CN)_6]$ in a narrow diameter tube. However, the material was best prepared in pure form as follows. A solution of $[Zn(H_2O)_6](ClO_4)_2$ (0.060 g, 0.22 mmol) in 2 mL of methanol was added to a solution of $Na_4[Re_6Se_8(CN)_6]$ (0.060 g, 0.030 mmol) in 2 mL of methanol. After the solution was left standing for 12 h, the resulting orange precipitate was collected by centrifugation, washed with methanol, and quickly dried in air to give 0.046 g (68%) of $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}14H_2O{\cdot}2MeOH$. IR (KBr): ν_{CN} 2150 cm^{-1}. Anal. Calcd for $C_{14}H_{48}N_{12}O_{22}Re_{12}Se_{16}Zn_4$: C, 3.74; H, 1.08; N, 3.74; Na, 0.00; Zn, 5.82. Found: C, 3.71; H, 1.12; N, 3.75; Na, <0.06; Zn, 5.94.

$[Zn(H_2O)]_2[Re_6Se_8(CN)_6]{\cdot}13H_2O$ (3). A solution of $[Zn(H_2O)_6](ClO_4)_2$ (0.10 g, 0.37 mmol) in 10 mL of water was added to a solution of $Na_4[Re_6Se_8(CN)_6]$ (0.10 g, 0.050 mmol) in 10 mL of water. After the solution was left standing for 12 h, large orange-red crystals of product had formed. The crystals were collected by centrifugation, separated from a small amount of orange powder impurity (compound **2**) by sonication, washed with water, and dried in air to give 0.076 g (68%) of $[Zn(H_2O)]_2[Re_6Se_8(CN)_6]{\cdot}8H_2O$. IR (KBr): ν_{CN} 2144 cm^{-1}. Anal. Calcd for $C_6H_{20}N_6O_{10}Re_6Se_8Zn_2$: C, 3.25; H, 0.91; N, 3.79. Found: C, 3.29; H, 0.75; N, 3.65.

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Table 1. Crystallographic Data[a] and Structure Refinement Parameters for $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (**1**), $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (**2**), and $[Zn(H_2O)]_2[Re_6Se_8(CN)_6]{\cdot}13H_2O$ (**3**)

	1	**2**	**3**
formula	$C_{12}H_{48}N_{12}Na_2$-$O_{24}Re_{12}Se_{16}Zn_3$	$C_{12}H_{48}N_{12}O_{24}$-$Re_{12}Se_{16}Zn_4$	$C_6H_{34}N_6O_{15}$-$Re_6Se_8Zn_2$
formula wt	4484.47	4503.86	2310.01
T, K	154	142	159
space group	$R\bar{3}c$	$R\bar{3}c$	$C2/m$
Z	6	6	2
a, Å	17.087(1)	17.192(1)	18.9899(2)
b, Å			10.8806(3)
c, Å	49.643(6)	49.369(5)	8.5788(3)
β, deg			108.218(2)
V, Å^3	12552(2)	12636(2)	1683.71(8)
μ, mm^{-1}	25.142	25.241	31.584
d_{calc}, g/cm^3	3.560	3.551	4.556
R_1, $wR2$,[b]%	4.46, 8.11	2.78, 6.87	3.99, 8.91

[a] Obtained with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[w(|F_o|^2)]\}^{1/2}$.

X-ray Structure Determinations. Single crystals were coated in Paratone-N oil, attached to quartz fibers, transferred to a Siemens SMART diffractometer, and cooled in a dinitrogen stream. Lattice parameters were initially determined from a least-squares refinement of more than 40 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 empirical absorption correction was applied to each data set using SADABS. Space group assignments were based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods, with the aid of difference Fourier maps, and were refined with successive full-matrix least-squares cycles. The sodium ions in the structure of **1** and the solvate water molecules in both **1** and **2** are disordered over multiple positions, and were modeled with partial occupancies accordingly. In these structures, disordered atoms were refined with isotropic thermal parameters, and all other atoms were refined anisotropically. The oxygen atoms of solvate and bound water molecules are fully ordered in the structure of **3** and were refined isotropically; all other atoms were refined anisotropically. Hydrogen atoms were not included in any of the refinements. Crystallographic parameters are listed in Table 1.

