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Cyano-Bridged Re_6Q_8 (Q = S, Se) Cluster-Metal Framework Solids: A New Class of Porous Materials

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The potential capability of designing porous materials for use as molecular sieves and catalysts has led to a recent surge in research involving the synthesis of extended solid frameworks from soluble molecular components.[1] Very often, an objective in such research is to develop techniques for producing frameworks with larger pore sizes. A simple yet relevant observation in this regard is that, for a given packing of solid spheres, as the diameter of the spheres increases, the percentage of void space remains constant; *however, the volume of each void increases*. Thus, one approach to enlarging the cavities defined by a framework is to isotropically expand the dimensions of some or all of its molecular precursors, while preserving their rigidity and directional bonding requirements. For example, a metal ion with a strong preference for a specific coordination geometry might be replaced by a multinuclear cluster core with a similar preference. To date, the use of clusters in constructing extended materials by standard solution routes has been limited to the production of porous three-dimensional frameworks from tetrahedral $[Ge_4S_{10}]^{4-}$ clusters,[2] and one- or two-dimensional frameworks from metal−metal bonded dinuclear clusters of the type $[M_2(O_2CR)_4]$.[3] We are now exploring the feasibility of constructing frameworks in which octahedrally ligated metal ions are replaced by larger M_6X_8 cluster cores with the face-capped octahedral geometry.[4] This approach has indeed led to the successful synthesis of direct cluster-expanded analogues of the porous metal−cyanide frameworks in both Prussian Blue and $Na_2Zn_3[Fe(CN)_6]_2{\cdot}5H_2O$.[5] Herein, however, we report the emergence of an unexpected wealth of new porous framework structure types accessible by direct reaction of $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) clusters with metal ions in solution.

Water-soluble salts of the $[Re_6Q_8(CN)_6]^{4-}$ clusters are conveniently prepared as $NaCs_3Re_6S_8(CN)_6$ (**1**) and $NaCs_3Re_6Se_8(CN)_6$ (**2**) by high-temperature exchange reactions of NaCN with $Cs_5Re_6S_8Br_7$ and $Cs_4Re_6Se_8I_6$,[6] respectively. An alternative preparation employing Re_6Te_{15} as a reactant has been described for $[Re_6Se_8(CN)_6]^{4-}$,[7] as well as for the related clusters $[Re_6Te_{8-n}Se_n(CN)_6]^{4-}$ (n = 0, 1, 4, 7)[7] and $[Re_6S_{8-x}Te_x(CN)_6]^{4-}$ (x = 0.60, 1.32).[8] Single-crystal X-ray analyses[9] of compounds **1** and **2** revealed the structure of the clusters (Figure 1) with the expected $[Re_6Q_8]^{2+}$ core geometry[6] consisting of a central Re_6 octahedron with μ_3-Q atoms capping each face. A cyanide ligand projects from each Re apex in an approximately linear fashion; as the chalcogen atom varies from S to Se to Te,[7] the mean Re−C−N bond angle increases from 172.7(8)° to 175(2)° to 178.8(1)°, respectively. This somewhat subtle trend parallels both a lengthening of the Re−Re bonds and a decrease in the C≡N stretching frequency, likely indicating a corresponding increase in the degree of interaction between the Re 5d orbitals and the π^* orbitals of the cyanide. The span of the $[Re_6Q_8(CN)_6]^{4-}$ clusters, as measured by the mean distance between N atoms of trans cyanide ligands, is 10.20(2) and 10.237(1) Å for Q = S and Se, respectively. This represents an expansion by more than 4 Å over the octahedral $[Fe(CN)_6]^{4-}$ complex [mean *trans*-N···N, 6.17(9) Å; mean Fe−C−N, 177(2)°] in $K_4Fe(CN)_6$.[10] And, like their smaller hexacyanometalate predecessors,[11] the clusters react with metal ions in solution to generate extended framework materials.

