

A Solid-State Route to Molecular Clusters: Access to the Solution Chemistry of $[\text{Re}_6\text{Q}_8]^{2+}$ (Q = S, Se) Core-Containing Clusters via Dimensional Reduction

Jeffrey R. Long, Logan S. McCarty, and R. H. Holm*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Abstract: A general method for accessing the solution chemistry of cluster constituents of solid phases exhibiting extended cluster frameworks is demonstrated. The approach is described in terms of simple metal–anion (M–X) frameworks and involves the formal incorporation of AX into a parent structure, resulting in termination of the X bridges between M centers while balancing the charge of the resulting framework with external cations A. The new structures obtained display frameworks of reduced connectedness and dimensionality. By replacing single metal centers with multinuclear cluster cores, this dimensional reduction approach is extended to cluster-containing frameworks. Its utility is demonstrated via application to the phases $\text{Re}_6\text{Q}_8\text{Cl}_2$ (Q = S, Se), exhibiting three- and two-dimensional arrays of face-capped octahedral $[\text{Re}_6(\mu_3\text{-Q})_8]^{2+}$ cluster cores covalently linked through extremely tight Re_2Q_2 rhombic interactions of the type common to many intractable cluster frameworks (including the Chevrel phases). Stoichiometric solid-state reactions incorporating TlCl supplement the cores with additional terminal ligands, producing less connected frameworks: two-dimensional $[\text{Re}_6\text{Se}_8\text{Cl}_3]^{1-}$ sheets, one-dimensional $[\text{Re}_6\text{Q}_8\text{Cl}_4]^{2-}$ chains, and ultimately, isolated $[\text{Re}_6\text{Q}_8\text{Cl}_6]^{4-}$ clusters. The connectivities for such $[\text{M}_6\text{Q}_8]$ frameworks are enumerated; of the 28 possibilities, three previously unknown frameworks are achieved in the structures of $\text{TlRe}_6\text{Se}_8\text{Cl}_3$, $\text{CsRe}_6\text{Se}_8\text{I}_3$, and $\text{Cs}_2\text{Re}_6\text{Se}_8\text{Br}_4$, described herein. Alternatively, employing cesium halide as a dimensional reduction agent directly provides the unprecedented molecular clusters in water-soluble form as the phases $\text{Cs}_5\text{Re}_6\text{S}_8\text{X}_7$ (X = Cl, Br), $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$, and $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$. The species $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ (X = Cl, Br, I) are precipitated from aqueous base upon addition of $(\text{Bu}_4\text{N})\text{X}$ to give the soluble molecular products $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$, $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Br}_6]\cdot\text{H}_2\text{O}$, and $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{I}_6]\cdot\text{H}_2\text{O}$. Treatment of yellow acetonitrile solutions of these compounds with anhydrous acid induces an immediate color change to red owing to the formation of the protonated clusters $[\text{Re}_6\text{S}_7(\text{SH})\text{X}_6]^{3-}$. Reversible uptake of a single proton is confirmed by the single-crystal X-ray structure determinations of $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Cl}_6]$, $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6]\cdot 2\text{Me}_2\text{CO}$, and $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{I}_6]\cdot 2\text{Me}_2\text{CO}$, as well as spectrophotometric titrations and elemental analyses. The $\text{p}K_a$ of $[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6]^{3-}$ in acetonitrile is estimated at 20. An analogous workup of red $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$ affords $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]\cdot 2\text{Me}_2\text{CO}$.

Introduction

Large classes of transition metal clusters are produced either exclusively or most reliably by means of high-temperature solid-state reactions.^{1,2} Typically, these clusters occur within the confines of an extended covalent framework, requiring that a certain extent of intercluster bond cleavage precede their (potential) liberation from parent solids as discrete molecular units. Over the years, the pursuit of soluble cluster species has resulted in development of an arsenal of low-temperature techniques for excising clusters from such environs.² The methods employed generally involve a heterogeneous reaction between the cluster-containing solid and a solution of some appropriate bridge-displacing ligand; however, success is largely contingent upon the accessibility of the clusters within the solid framework. As an instructive example, consider the series of n -dimensional phases $\text{Re}_6\text{Se}_{4+n}\text{Cl}_{10-2n}$ ($n = 1-3$). The two-dimensional structure of $\text{Re}_6\text{Se}_6\text{Cl}_6$ (Figure 1) consists of face-

capped octahedral $[\text{Re}_6\text{Se}_6\text{Cl}_2]^{4+}$ cores with four Re apices linked to neighboring cores via chloride bridges and the remaining two *trans* Re apices terminated by chloride ligands.³ When $\text{Re}_6\text{Se}_6\text{Cl}_6$ is stirred in a refluxing acetonitrile solution of $(\text{R}_4\text{N})\text{Cl}$ (R = Et, Pr), the Cl^- ions displace the bridges between cores, breaking up the extended sheetlike framework to afford a soluble molecular cluster, $[\text{Re}_6\text{Se}_6\text{Cl}_3]^{2-}$.⁴ One-dimensional $\text{Re}_6\text{Se}_5\text{Cl}_8$, exhibiting a structure composed of $[\text{Re}_6\text{Se}_5\text{Cl}_3]^{5+}$ cores linked through just two *trans* chloride bridges (the remaining four apices are capped by terminal chloride ligands),^{3,5} reacts under similar conditions to yield $[\text{Re}_6\text{Se}_5\text{Cl}_9]^{1-}$.⁴ Conversely, the three-dimensional phase $\text{Re}_6\text{Se}_7\text{Cl}_4$, wherein the $[\text{Re}_6\text{Se}_7\text{Cl}]^{3+}$ cores are each linked to six neighbors through chloride bridges,^{3,5} has proven inert to a variety of excision techniques; presumably its tightly-packed three-dimensional framework renders the structure impervious to attack by bridge-displacing ligands.⁴

Conspicuously absent in the foregoing discussion is the phase $\text{Re}_6\text{Se}_8\text{Cl}_2$, formulated by extending the series from $\text{Re}_6\text{Se}_7\text{Cl}_4$ with one further substitution of an Se^{2-} for two Cl^- atoms. Its structure (Figure 2) consists of $[\text{Re}_6\text{Se}_8]^{2+}$ cores, each with two