Ion-Exchange Experiments. A solution of the perchlorate or nitrate salt of the hydrated metal ion or of $[Cr(en)_3](SCN)_3$ in 10 mL of methanol was stirred over a precisely weighed quantity (ca. 100 mg) of solid **1** for 10 h. The solution and subsequent methanol washes (3 × 20 mL) were separated from the exchanged solid by centrifugation and combined. The integrity of the crystal structure of the exchanged solid was checked by X-ray powder diffraction. The separated solutions were reduced to dryness, and the resulting residue was dissolved in 25.00 mL of an aqueous solution that was 0.55 M in ammonium hydroxide and 0.33 M in ammonium chloride. An Orion model 97-12 Na^+ ion-selective electrode was then used to determine the Na^+ ion concentration of this solution by comparison with calibration curves obtained from standards having concentrations in a similar range. For each paramagnetic metal ion, the effective magnetic moment of the exchanged solid was measured at 295 K using a Quantum Design SQUID magnetometer, and was found to be within 1% of the expected moment (as calculated using previously reported data for the metal complex).[18]

Other Physical Measurements. X-ray powder diffraction data were collected using Cu Kα ($\lambda = 1.5406$ Å) radiation on a Siemens D5000 diffractometer. Thermogravimetric analyses were performed under a dinitrogen atmosphere at a ramp rate of 1 °C/min, using a TA Instruments TGA 2950. Infrared spectra were recorded on a Mattson Infinity System FTIR spectrometer. Cyclic voltammetry was performed using a Bioanalytical systems CV-50W voltammagraph, 0.1 M KNO_3 supporting electrolyte, and a glassy carbon working electrode. Potentials were determined vs a Ag/AgCl reference electrode. Diffuse reflectance spectra of solids were acquired relative to $BaSO_4$ on a Perkin-Elmer Lambda 9 spectrophotometer equipped with a 60 mm integrating sphere. Absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer.

Results and Discussion

The synthesis of $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (**1**), a cluster-expanded analogue of $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$, is accomplished by employing $Na_4[Re_6Se_8(CN)_6]$[3b,16,19] in place of $Na_4[Fe(CN)_6]$ in reaction 1.

$$3[Zn(H_2O)_6]^{2+} + 2Na_4[Re_6Se_8(CN)_6] \rightarrow Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O + 6Na^+ \quad (2)$$

However, to avoid impurities, the reaction is best carried out in the presence of a large excess of both the cluster reactant and Na^+ ions. Similar conditions have been recognized as helpful in obtaining the ferrocyanide-based materials in pure form.[11bc] Reactions analogous to reaction 2 have now been used to synthesize a variety of open framework solids, most of these with unprecedented structure types.[3,7b,8] Interestingly, the reactions are highly sensitive to the choice of transition metal ion, cluster chalcogen element (Q = S, Se, or Te), and cluster countercation, as well as to the relative reactant concentrations. As will be shown here, this last factor is of particular importance for reaction 2, leading to formation of no less than three different phases.