Reaction of $[Re_6S_8(CN)_6]^{4-}$ with Fe^{2+} in aqueous solution yields, after several days, the two-dimensional phase $Cs_2[\textit{trans}\text{-}Fe(H_2O)_2][Re_6S_8(CN)_6]$ (**3**). Its structure[9] contains $\{[\textit{trans}\text{-}Fe(H_2O)_2][Re_6S_8(CN)_6]\}^{2-}$ sheets

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(9) Crystallographic analyses. **1**: $C_6Cs_3N_6NaRe_6S_8$, T = 120 K, orthorhombic, $Pmna$, a = 11.2390(4) Å, b = 8.9229(3) Å, c = 13.0650(5) Å, V = 1310.22(8) Å^3, Z = 2, D_{calc} = 4.947 g/cm^3, R_1 = 0.0262, wR_2 = 0.0456. **2**: $C_6Cs_3N_6NaRe_6Se_8$, T = 165 K, orthorhombic, $Pmn2_1$, a = 11.3414(2) Å, b = 8.8725(1) Å, c = 13.6372(2) Å, V = 1372.26(4) Å^3, Z = 2, D_{calc} = 5.631 g/cm^3, R_1 = 0.0337, wR_2 = 0.0700. **3**: $C_6H_4Cs_2FeN_6O_2Re_6S_8$, T = 146 K, orthorhombic, $Imma$, a = 18.5451(8), b = 10.6492(5), c = 13.2036(5) Å, V = 2607.6(2) Å^3, Z = 4, D_{calc} = 4.808 g/cm^3, R_1 = 0.0486, wR_2 = 0.1082. **4**: $C_6H_{18}N_6O_9Re_6S_8Zn_2$, T = 160 K, orthorhombic, $Pbcn$, a = 10.9529(5), b = 16.6531(8), c = 32.989(2) Å, V = 6017.1(5) Å^3, Z = 8, D_{calc} = 4.024 g/cm^3, R_1 = 0.0564, wR_2 = 0.1211. **5**: $C_{12}H_{36}Cs_2Fe_3N_{12}O_{18}Re_{12}Se_{16}$, T = 159 K, trigonal, $R\bar{3}c$, a = 26.9542(4) Å, c = 33.3838(7) Å, V = 21004.8(6) Å^3, Z = 12, D_{calc} = 4.333 g/cm^3, R_1 = 0.0601, wR_2 = 0.0785. Data ($2 < 2\theta < 52°$) were collected on a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation and were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods, with the aid of successive difference Fourier maps, and were refined against all data using SHELXTL 5.0.

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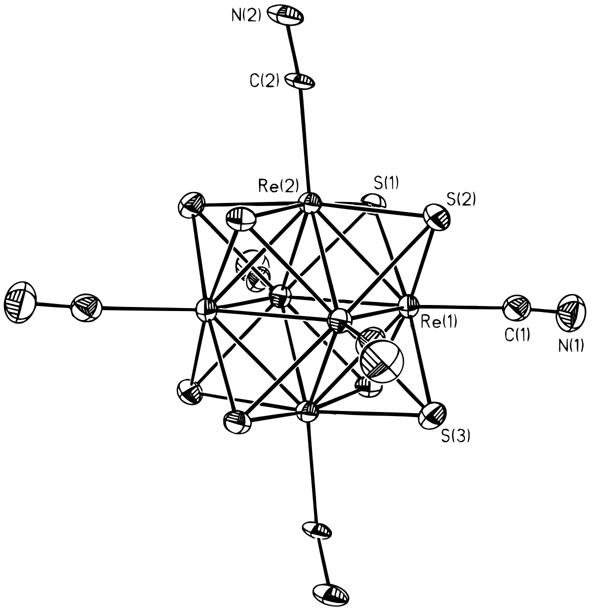

Figure 1. Structure of the $[Re_6S_8(CN)_6]^{4-}$ cluster in **1**, showing 70% probability ellipsoids. The cluster resides on a $2/m$ symmetry site with atoms Re(2), S(2), and S(3) in the mirror plane. Selected mean interatomic distances (Å) and angles (deg): Re−Re, 2.602(4); Re−S, 2.413(9); Re−C, 2.122(9); C−N, 1.16; S−Re−C, 93(4); Re−C−N, 172.7(8). Analogous mean interatomic distances (Å) and angles (deg) for the $[Re_6Se_8(CN)_6]^{4-}$ cluster in **2**: Re−Re, 2.634(4); Re−Se, 2.52(1); Re−C, 2.10(2); C−N, 1.173(5); Se−Re−C, 92(4); Re−C−N, 175(2).