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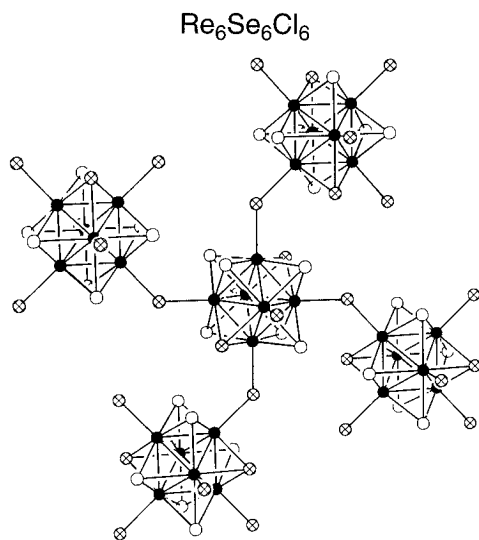


Figure 1. Local cluster environment in the $\text{Re}_6\text{Se}_6\text{Cl}_6$ ($=[\text{Re}_6\text{Se}_6^{\text{I}}\text{Cl}_6^{\text{I}}]\text{Cl}_2^{\text{II}}\text{Cl}_2^{\text{III}}$) structure; its sheetlike cluster framework extends within the plane of the page. Black, white, and cross-hatched spheres represent Re, Se, and Cl atoms, respectively. Core Se and Cl atoms are statistically disordered; the positions shown have been arbitrarily designated. Selected mean interatomic distances (Å) and angles (deg) are as follows: Re–Re 2.614(3), Re–Qⁱ (Q = Se, Cl) 2.506(9), bridging Re–Cl 2.465(7), terminal Re–Cl 2.360, intercore Re–Cl–Re 132.7.³

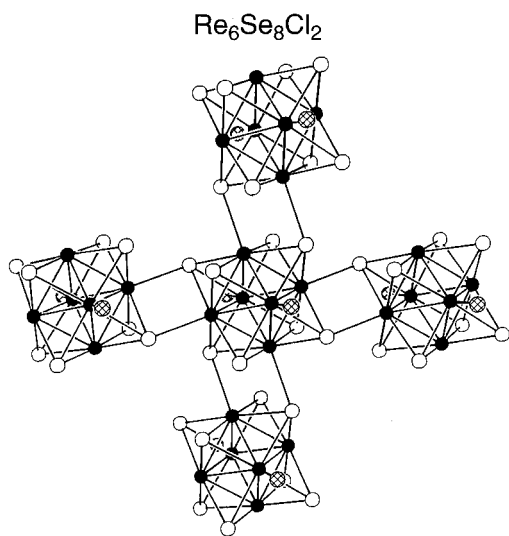


Figure 2. Local cluster environment in the structure of $\text{Re}_6\text{Se}_8\text{Cl}_2$ ($=[\text{Re}_6\text{Se}_4^{\text{I}}\text{Se}_2^{\text{II}}\text{Cl}_2^{\text{III}}]\text{Se}_4^{\text{IV}}$); the cluster framework extends within the plane of the page. Selected mean interatomic distances (Å) and angles (deg) are as follows: Re–Re 2.64(2), non-rhomb Re–Se 2.52(1), Re–Cl 2.38(1), Re–Re–Re 60.0(5); within Re_2Se_2 rhombs Re–Se 2.62(1), $\text{Re}\cdots\text{Re}$ 3.43(2).⁶

attendant terminal chlorides at *trans* Re apices, directly linked in two dimensions via rhombic Re_2Se_2 interactions.⁶ These rigid, compact core–core linkages bestow $\text{Re}_6\text{Se}_8\text{Cl}_2$ with a tightly-bound framework that is completely intractable, despite its two-dimensional nature. As a result of the described differences in framework dimensionality and connectivity, low-temperature excision methods have provided access to the solution chemistry of molecular species containing $[\text{Re}_6\text{Se}_5\text{Cl}_3]^{5+}$ and $[\text{Re}_6\text{Se}_6\text{Cl}_2]^{4+}$ cores,⁴ but an analogous chemistry has failed to develop around the $[\text{Re}_6\text{Se}_7\text{Cl}]^{3+}$ and $[\text{Re}_6\text{Se}_8]^{2+}$ cluster cores.⁷ Similarly, the mixed sulfur–chlorine cores

$[\text{Re}_6\text{S}_{4+n}\text{Cl}_{4-n}]^{(6-n)+}$ ($n = 1-3$) have been achieved in soluble molecular form,⁸ while $[\text{Re}_6\text{S}_8]^{2+}$ has not. The pure *binary* cores $[\text{Re}_6\text{Q}_8]^{2+}$ (Q = S, Se) thus present an attractive but unrealized target for study in solution, particularly in view of the complex substitution chemistry associated with the chlorides in the mixed core species.^{4,8,9} Such cores are encountered in the phases $\text{Re}_6\text{Q}_8\text{X}_2$ (X = Cl, Br),^{6,10} as well as other framework solids, none of which offer a soluble molecular cluster: $\text{Li}_4\text{Re}_6\text{S}_{11}$, $\text{M}^{\text{I}}_4\text{Re}_6\text{Q}_{12}$ ($\text{M}^{\text{I}} = \text{K}, \text{Ti}$), $\text{Cs}_4\text{Re}_6\text{Q}_{13}$, $\text{M}^{\text{I}}_{10}\text{Re}_6\text{S}_{14}$ ($\text{M}^{\text{I}} = \text{Rb}, \text{Cs}$), $\text{Re}_6\text{Se}_8\text{Te}_7$, and $\text{Cs}_4\text{Re}_6\text{S}_{16}$, *inter alia*.¹¹

Rhombic intercore linkages of the type observed in $\text{Re}_6\text{Se}_8\text{Cl}_2$ occur in most of the currently intractable cluster frameworks² (many containing clusters with no molecular analogues), including the Chevrel phases wherein they link $[\text{Mo}_{3n}\text{Q}_{3n+2}]^{z-}$ ($n = 2-6, 8, 10$; Q = S, Se) cores into three-dimensional frameworks.¹² In order to gain access to this realm of cluster chemistry which lies beyond the scope of low-temperature excision techniques or solution synthesis, our recent efforts have focused on the development of a general high-temperature method, termed *dimensional reduction*, for deconstructing solid frameworks.¹³ Herein, the concept of dimensional reduction is elaborated and exemplified as an effective means of producing soluble $[\text{Re}_6\text{Q}_8]^{2+}$ core-containing clusters; initial investigations into the solution properties of these species are also reported.