Single crystals of compound **1** were grown by layering the reactant solutions in a narrow diameter tube. X-ray analysis revealed a structure in which the framework is perfectly isotypic with that of $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$[10] (Figure 1), adopting the same $R\bar{3}c$ space group, and differing only in the substitution of $[Re_6Se_8]^{2+}$ cluster cores onto the Fe^{2+} ion sites. This substitution results in the expansion of the hexagonal bipyramidal cages of the framework (see Figure 2), which each now contain two Na^+ cations and 24 water molecules. As calculated[3b] based on the estimated van der Waals radii of the framework atoms, the volume enclosed by these cages has increased from 421 Å^3 (57% of the total volume) to 1340 Å^3 (64%) upon expansion. The largest openings through which the cavities in **1** can be accessed consist of pseudohexagonal $(Re_6Se_8)_3(CN)_6Zn_3$ rings situated over alternate "faces" of the hexagonal bipyramidal cages. By incorporating tetrahedral Zn^{2+} ions in this fashion, a significantly more open structure is achieved than observed for the frameworks of matching composition and charge in the phases $Cs_2[M(H_2O)]_3[Re_6Se_8(CN)_6]_2{\cdot}xH_2O$ (M = Mn, Fe, Co, Ni, Cd),[3a,7b] where the M^{2+} ions adopt an octahedral coordination geometry. Thermogravimetric analysis and X-ray powder diffraction data indicate that, similar to $K_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$,[12] **1** can be completely desolvated, and retains its crystal structure with extended heating at temperatures up to 250 °C.

The expanded cavities and framework openings in the structure of **1** suggest its potential utility in absorbing large cationic complexes via exchange for the Na^+ ions. In fact, when its preparation is attempted using a slight excess of the zinc

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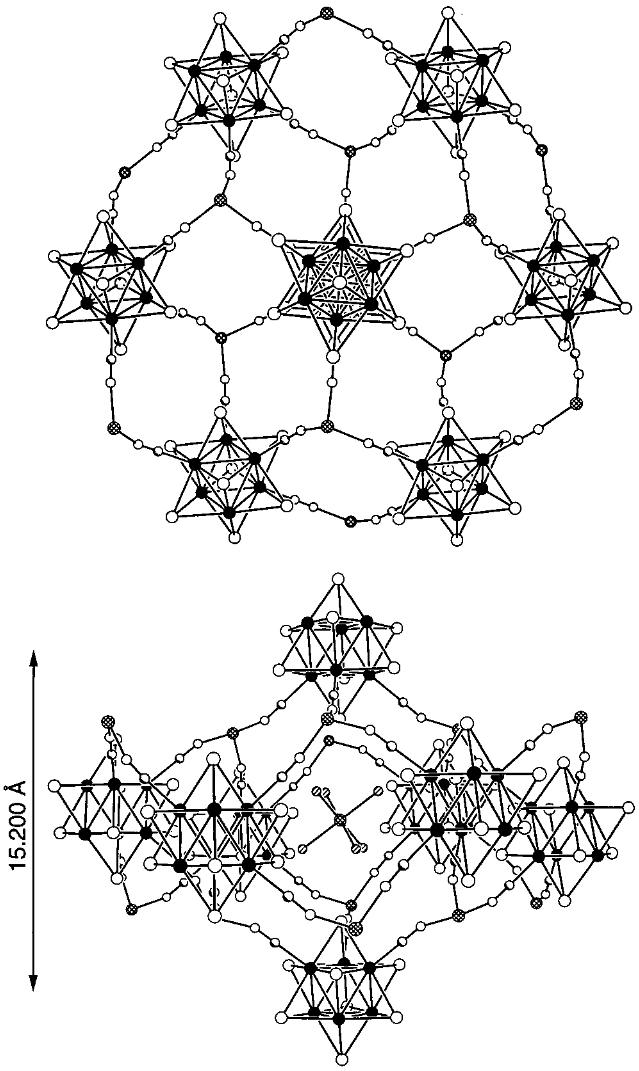

Figure 2. Top and side views of a hexagonal bipyramidal cage unit (with vertices located at the center of each cluster) in the structure of $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (**2**). Black, large white, shaded, small white, crosshatched, and hatched spheres represent Re, Se, C, N, Zn, and O atoms, respectively. The cage is centered by a $[Zn(H_2O)_6]^{2+}$ complex situated on a $\bar{3}$ symmetry site. The framework in $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (**1**) is essentially identical, except that its cages each encapsulate two hydrated Na^+ ions rather than a $[Zn(H_2O)_6]^{2+}$ complex. Comparison with Figure 1 shows how this framework is related to that of $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$ simply by replacing the Fe^{2+} ions with $[Re_6Se_8]^{2+}$ cluster cores. Mean interatomic distances and angles are listed in Table 2.