(Figure 2) consisting of a square lattice of alternating cluster cores and iron atoms linked by cyanide bridges. Hence, each iron atom is bound by the N terminus of four cyanide ligands, with two trans water molecules completing its octahedral coordination sphere. Likewise, each cluster unit is connected through only four of its cyanide ligands, leaving two trans cyanide ligands uncoordinated. This square net, however, is ruffled along its diagonal (the a axis), creating a wave with an amplitude of 1.65 Å and period of $a = 18.5451(8)$ Å. The pairwise tilting of the clusters in the wave serves to encase half of the Cs^+ ions in intervening channels. The remaining Cs^+ ions are centered in half of the holes (those with the larger openings in Figure 2) in the two-dimensional net. The isostructural phases Cs_2[*trans*-$M(H_2O)_2][Re_6S_8(CN)_6]$ (M = Mn, Zn, Cd) are formed in analogous aqueous reactions.[12a]

Incorporating Cs^+ ions into the structure may, in at least one case, be prevented by maintaining a relatively high transition metal ion concentration throughout the reaction. Thus, reaction of $[Re_6S_8(CN)_6]^{4-}$ with a *saturated* aqueous solution of Zn^{2+} yields, upon heating, the Zn-rich three-dimensional phase $[Zn(H_2O)]_2[Re_6S_8(CN)_6]\cdot 7H_2O$ (**4**). The structure[9] adopted by this compound features two interpenetrating neutral frameworks (Figure 3) wherein Re−CN−Zn bridges link each cluster core to six Zn neighbors, and each Zn center is tetrahedrally coordinated by three cyanide ligands and one water molecule. The frameworks are perhaps best viewed as being built up from one-dimensional columns consisting of a double row of octahedral $[Re_6S_8(CN)_6]^{4-}$ clusters, each connected to four equivalent clusters through *two* Zn^{2+} ions (i.e., through rhombic $(Re_6S_8)_2(CN)_4Zn_2$ interactions).[13] The columns (four of which are depicted in Figure 3) are cross-linked, each to four neighboring columns, via Re−CN−Zn−NC−Re linkages to give a three-dimensional framework with wide elliptical tunnel-like openings. These openings are then occupied by columns from an identical interpenetrating framework. The columns themselves exhibit a series of alternating cuboidal $[Re_6S_8(CN)_3]_3Zn_4$ pockets filled with guest water molecules which overflow to line the interfaces between frameworks. The molar nonframework volume, V_M^{nf}, of this structure was calculated using a Monte Carlo method to be 205 $cm^3\ mol^{-1}$ (45.3%) on the basis of the estimated van der Waals radii of the framework atoms.[14]

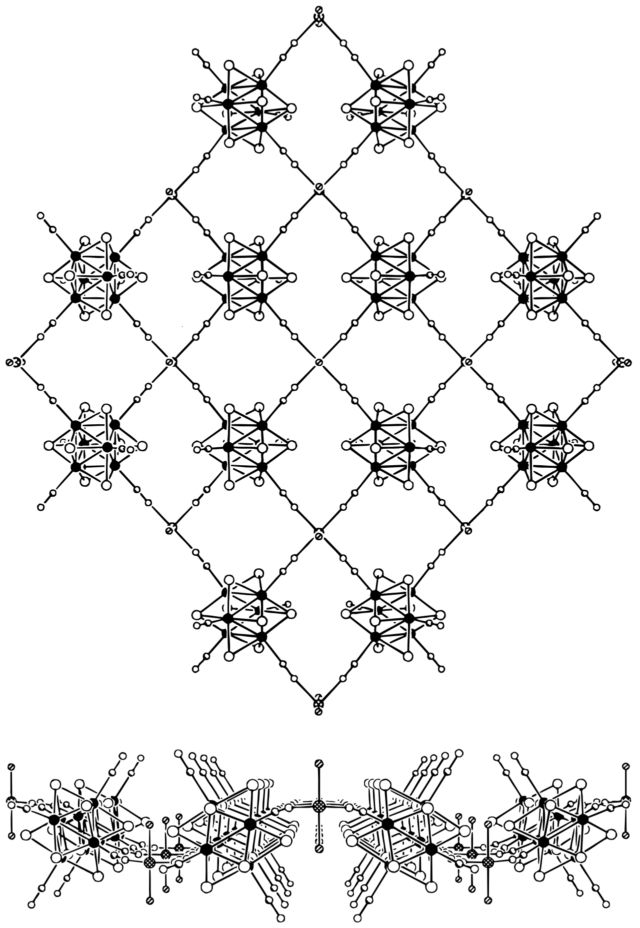

Figure 2. A portion of a two-dimensional sheet in **3** viewed down the perpendicular c (upper) and b (lower) crystal axes. Large black, white, and crosshatched spheres represent Re, S, and Fe atoms, respectively, while smaller highlighted, white, and diagonally shaded spheres represent C, N, and O atoms, respectively. Selected mean interatomic distances (Å) and angles (deg): Re−Re, 2.606(4); Re−S, 2.41(1); Re−C, 2.14(4); C−N, 1.14(1); Fe−N, 2.19; Fe−O, 2.12; S−Re−C, 93(2); Re−C−N, 177(5); Fe−N−C, 170; N−Fe−N, 90(4); N−Fe−O, 90(3).