Dimensional Reduction

We begin with a development of the concept of dimensional reduction which is more general and detailed than our prior brief introduction to the subject.¹³ Thereafter, experimental applications of the concept to certain rhenium–chalcogenide–halide phases are described.

(a) Metal–Anion Frameworks. The general premise underlying the approach is exemplified in Figure 3, which illustrates the stepwise deconstruction of a rudimentary three-dimensional metal–anion framework. The initial structure consists of octahedral metal centers, M, covalently linked in three dimensions by bridging anions, X. Successive incorporation of additional equivalents of X reduces the connectivity of

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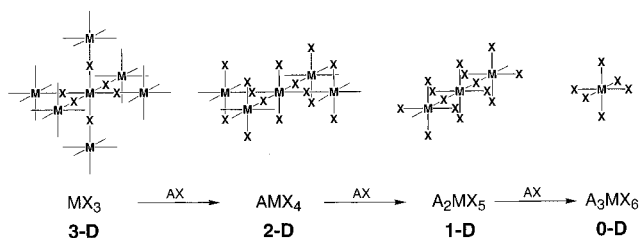


Figure 3. Dimensional reduction of MX_3 (M = metal, X = bridging anion). By incorporating additional X atoms, the bridges between metals are terminated. Each equivalent added reduces the dimension of the structure by one, and is accompanied by a charge-compensating cation, A . These cations (not shown) reside in the voids between the resulting sheets, chains, and molecules.

the framework by terminating intermetal bridges, producing structures containing sheets, chains, and, finally, discrete molecular units. To preserve the electronic configuration (and subsequently the ligand geometry) of its metal centers, each X added to the structure is accompanied by a charge-compensating cation, A .¹⁴ These cations reside external to the negatively-charged $M-X$ framework (*i.e.*, between anionic sheets, chains, or isolated molecules), and are not depicted in Figure 3. With each equivalent of AX incorporated in the MX_3 structure, the overall dimensionality of the ensuing framework is reduced by one—hence the term dimensional reduction. The scheme presented in Figure 3 is not necessarily intended to imply a specific reaction pathway (although it may do so in certain cases), but rather to embody a formalism with which lower-dimensional compounds are readily extrapolated from existing structures.

It is important to emphasize that this formalism does not predict explicit structures. Instead, it utilizes a mode of framework connectivity based upon that of a parent structure, MX_x , to predict the connectedness of a new phase, A_nMX_{x+n} . The *connectedness* of a framework shall be defined as the mean degree of connectivity of its metal centers (*i.e.*, the mean number of neighboring metals directly connected to a metal center through $M-X-M$ linkages). Consider the MX_3 framework at the far left in Figure 3, in which each MX_6 octahedron shares all six of its corners with neighboring MX_6 octahedra. This structure is efficiently described by the polyhedra connectivity partitioning nomenclature recently introduced.^{15,16} The appropriate descriptor is $O_1(1_6)^{-3}MX_3$, where the subscript 6 indicates its connectedness. The framework should be viewed as the parent solid whence all possible dimensionally reduced products are derived. Thus, extending our methodology of cluster enumeration,¹⁵ an infinite number of potential substructures⁶ may be envisioned, including the three depicted in Figure 3: $O_1(1_4)^{-2}[MX_4]^{2-}$, $O_1(1_2)^{-1}[MX_5]^{2-}$, and $O(1_0)^{-1}[MX_6]^{3-}$ ($A = A^{+}$). Each equivalent of X incorporated reduces

(14) In general, A will be considerably more electropositive than M .

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(16) A brief summation of the PCP notation pertaining only to extended solids follows. Note that the definition for the partitioning has been slightly revised from that previously proposed.¹⁵ Consider a general descriptor with the following formula.

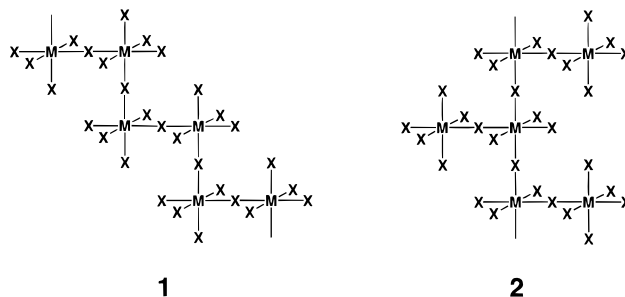
$$P_v(\dots n_i \dots)^{-d} M_m X_x$$

The descriptor indicates that the structure of the solid $M_m X_x$ contains M centers, with a polyhedral coordination geometry P ($P = O$ for octahedral, T for tetrahedral, and so on, as designated in ref 15), connected to neighboring M centers through linkages consisting of v bridging X atoms. The number n is obtained from the sum of the crystallographic site occupancy factors for any M centers connected in this fashion to exactly i neighboring M centers; all n are scaled by their greatest common denominator to ensure integral values. Finally, d ($=1, 2, \text{ or } 3$) specifies the overall dimensionality of the infinitely extended framework.

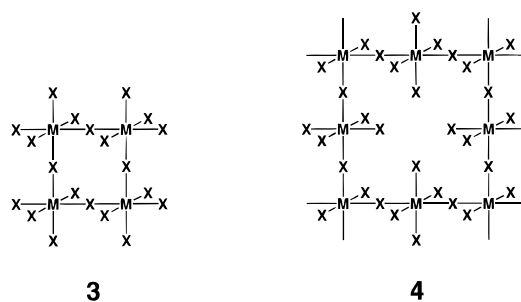
the connectedness of the framework by exactly two, permitting formulation of a mean general descriptor

$$O_1(1_{6-2n})^{-?}[MX_{3+n}]^{nz-} \quad 0 < n \leq 3 \quad (1)$$

for any product, A_nMX_{x+n} . Such general descriptors will often correspond to a vast number of possible isomeric structures, any one of which might be adopted. For example, the chain $O_1(1_2)^{-1}[MX_5]^{2-}$ in Figure 3 consists of MX_6 octahedra sharing *trans* apices. If, instead, the octahedra share *cis* apices, then an isomer with the exact same PCP descriptor emerges, as shown in **1**. From the perspective of the M and X atoms, the