Table 2. Selected Mean Interatomic Distances (Å) and Angles (deg) from the Structures of $Na_2Zn_3[Re_6Se_8(CN)_6]_2{\cdot}24H_2O$ (**1**), $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (**2**), and $[Zn(H_2O)]_2[Re_6Se_8(CN)_6]{\cdot}13H_2O$ (**3**)

	1	**2**	**3**
Re−Re	2.627(2)	2.634(1)	2.638(6)
Re−Se	2.517(8)	2.525(8)	2.522(9)
Re−C	2.095(7)	2.089(7)	2.109(1)
C−N	1.16(2)	1.167(5)	1.14(1)
Zn−N	1.946(5)	1.962(3)	1.983(2)
Zn−O		2.126(1)	2.00
Se−Re−C	92(2)	92(2)	92(3)
Re−C−N	177.5(7)	177(2)	173.9(1)
Zn−N−C	161(1)	161(2)	165.2
N−Zn−N	110(6)	110(4)	115.7(8)
O−Zn−O		90(1)	
N−Zn−O			102(4)

Table 3. Exchange of $[M(H_2O)_6]^{n+}$ into Solid **1**

	Na^+ released[a]	% exchange	μ_{eff} (μ_B)[b]
Mg^{2+}	0.85	43	
Cr^{3+}	1.83	92	4.89[c]
Mn^{2+}	1.17	59	3.45
Ni^{2+}	1.50	75	2.46
Zn^{2+}	1.68	84	

[a] Number of equivalents per formula unit of **1**. [b] At 295 K. [c] Moment and electronic absorption spectrum (Figure 3) indicate oxidation of 45% of the cluster cores to $[Re_6Se_8]^{3+}$ ($S = {}^1/_2$).

reactant, $[Zn(H_2O)_6]^{2+}$ incorporates instead of the Na^+ ions, leading to crystallization of $[Zn(H_2O)_6]Zn_3[Re_6Se_8(CN)_6]_2{\cdot}18H_2O$ (**2**). This compound exhibits a framework isostructural with that of **1**, but featuring cationic zinc complexes at the center of its hexagonal bipyramidal cages (Figure 2), wherein each is surrounded by 18 solvate water molecules. Direct exchange experiments with preformed samples of solid **1** were conducted for a range of $[M(H_2O)_6]^{n+}$ species dissolved in methanol.[20] The extent of the exchange was assessed by measuring the amount of Na^+ released into solution using an ion-selective electrode. The results obtained are summarized in Table 3, and demonstrate the successful uptake of Mg^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, with no perturbation of the framework structure (as probed by powder X-ray diffraction). For paramagnetic ions, the extent of the exchange was also calculated from the measured effective magnetic moment of the product, and found to be within 1% of the potentiometrically determined value. This exchange behavior is reminiscent of the water-softening properties of zeolites; however, as with traditional zeolites, certain metal ions were found to modify the framework of the material. X-ray powder diffraction data indicate that exchanges attempted with Fe^{2+}, Co^{2+}, and Cu^{2+} all resulted in the loss of framework structure and formation of an amorphous phase. A satisfactory explanation for why these ions should destroy the framework structure is not immediately forthcoming, particularly in view of the range of stability and lability parameters characterizing those metal ion complexes that simply exchange with no loss of crystallinity. Clearly there is sufficient space for larger cationic complexes to fit within the cavities of the $\{Zn_3[Re_6Se_8(CN)_6]_2\}^{2-}$ framework, and indeed, analogous exchange experiments indicate that 75% of the Na^+ ions in compound **1** can be exchanged for $[Cr(en)_3]^{3+}$.[21] The possibility of building still larger complexes within the cavities by first exchanging in $[M(H_2O)_6]^{n+}$ and subsequently adding the free ligand is currently under investigation.