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[12] (12) Unit cell parameters were refined using X-ray powder diffraction data. (a) M = Mn, $a = 18.661(2)$ Å, $b = 10.760(1)$ Å, $c = 13.309(2)$ Å; M = Zn, $a = 18.481(2)$ Å, $b = 10.657(1)$ Å, $c = 13.270(2)$ Å; M = Cd, $a = 18.821(3)$ Å, $b = 10.830(2)$ Å, $c = 13.347(3)$ Å. (b) M = Mn, $a = 27.106(3)$ Å, $c = 33.683(8)$ Å; M = Co, $a = 26.896(2)$ Å, $c = 33.468(5)$ Å; M = Ni, $a = 26.694(2)$ Å, $c = 33.250(5)$ Å; M = Cd, $a = 27.277(2)$ Å, $c = 33.948(4)$ Å.

[13] (13) These columns are equivalent to a double chain excised from a CdI_2 sheet with $[Re_6S_8(CN)_6]^{4-}$ clusters on the Cd sites and $[Zn(H_2O)]^{2+}$ on the I sites.

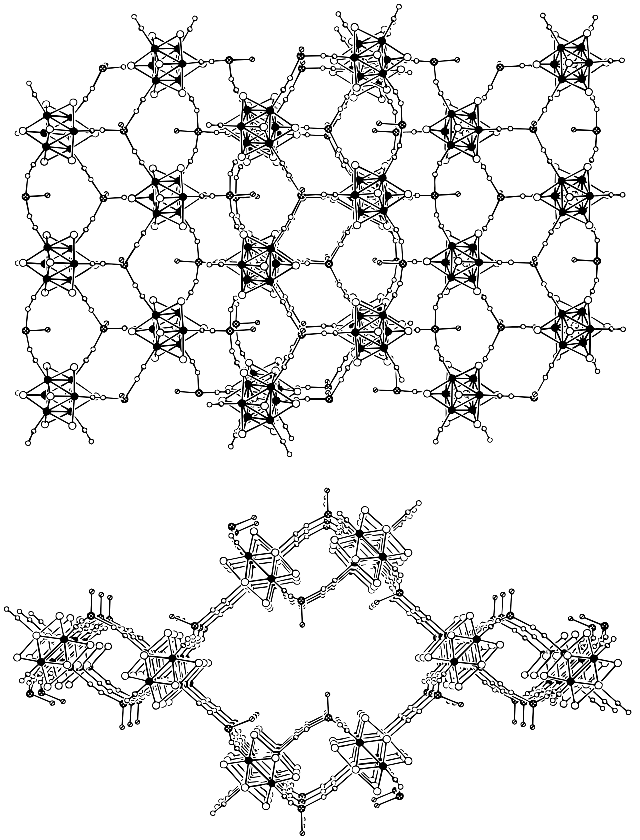

Figure 3. A portion of one of the two equivalent interpenetrating frameworks in the structure of **4** viewed down the perpendicular *b* (upper) and *a* (lower) crystal axes. Atom representations are the same as in Figure 2, except for the crosshatched spheres, which here represent Zn atoms. Selected mean interatomic distances (Å) and angles (deg): Re−Re, 2.606(3); Re−S, 2.410(7); Re−C, 2.13(1); C−N, 1.14(2); Zn−N, 1.96(2); Zn−O, 1.98(1); S−Re−C, 93(3); Re−C−N, 175(2); Zn−N−C, 170(7); N−Zn−N, 112(5); N−Zn−O, 106(9).