differences between the two structures are rather subtle and at long range, and the role of the cation A in crystal packing is likely to be a deciding factor in structural preference. So, while dimensional reduction predicts that the connectedness of a phase containing $[MX_5]^{2-}$ should be two, it does not distinguish between any of the many possible isomeric structures. As mentioned, the connectedness of a framework is actually the *mean* degree of connectivity of its metal centers. For instance, another possible $[MX_5]^{2-}$ isomer has the $O_1(1_3)^{-1}[MX_5]^{2-}$ chain structure depicted in **2**. This structure contains two nonequivalent octahedral M sites (in equal proportions), one of degree three and the other of degree one, resulting in a mean degree, or connectedness, of two. As indicated in eq 1, the dimensionality of a given phase is structure dependent, and does not necessarily follow from its connectedness (although, obviously, there is an inexact correlation between the two). A zero-dimensional structure, $O_1(4_2)^{-1}[M_4X_{20}]^{8-}$, with empirical formula $[MX_5]^{2-}$ and a connectedness of two is shown in **3**. Finally, it is worth noting that the value of n in descriptor 1 is not restricted to integers, but may take on any rational number between 0 and 3. In other words, the steps in Figure 3 are not discrete, but represent a numerically (and structurally) convenient sampling from a virtual continuum of empirical formulae. Eradicating a square lattice consisting of one fourth of the total MX_6 octahedra from the two-dimensional sheet in Figure 3 results in a new sheet, $O_1(1_4 2_2)^{-2}[M_3X_{14}]^{5-}$, with the structure shown in **4**. This is just one of the possible structures corresponding to a value of $n = 5/3$ in eq 1; examination of **4** confirms that it does indeed have the predicted connectedness of $6 - 2(5/3) = 8/3$ (for every one MX_6 octahedron of degree four, there are two of degree two).



When applied to a known parent structure, the dimensional reduction formalism may serve both as a means of formulating new synthetic targets of altered connectedness/dimensionality and as a means of relating *established* framework solids throughout chemistry. As an instance of the latter, all four of the structures illustrated in Figure 3 have been demonstrated for the phases $K_n\text{FeF}_{3+n}$ ($n = 0, 1, 2, 3$).¹⁷ In addition, the surprisingly diverse crystal chemistry of the ternary ferric fluorides furnishes examples of frameworks 1–4, as encountered in SrFeF_5 , BaFeF_5 , $\text{Pb}_3\text{Fe}_2\text{F}_{12}$ ($=\text{Pb}_4[\text{Fe}_4\text{F}_{20}] \cdot 2\text{PbF}_2$), and $\text{Na}_5\text{Fe}_3\text{F}_{14}$, respectively.¹⁸ Some further examples are collected in Table 1.^{9,19–31} These include a selection of metal oxide, chalcogenide, and halide frameworks featuring a variety of different polyhedra-based connectivity modes. With hundreds of different frameworks based on corner-sharing SiO_4 tetrahedra, the silicates represent by far the most thoroughly explored dimensional reduction system.³² The incorporation of AO in an appropriate SiO_2 parent structure invokes a mean general descriptor

$$T_1(1_{4-2n})-\infty[\text{SiO}_{2+n}]^{2n-} \quad 0 < n \leq 2 \quad (2)$$

encompassing these many phases.

(b) Cluster Frameworks. The basic tenets of dimensional reduction apply equally to frameworks built up from multi-

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Table 1. Selected Examples of Solids with Metal–Anion Frameworks Related by Dimensional Reduction

mode ^a	3-D	2-D	1-D	0-D	ref
S ₂	PdS	K ₂ Pd ₃ S ₄	K ₂ PdS ₂		19
T ₁	SiO ₂	BaSi ₂ O ₅	Na ₂ SiO ₃	K ₄ SiO ₄	20
T ₁		P ₂ O ₅	NaPO ₃	Na ₃ PO ₄	21
T ₁	Ga ₂ Se ₃			Cs ₈ Ga ₄ Se ₁₀	22
T ₁	HgS		K ₂ Hg ₃ S ₄	K ₆ HgS ₄	23
T ₂	MnS	K ₂ Mn ₃ S ₄	K ₂ MnS ₂	K ₆ MnS ₄	24
T ₂	Cu ₂ Q ^b	KCuQ ^b			25
T ₂	ZnS	Na ₂ Zn ₃ S ₄	Na ₂ ZnS ₂	Na ₆ ZnS ₄	26
SPy _{2,1}		V ₂ O ₅	KVO ₃		27
O ₁	WO ₃		Ba ₂ WO ₅	Ba ₃ WO ₆	28
O ₁	FeF ₃	KFeF ₄	K ₂ FeF ₅	K ₃ FeF ₆	17
O _{2,1}	PtO ₂			Li ₈ PtO ₆	29
O ₂		CdCl ₂		K ₄ CdCl ₆	30

^a Principal framework connectivity mode in PCP notation. ^b Q = S, Se.

Table 2. Structurally Proven Examples of Solids with Cluster Frameworks Related by Dimensional Reduction

mode ^a	3-D	2-D	1-D	0-D	ref
Cl ^{a-a}		Re ₃ Cl ₉		A ₃ Re ₃ Cl ₁₂ ^b	33
Cl ^{a-a}	K ₂ Zr ₆ BCl ₁₅	Cs ₃ Zr ₆ BCl ₁₆	Ba ₂ Zr ₆ BCl ₁₇	Rb ₅ Zr ₆ BCl ₁₈	34
Cl ^{a-a}		Nb ₆ Cl ₁₄		K ₄ Nb ₆ Cl ₁₈	35
Cl ^{a-a}		Mo ₆ Cl ₁₂	NaMo ₆ Cl ₁₃	PbMo ₆ Cl ₁₄	36
Cl ^{a-a}			Re ₆ S ₅ Cl ₈	RbRe ₆ S ₅ Cl ₉	8
S ^{a-a}	Li ₄ Re ₆ S ₁₁			A ₁₀ Re ₆ S ₁₄ ^b	37

^a Principal cluster framework connectivity mode. ^b A = Rb, Cs.

nuclear cluster cores. Replacing the single metal centers M in Figure 3 with cluster cores of general formula $[\text{M}_m\text{Q}_q]$ (where Q represents an anionic ligand or atom intimately bonded with multiple intracluster metals, M) leads to the analogous deconstruction of an $[\text{M}_m\text{Q}_q]\text{X}_3$ parent cluster framework. A similar replacement extends the other facets of the formalism (as detailed above for the simpler metal–anion frameworks) to cluster frameworks. Over the years, a number of cluster phases have been structured featuring frameworks readily related by dimensional reduction. These phases, which were not previously correlated by the dimensional reduction argument, are collected in Table 2.^{8,33–37} With the exception of $\text{Li}_4\text{Re}_6\text{S}_{11}$, all of the parent phases (those of maximal dimensionality) have proven amenable to cluster excision,^{2,7b,8a} rendering the dimensionally reduced products extraneous for purposes of cluster solubilization.