Compound **1** and its ion-exchanged variants all undergo a color change from orange to green upon prolonged exposure to air. This change is not observed when the samples are stored under dinitrogen, and we attribute it to the one-electron oxidation of the $[Re_6Se_8]^{2+}$ cluster cores in the solid framework by dioxygen. An analogous oxidation is apparent in the cyclic voltammagram of $Na_4[Re_6Se_8(CN)_6]$ in aqueous solution, which reveals a $[Re_6Se_8(CN)_6]^{3-/4-}$ couple centered at $E_{1/2} = 0.62$ V vs Ag/AgCl.[22] Furthermore, the diffuse reflectance spectra of the green solids exhibit bands matching those centered at 545

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(20) Exchanges were studied in methanol, because experiments in water were typically complicated by simultaneous formation of an impurity phase.

(21) The absorbed $[Cr(en)_3]^{3+}$ is also evident in the infrared spectrum of the exchanged solid, which exhibits no change in its framework structure (as again probed by X-ray powder diffraction).

(22) Note that this potential is slightly (~0.25 V) more positive than that observed in acetonitrile solution: Yoshimura, T.; Ishizaka, S.; Sasaki, Y.; Kim, H.-B.; Kitamura, N.; Naumov, N. G.; Sokolov, M. N.; Fedorov, V. E. *Chem. Lett.* **1999**, 1121.

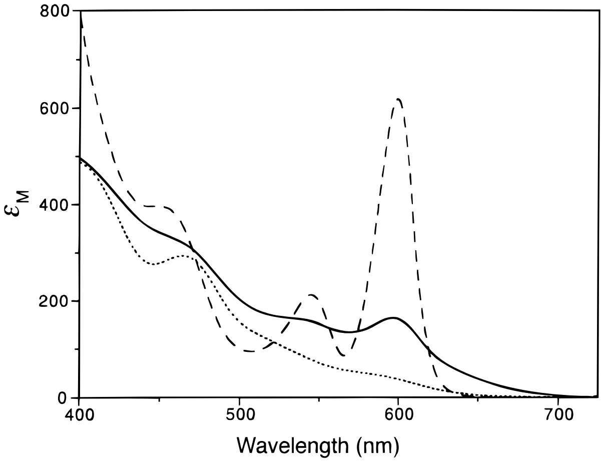

Figure 3. Electronic absorption spectra of the solid compound **1** before (dotted line) and after (solid line) exchange of $[Cr(H_2O)_6]^{3+}$, and of $Na_3[Re_6Se_8(CN)_6]$ in aqueous solution (dashed line). The units along the vertical axis correspond to the solution spectrum, and are arbitrary for the two solid spectra.

and 599 nm in the absorption spectrum of a green aqueous solution of $[Re_6Se_8(CN)_6]^{3-}$ (Figure 3). Typically, emergence of the green color in the solids is gradual, only becoming noticeable after approximately 1 day. However, the exchange of $[Cr(H_2O)_6]^{3+}$ into compound **1** induces a more rapid change, with the green color already apparent immediately following the (10 h) exchange reaction. At this stage, the exchanged product displays an electronic absorption spectrum substantially different from that of the original compound **1** (see Figure 3) and an effective magnetic moment indicating oxidation of 45% of the framework clusters. We propose that the increased rate is due to the greater acidity of $[Cr(H_2O)_6]^{3+}$ ($pK_a \approx 4$), which provides protons for the acid-promoted oxidation of the clusters by absorbed dioxygen. Consistent with our claim, exchange of $[Cr(en)_3]^{3+}$, a much less likely source of protons, results in a solid product that oxidizes only very slowly. Significantly, no loss of crystallinity is apparent in the X-ray powder diffraction patterns of these oxidized materials.