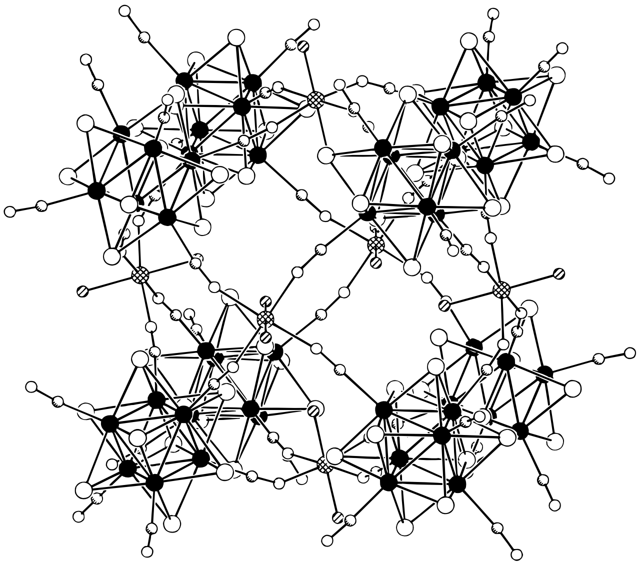

Figure 4. An octacluster cage in the structure of **5**. Atom representations are the same as in Figure 2, except for the large white spheres, which here represent Se atoms. A crystallographically imposed 3-fold rotation axis runs along the body diagonal of the cube, penetrating the lower left back and upper right front clusters. Note the resemblance of the overall cage structure to the face-capped octahedral geometry of the individual cluster cores. Selected mean interatomic distances (Å) and angles (deg): Re−Re, 2.628(6); Re−Se, 2.522(5); Re−C, 2.095(6); C−N, 1.158(5); Fe−N, 2.13(1); Fe−O, 2.14; Se−Re−C, 92(2); Re−C−N, 175.3(5); Fe−N−C, 157(11); N−Fe−N, 90.1(8); N−Fe−O, 90(3).

Reaction of $[\mathrm{Re_6Se_8(CN)_6}]^{4-}$ with Fe^{2+} in aqueous solution generates the three-dimensional phase $\mathrm{Cs_2}$[*trans*-$\mathrm{Fe(H_2O)_2]_3[Re_6Se_8(CN)_6]_2 \cdot 12H_2O}$ (**5**). While retaining the octahedral *trans*-$\mathrm{Fe(NC)_4(H_2O)_2}$ coordination mode, the connectivity of this phase differs from that of **3** in that all six of the cluster cyanide ligands are coordinated by iron atoms. Its porous structure[9,15] is characterized by cubic $\mathrm{[Re_6Se_8(CN)_3]_8Fe_6}$ cages (Figure 4) with a cluster at each corner and cyanide-bound Fe atoms capping each face. Alternatively, the cage may be described as a rhombic dodecahedron with $\mathrm{Re_6Se_8}$ cluster cores centered at eight of the vertexes (in the form of a cube) and Fe atoms situated at the remaining six vertexes, with Re−CN−Fe bridges spanning the edges. Each cage encloses a volume of approximately 720 Å^3, containing at least 15 water molecules (six of which are bound to Fe atoms) and accessible through rhombic $\mathrm{(Re_6Se_8)_2(CN)_4Fe_2}$ openings. The nearly spherical cages are packed in a body-centered cubic arrangement, wherein each makes contact (through a shared $[\mathrm{Re_6Se_8}]^{2+}$ cluster core) with a cube of eight surrounding cages. The space between cages comprises a three-dimensional network of tunnels in which the Cs^+ ions and additional water molecules reside. Compound **5** was calculated to have $V_{\mathrm{M}}^{\mathrm{nf}} = 566$ cm^3 mol^{-1} (53.7%).[14] The isostructural phases $\mathrm{Cs_2}$[*trans*-$\mathrm{M(H_2O)_2]_3[Re_6Se_8(CN)_6]_2 \cdot }x\mathrm{H_2O}$ (M = Mn, Co, Ni, Cd) are formed in analogous aqueous reactions.[12b]

It remains to be established whether the new class of porous materials exemplified here by compounds **4** and **5** will display a range of molecular sieve, ion exchange, and catalytic properties comparable to (or perhaps more extensive than) those observed in noncluster metal−cyanide framework solids.[11b,16] An important initial consideration for such applications is the robustness of the framework. Thermogravimetric analyses of compounds **3**, **4**, and **5** indicate their complete dehydration at 110, 190, and 80 °C, respectively, with no significant loss of framework mass below 500 °C. X-ray powder diffraction experiments demonstrate retention of crystallinity in compound **3** below 400 °C, whereas compounds **4** and **5** are both observed to undergo transformations to a new crystalline structure at ca. 200 °C. Certainly, the ability to distribute a variety of transition metals as potentially accessible reaction sites in open framework solids merits further attention with respect to the possible design of new heterogeneous catalysts. Future work will focus on probing the inclusion chemistry of these and related materials.