Most of the more intractable cluster frameworks are partially or entirely linked by bonding interactions directly between cores,

(31) The correlation between cation/anion incorporation and dimensionality has been specifically recognized in the structures of certain metal chalcogenides: (a) Kanatzidis, M. G.; Park, Y. *Chem. Mater.* **1990**, 2, 99. (b) Axtell, E. A.; Liao, J.-H.; Pikramenou, Z.; Park, Y.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, 115, 12191. (c) Lu, Y.-J.; Ibers, J. A. *Comments Inorg. Chem.* **1993**, 14, 229.

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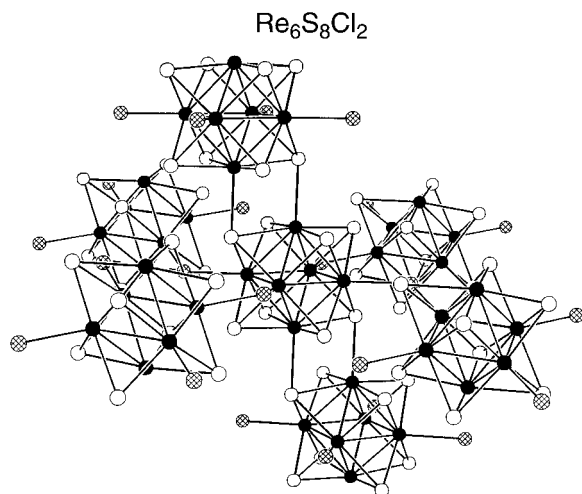


Figure 4. Local cluster environment in the three-dimensional $\text{Re}_6\text{S}_8\text{Cl}_2$ ($=[\text{Re}_6\text{S}_6^i\text{S}_2^{i-a}]_2\text{S}_2^{a-i}\text{Cl}_4^{a-a}$) parent structure. Black, white, and cross-hatched spheres represent Re, S, and Cl atoms, respectively. Selected mean interatomic distances (Å) and angles (deg) are as follows: Re–Re 2.59(1), non-rhomb Re–S 2.39(1), Re–Cl 2.46(1), Re–Re–Re 60.0(4); within Re_2S_2 rhombs Re–S 2.50(2).^{10b}

rather than through some intermediate bridging atom, as in $\text{Re}_6\text{Se}_6\text{Cl}_6$ (Figure 1) and all of the phases listed in Table 2.² The three-dimensional framework of $\text{Re}_6\text{S}_8\text{Cl}_2$ provides such an example. Its structure^{10b} is built up from electron-precise face-capped octahedral $[\text{Re}_6\text{S}_8]^{2+}$ cluster cores, each linked to six neighboring cores via two rhombic Re_2S_2 interactions (situated at *trans* apices of the Re_6 octahedron) and four μ_2 -Cl atoms. Thus, a total of eight bonds astrick each cluster, making the compound impervious to excision. By focusing on the local environment of a single cluster, Figure 4 attempts to convey the connectivity of the framework; however, due to its tightly-packed three-dimensional nature, the drawing is crowded and difficult to penetrate.

A notation specific to cluster frameworks has been developed as an aid in both visualizing structures and unambiguously communicating connectivities.³⁸ It is now advantageous to provide a brief explanation of this notation, which will be generously employed hereafter. To begin, attention should be directed at a *single* cluster within the framework.³⁹ Utilizing the $\text{Re}_6\text{S}_8\text{Cl}_2$ structure as an example, consider the central cluster in Figure 4. Square brackets are used to designate the cluster core, which consists of six Re atoms and eight *inner* S ligands. Outer (*ausser*) ligands that are not a part of the core, but which are directly bonded to core metal atoms, are listed outside the brackets.



Inner ligands that serve as an outer ligand for a neighboring core are labeled with a superscript “i-a”, while those which do not are labeled “i”. Outer ligands that serve as an inner or outer ligand for a neighboring core are labeled with a superscript

(38) Schäfer, H.; von Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833.

(39) The notation makes the simplifying assumption that all clusters in the framework are equivalent. This assumption, which will be tentatively adopted here, obliterates many of the intricacies of dimensional reduction considered above for metal–anion frameworks. However, it should be kept in mind that frameworks composed of more than one type of cluster are not entirely unknown; several examples have been uncovered among the Chevrel phases: (a) Chevrel, R.; Sergent, M.; Seeber, B.; Fischer, Ø.; Grüttnar, A.; Yvon, K. *Mater. Res. Bull.* **1979**, *14*, 567. (b) Chevrel, R.; Potel, M.; Sergent, M.; Decroux, M.; Fischer, Ø. *J. Solid State Chem.* **1980**, *34*, 247.

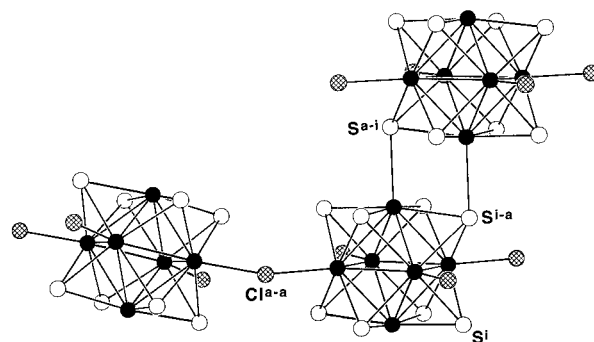
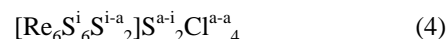
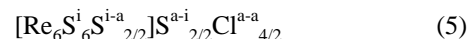


Figure 5. A piece of the $\text{Re}_6\text{S}_8\text{Cl}_2$ structure clearly displaying the two different types of intercluster linkages. The various ligand designations present in its cluster connectivity notation are as indicated.

“a-i” or “a-a”, respectively, while those which do neither are labeled “a”.