When reaction 1 is carried out using an excess of $[Zn(H_2O)_6]^{2+}$, the zinc-enriched compound $[Zn(H_2O)]_2[Fe(CN)_6]\cdot 0.5H_2O$[11bc,23] is obtained instead of $Na_2Zn_3[Fe(CN)_6]_2\cdot 9H_2O$. Similarly, as the molar ratio of $[Zn(H_2O)_6]^{2+}$:$Na_4[Re_6Se_8(CN)_6]$ employed in analogous reactions increases, the amount of compound **2** produced decreases, owing to the gradual emergence of a new phase identified as $[Zn(H_2O)]_2[Re_6Se_8(CN)_6]\cdot 13H_2O$ (**3**). The structure of **3** is characterized by two-dimensional sheets, each consisting of a triangular lattice of $[Re_6Se_8(CN)_6]^{4-}$ clusters connected through tetrahedral Zn^{2+} ions with an $(NC)_3(H_2O)$ coordination sphere (see Figure 4). This is, once again, a direct expansion of the framework in the iron-containing analogue,[23b] with $[Re_6Se_8]^{2+}$ cluster cores directly substituted onto the Fe^{2+} ion positions. More simply, the structure can be viewed as an expansion of the CdI_2 structure, with $[Re_6Se_8(CN)_6]^{4-}$ clusters and $[Zn(H_2O)]^{2+}$ moieties residing on the Cd^{2+} and I^- sites, respectively. Interestingly, compound **3** is converted to compound **2** with sustained exposure to methanol; an analogous transformation has been reported for the ferrocyanide-based solids.[24]

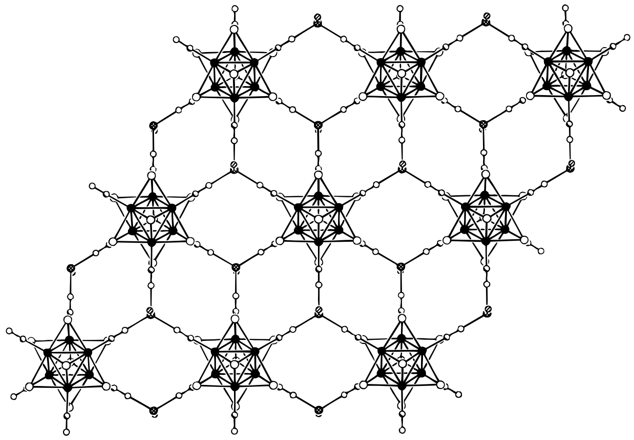

Figure 4. A portion of a two-dimensional sheet in the structure $[Zn(H_2O)]_2[Re_6Se_8(CN)_6]\cdot 13H_2O$ (**3**). Atom representations are the same as in Figure 2. Each cluster resides on a site of 2/*m* crystallographic symmetry, with the 2-fold rotational axes running horizontally within the plane of the drawing. Mean interatomic distances and angles are listed in Table 2.

In sum, the reaction chemistry between Zn^{2+} and $[Re_6Se_8(CN)_6]^{4-}$ has been found to closely parallel that between Zn^{2+} and $[Fe(CN)_6]$,$^{4-}$ permitting synthesis of $Na_2Zn_3[Re_6Se_8(CN)_6]_2\cdot 24H_2O$, an expanded form of $Na_2Zn_3[Fe(CN)_6]_2\cdot 9H_2O$ with an enhanced ion-exchange capacity. Future work will focus on assembling reactive cationic complexes in the cavities of this new material with the intention of rendering known homogeneous catalysts heterogeneous.

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Supporting Information Available: Tables of crystal data, structure solution and refinement parameters, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **1**, **2**, and **3** (PDF). 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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