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(14) For comparison, the calculated $V_{\mathrm{M}}^{\mathrm{nf}}$ values for α-$\mathrm{SiO_2}$, zeolite A ($\mathrm{Na_{12}[Al_{12}Si_{12}O_{48}]}$), and zeolite ZSM-5 ($\mathrm{H_2[Al_2Si_{94}O_{192}]\cdot 24H_2O}$) are 2.0 cm^3 mol^{-1} (8.9%), 641 cm^3 mol^{-1} (57.7%), and 1420 cm^3 mol^{-1} (43.9%), respectively.

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Experimental Section. Crystals suitable for single-crystal X-ray analysis[9] were either selected directly from the reaction products or were grown separately by layering solutions of the reactants in a narrow diameter tube. Product identity and purity were confirmed by comparison of the observed X-ray powder diffraction (Siemens D5000, Cu Kα radiation) pattern with a calculated pattern generated from the single-crystal results. Analyses (EMA) were performed with a Cameca SX-51 electron microprobe employing five wavelength-dispersive spectrometers.

$\mathrm{NaCs_3Re_6S_8(CN)_6}$ (1). A mixture of NaCN (0.39 g, 8.0 mmol) and $\mathrm{Cs_5Re_6S_8Br_7}$[6] (2.6 g, 1.0 mmol) was intimately ground in a pure dinitrogen atmosphere, and sealed in a fused silica ampule under vacuum. The sample was heated at 635 °C for 25 h and cooled at 1 °C/min to ambient temperature. The resulting orange solid was stirred in 100 mL of methanol for 10 min, collected by filtration, and washed with successive aliquots of methanol (3 × 10 mL) and ethanol (5 × 10 mL). The solid was twice recrystallized from water and dried to yield 1.7 g (87%) of orange-red crystalline product. IR (KBr): ν_{CN} 2105, 2129 cm^{-1}.

$\mathrm{NaCs_3Re_6Se_8(CN)_6}$ (2). This compound was prepared from $\mathrm{Cs_4Re_6Se_8I_6}$[6] (2.1 g, 0.69 mmol) by a procedure analogous to that described for the preparation of **1**. The product was obtained as 1.3 g (81%) of red crystalline solid. IR (KBr): ν_{CN} 2092, 2116 cm^{-1}.

$\mathrm{Cs_2}$[*trans*-$\mathrm{Fe(H_2O)_2}$][$\mathrm{Re_6S_8(CN)_6}$] (3). A 20 mL aqueous solution of $\mathrm{(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O}$ (0.40 g, 1.0 mmol) was added to a 20 mL aqueous solution of **1** (0.14 g, 0.072 mmol). After 4 days, orange platelike crystals had formed. The supernatant solution was decanted and the crystals were washed with successive aliquots of water (3 × 25 mL) and dried in air to give 0.12 g (88%) of product. IR (KBr): ν_{CN} 2136 (broad) cm^{-1}.

$\mathrm{[Zn(H_2O)]_2[Re_6S_8(CN)_6]\cdot 7H_2O}$ (4). A saturated 20 mL aqueous solution of $\mathrm{Zn(SO_4)\cdot 7H_2O}$ was combined with a 20 mL aqueous solution of **1** (0.12 g, 0.061 mmol), and the mixture was boiled to dryness. The resulting solid was washed with successive aliquots of water (3 × 50 mL) to give 0.067 g (60%) of product as small orange hexagonal plate crystals. IR (KBr) ν_{CN} 2162 cm^{-1}. EMA: $\mathrm{Zn_{1.8(2)}Re_6S_{8.5(3)}}$

$\mathrm{Cs_2}$[*trans*-$\mathrm{Fe(H_2O)_2]_3[Re_6Se_8(CN)_6]_2\cdot 12H_2O}$ (5). This compound was prepared from **2** (0.18 g, 0.077 mmol) by a procedure analogous to that described for the preparation of **3**. The product was obtained as 0.15 g (85%) of large red cubic crystals. IR (KBr): ν_{CN} 2124 (broad) cm^{-1}. EMA: $\mathrm{Cs_{1.9(2)}Fe_{3.15(7)}Re_{12}Se_{16.2(2)}}$

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Supporting Information Available: Tables of X-ray crystallographic data for 1−5 (35 pages); observed and calculated structure factors for 1−5 (34 pages). Ordering information is given on any masthead page.

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