Examples of some of these types of ligands are indicated on a smaller piece of the $\text{Re}_6\text{S}_8\text{Cl}_2$ structure in Figure 5 (the core on the lower right is considered the central cluster). Finally, denominators corresponding to the number of distinct cores to which each type of ligand is bonded are added to the formula (denominators of 1 are omitted).



Note that summing the atoms in a correct formulation will always result in the proper stoichiometry.

Like their metal–anion brethren, cluster frameworks can exhibit structural isomerism. The $\text{Re}_6\text{S}_8\text{Cl}_2$ structure is also assumed by the isotopic phases $\text{Re}_6\text{S}_8\text{Br}_2$ and $\text{Re}_6\text{Se}_8\text{Br}_2$;¹⁰ however, for reasons which are not entirely clear, $\text{Re}_6\text{Se}_8\text{Cl}_2$ adopts a different structure. The latter structure⁶ (Figure 2) is built up from analogous $[\text{Re}_6\text{Se}_8]^{2+}$ cores, each with two attendant terminal chlorides (Cl^a) at *trans* rhenium apices and four rhombic Re_2Se_2 interactions directly linking neighboring cores. The ensuing connectivity notation for this rigid two-dimensional framework is $[\text{Re}_6\text{Se}_4^i\text{Se}_2^{i-a}]_2\text{Se}_2^{a-i}\text{Cl}_4^{a-a}$. Significantly, the connectedness of both isomeric frameworks is eight.⁴⁰

In general, the excision techniques currently available are only effective for cluster cores linked exclusively through μ_2 -halide bridges in frameworks with a connectedness of six or less.² Thus, neither $\text{Re}_6\text{S}_8\text{Cl}_2$ nor $\text{Re}_6\text{Se}_8\text{Cl}_2$ is amenable to cluster excision. In view of this, the multitude of solids containing $[\text{Re}_6\text{Q}_8]^{2+}$ ($\text{Q} = \text{S}, \text{Se}$) cluster cores,² and the lack of any corresponding species in solution, the $\text{Re}_6\text{S}_8\text{Cl}_2$ and $\text{Re}_6\text{Se}_8\text{Cl}_2$ structures were chosen as prototypes for testing the validity of the dimensional reduction approach.

Experimental Section

Preparation of Compounds. The preparation of $\text{Cs}_3\text{Re}_6\text{S}_8\text{Cl}_7$ has been reported elsewhere.¹³ The reactants Re (–325 mesh, Cerac), S (–100 mesh, Aldrich), Se (–325 mesh, Strem), ReBr_5 (–100 mesh, Cerac), Br_2 (Fluka), I_2 (Strem), HBr (48%, Mallinckrodt), HI (47%, Fluka), $(\text{Bu}_4\text{N})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; Aldrich), SOCl_2 (Mallinckrodt), and SOBr_2 (Fluka) were used as purchased, without further purification. Alkali metal halides CsBr (Strem) and CsI (–20 mesh, Cerac) were ground and dried for two days at 200 °C prior to use. Fused silica ampules with dimensions i.d. \times o.d. \times l = 7 \times 10 \times 120 mm were

(40) Due to the capacity of multinuclear cluster cores for forging multiple bond linkages (see Figure 2), we will now employ a slightly revised definition of connectedness as the minimum number of bonds that must be broken to completely liberate a cluster core from its surrounding framework.

dried overnight at 150 °C. High temperature reactions were carried out in tube furnaces (Marshall, Lindberg or Carbolite) equipped with programmable Eurotherm temperature controllers; furnace temperatures were typically ramped up at 2 °C/min. Products were identified by single crystal X-ray structure determinations and subsequent X-ray powder diffraction (XRPD) patterns. Solid phases exhibiting large crystal faces were subjected to an electron microprobe analysis (EMPA).

Cs₅Re₆S₈Br₇. Liquid Br₂ (*ca.* 0.2 g) was added to a tared fused silica ampule; the ampule and its contents were accurately weighed and cooled with liquid nitrogen. A mixture of Re, S, and CsBr (stoichiometric amounts bringing the total mass of reactants to *ca.* 4 g) was intimately ground and added to the ampule, which was then evacuated and sealed. The sample was heated (with reactants situated at the cooler end of the ampule) at 850 °C for 6000 min, cooled at 0.2 °C/min to about 500 °C, and air-quenched. The product crystallized as thick yellow-orange hexagonal plates. EMPA: Cs_{5.15(6)}Re_{6.00(5)}S_{8.02(2)}Br_{7.5(2)}.

Cs₆Re₆S₈I₈. A fused silica ampule was charged with a *ca.* 2-g mixture of Re, S, I₂, and CsI in proportions corresponding to an overall stoichiometry of Cs₈Re₅S₈I₁₀ (two extra equivalents of CsI) and sealed under static vacuum. The sample was heated (with reactants situated at the cooler end of the ampule) at 850 °C for 6000 min, cooled at 0.2 °C/min to about 500 °C, and air-quenched. The product crystallized as thick yellow rectangular plates along with CsI and varying amounts of an insoluble black phase of unknown composition. EMPA: Cs_{6.17(5)}Re_{6.00(9)}S_{7.7(1)}I_{8.25(5)}.

Cs₂Re₆Se₈Br₄. A 0.500-g mixture of Re, Se, ReBr₅, and CsBr in proportions corresponding to an overall stoichiometry of Cs₅Re₆Se₈Br₇ (three extra equivalents of CsBr) was intimately ground in a pure dinitrogen atmosphere and sealed in a fused silica ampule under vacuum. The sample was heated (with reactants situated at the cooler end of the ampule) at 800 °C for 6000 min, cooled at 0.2 °C/min to about 400 °C, and air-quenched. The product crystallized (along with the excess CsBr) as metallic black needles.

CsRe₆Se₈I₃. A fused silica ampule was charged with a stoichiometric 0.800-g mixture of Re, Se, I₂, and CsI and sealed under vacuum. The sample was heated (with reactants situated at the cooler end of the ampule) at 850 °C for 6000 min, cooled at 0.2 °C/min to about 400 °C, and air-quenched. The product crystallized as metallic black elongated rhombic plates. EMPA: Cs_{1.1(1)}Re_{6.0(1)}Se_{8.0(1)}I_{3.13(8)}.

Cs₄Re₆Se₈I₆. A fused silica ampule was charged with a stoichiometric *ca.* 2-g mixture of Re, Se, I₂, and CsI and sealed under static vacuum. The sample was heated (with reactants situated at the cooler end of the ampule) at 850 °C for 6000 min, cooled at 0.2 °C/min to about 500 °C, and air-quenched. The product crystallized as thick red rhombic plates. Occasional minor impurities of CsRe₆Se₈I₃ (insoluble) and CsI were also observed. EMPA: Cs_{4.5(2)}Re_{6.0(2)}Se_{7.6(9)}I_{6.4(2)}.

(Bu₄N)₄[Re₆S₈Cl₆]. A 1.70-g portion of the product recovered from a reaction targeting Cs₅Re₆S₈Cl₇ was pulverized and stirred in 200 mL of 1 M aqueous HCl for 45 min. The mixture was filtered to give a small amount of gray-black solid and a bright yellow filtrate. Solid KOH (26 g, 0.46 mol) was added to the filtrate and stirred until it completely dissolved. Excess (Bu₄N)Cl (*ca.* 1 g) was added to the stirred solution which turned colorless upon formation of a yellow precipitate. The precipitate was collected by filtration and dissolved in 100 mL of acetonitrile to give a yellow-orange solution. The solution was reduced to dryness leaving a yellow-orange solid which was recrystallized by evaporation from a *ca.* 1:1 (v/v) mixture of acetone and toluene. The resulting yellow-orange plates were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 0.73 g (38%) of product. Absorption spectrum (MeCN): λ_{max} (ε_M) 377 (sh, 1860), 434 (1050), 537 (140) nm. Anal. Calcd for C₆₄H₁₄₄Cl₆N₄S₈Re₆: C, 30.07; H, 5.68; Cl, 8.32; N, 2.19; Re, 43.70; S, 10.03. Found: C, 29.88; H, 5.59; Cl, 8.38; N, 2.17; Re, 43.88; S, 10.11.

(Bu₄N)₃[Re₆S₇(SH)Cl₆]. The product recovered (1.96 g) from a reaction targeting Cs₅Re₆S₈Cl₇ was pulverized and stirred in 200 mL of 1 M aqueous HCl for 30 min. The mixture was filtered to give a small amount of gray-black solid and a bright yellow filtrate. Excess (Bu₄N)Cl (*ca.* 800 mg) was added to the stirred filtrate which turned colorless upon formation of a yellow precipitate. The precipitate was

collected by filtration and dissolved in 100 mL of acetonitrile to give a yellow-orange solution. Several drops of water and *ca.* 0.5 mL of SOCl₂ were added to the stirred solution which underwent an immediate color change to red. The solution was reduced to dryness leaving a red solid which was recrystallized by evaporation from a *ca.* 1:1 (v/v) mixture of acetone and toluene. The resulting red plates were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 1.31 g (66%) of product. Absorption spectrum (MeCN): λ_{max} (ε_M) 378 (sh, 1820), 489 (785), 544 (1190) nm. Anal. Calcd for C₄₈H₁₀₉Cl₆N₃S₈Re₆: C, 24.91; H, 4.75; Cl, 9.19; N, 1.82; Re, 48.26; S, 11.08. Found: C, 24.83; H, 4.68; Cl, 9.24; N, 1.77; Re, 48.34; S, 11.21.

(Bu₄N)₄[Re₆S₈Br₆]·H₂O. A 1.17-g portion of the product recovered from a reaction targeting Cs₅Re₆S₈Br₇ (as described above) was pulverized and stirred in 200 mL of 1 M aqueous HBr for 30 min. The mixture was filtered to give a small amount of gray-black solid and a bright yellow filtrate. Solid NaOH (26 g, 0.65 mol) was added to the filtrate and the mixture was stirred until the solid completely dissolved. Excess (Bu₄N)Br (*ca.* 600 mg) was added to the stirred solution which turned colorless upon formation of a yellow precipitate. The precipitate was collected by filtration and dissolved in 100 mL of MeCN to give a yellow-orange solution. The solution was reduced to dryness leaving a yellow-orange residue which was crystallized by evaporation from a *ca.* 1:1 (v/v) mixture of acetone and toluene. The resulting yellow-orange plates were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 0.73 g (58%) of pure product. Absorption spectrum (MeCN): λ_{max} (ε_M) 401 (sh, 1540), 443 (945), 545 (90) nm. Anal. Calcd for C₆₄H₁₄₆Br₆N₄O₈Re₆: C, 27.06; H, 5.18; Br, 16.87; N, 1.97; Re, 39.32; S, 9.03. Found: C, 27.15; H, 5.16; Br, 16.76; N, 1.89; Re, 39.26; S, 9.18.

(Bu₄N)₃[Re₆S₇(SH)Br₆]. The product recovered (3.48 g) from a reaction targeting Cs₅Re₆S₈Br₇ (as described above) was pulverized and stirred in 200 mL of 1 M aqueous HBr for 30 min. The mixture was filtered to give a small amount of red-brown solid and a bright yellow filtrate. Excess (Bu₄N)Br (*ca.* 1.5 g) was added to the stirred filtrate which turned colorless upon formation of a yellow precipitate. The precipitate was collected by filtration and dissolved in 100 mL of acetonitrile to give an orange solution. Several drops of water and *ca.* 1 mL of SOBr₂ were added to the stirred solution, which underwent an immediate color change to red. The solution was reduced to dryness leaving a red solid which was recrystallized by evaporation from a *ca.* 1:1 (v/v) mixture of acetone and toluene. The resulting red plates were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane and dried under vacuum to afford 2.44 g (71%) of pure product. Absorption spectrum (MeCN): λ_{max} (ε_M) 395 (sh, 2380), 492 (781), 541 (1270) nm. Anal. Calcd for C₄₈H₁₀₉Br₆N₃S₈Re₆: C, 22.33; H, 4.26; Br, 18.57; N, 1.63; Re, 43.28; S, 9.94. Found: C, 22.37; H, 4.31; Br, 18.88; N, 1.58; Re, 43.16; S, 9.79.

(Bu₄N)₄[Re₆S₈I₆]·H₂O. A 1.12-g portion of the product recovered from a reaction targeting Cs₆Re₆S₈I₈ (as described above) was pulverized and stirred in 200 mL of 1 M aqueous HI for 2 h. The mixture was filtered to give a large amount of gray-black solid and a yellow filtrate. Solid KOH (30 g, 0.53 mol) was added to the filtrate and stirred until it completely dissolved. A 50-mL aliquot of 0.05 M aqueous (Bu₄N)I was added to the stirred solution, which turned colorless upon formation of a yellow-orange precipitate. The precipitate was collected by filtration and dissolved in 100 mL of acetonitrile to give a yellow-orange solution. The solution was reduced to dryness leaving a yellow-orange solid that was crystallized by evaporation from a *ca.* 1:1 (v/v) mixture of acetone and toluene. The resulting yellow-orange plates were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 0.041 g (4.3%) of product. Absorption spectrum (MeCN): λ_{max} (ε_M) 393 (sh, 3290), 420 (2200), 507 (sh, 755) nm.

(Bu₄N)₃[Re₆S₇(SH)I₆]·2Me₂CO. The product recovered (2.69 g) from a reaction targeting Cs₆Re₆S₈I₈ (as described above) was pulverized and stirred in 200 mL of 1 M aqueous H₂SO₄ for 1 h. The mixture was filtered to give a large amount of gray-black solid and a yellow-orange filtrate. A 50-mL aliquot of 0.05 M aqueous (Bu₄N)I was added to the stirred filtrate which turned colorless upon formation of a brown precipitate. The precipitate was collected by filtration and dissolved in 100 mL of CH₂Cl₂ to give a red-brown solution. Three drops of concentrated aqueous H₂SO₄ were added, and the solution was stirred

Table 3. Crystallographic Data^a for $Cs_5Re_6S_8Br_7$, $Cs_6Re_6S_8I_8$, $Cs_2Re_6Se_8Br_4$, $CsRe_6Se_8I_3$, and $Cs_4Re_6Se_8I_6$

	$Cs_5Re_6S_8Br_7$	$Cs_6Re_6S_8I_8$	$Cs_2Re_6Se_8Br_4$	$CsRe_6Se_8I_3$	$Cs_4Re_6Se_8I_6$
formula wt	2597.6	3186.3	2334.3	2262.5	3041.9
space group	$R3c$	$Fm\bar{3}m$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	6	4	2	4	4
a, Å	9.957(2)	15.842(2)	6.544(3)	6.565(2)	10.099(3)
b, Å			18.687(7)	19.678(9)	28.922(8)
c, Å	54.55(2)		9.263(4)	15.793(6)	11.667(3)
β , deg			104.26(3)	96.77(3)	106.27(2)
V, Å ³	4685(2)	3976(1)	1098.0(8)	2026(1)	3271(2)
d_{calc} , g/cm ³	5.524	5.324	7.061	7.417	6.176
μ , mm ⁻¹	38.39	30.24	56.73	56.39	41.06
R ^b (R_w^c), %	7.56 (7.96)	5.39 (6.51)	6.70 (6.81)	7.64 (7.03)	5.03 (4.99)

^a Obtained at 223 K with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = \{ \sum [w(|F_o| - |F_c|)]^2 / \sum [w|F_o|^2] \}^{1/2}$.

Table 4. Crystallographic Data^a for $(Bu_4N)_4[Re_6S_8Cl_6]$, $(Bu_4N)_3[Re_6S_7(SH)Cl_6]$, $(Bu_4N)_4[Re_6S_8Br_6] \cdot H_2O$, and $(Bu_4N)_3[Re_6S_7(SH)Br_6] \cdot 2Me_2CO$

	$(Bu_4N)_4[Re_6S_8Cl_6]$	$(Bu_4N)_3[Re_6S_7(SH)Cl_6]$	$(Bu_4N)_4[Re_6S_8Br_6] \cdot H_2O$	$(Bu_4N)_3[Re_6S_7(SH)Br_6] \cdot 2Me_2CO$
formula	$C_{64}H_{144}Cl_6N_4Re_6S_8$	$C_{48}H_{109}Cl_6N_3Re_6S_8$	$C_{64}H_{146}Br_6N_4OR_6S_8$	$C_{54}H_{121}Br_6N_3O_2Re_6S_8$
formula wt	2556.2	2314.8	2841.0	2697.7
space group	$Pbca$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	4	2	4	2
a, Å	22.738(5)	12.445(5)	22.055(7)	13.957(5)
b, Å	16.585(6)	17.482(5)	16.832(6)	16.870(6)
c, Å	23.524(9)	18.190(6)	24.482(10)	18.552(8)
α , deg		95.98(2)		76.30(3)
β , deg		106.53(3)	90.87(3)	76.02(3)
γ , deg		103.67(3)		77.62(3)
V, Å ³	8871(5)	3624(2)	9088(5)	4061(3)
d_{calc} , g/cm ³	1.914	2.121	2.076	2.206
μ , mm ⁻¹	8.559	10.47	10.82	12.10
R (R_w), ^b %	6.06 (6.38)	5.03 (5.20)	4.83 (5.13)	6.00 (6.26)

^a Obtained at 223 K with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. ^b For definitions cf. Table 3.

Table 5. Crystallographic Data^a for $(Bu_4N)_4[Re_6S_8I_6] \cdot H_2O$, $(Bu_4N)_3[Re_6S_7(SH)I_6] \cdot 2Me_2CO$, and $(Bu_4N)_3[Re_6Se_7(SeH)I_6] \cdot 2Me_2CO$

	$(Bu_4N)_4[Re_6S_8I_6] \cdot H_2O$	$(Bu_4N)_3[Re_6S_7(SH)I_6] \cdot 2Me_2CO$	$(Bu_4N)_3[Re_6Se_7(SeH)I_6] \cdot 2Me_2CO$
formula	$C_{64}H_{146}I_6N_4OR_6S_8$	$C_{54}H_{121}I_6N_3O_2Re_6S_8$	$C_{54}H_{121}I_6N_3O_2Re_6Se_8$
formula wt	3122.9	2921.5	3353.8
space group	$P2_1/c$	$C2/c$	$C2/c$
Z	4	4	4
a, Å	22.170(7)	28.631(12)	28.227(11)
b, Å	17.326(5)	21.380(8)	21.940(9)
c, Å	24.682(9)	14.741(5)	14.995(6)
β , deg	91.73(3)	108.57(3)	105.22(3)
V, Å ³	9477(5)	8553(6)	8961(6)
d_{calc} , g/cm ³	2.189	2.269	2.486
μ , mm ⁻¹	9.800	10.85	13.42
R (R_w), ^b %	8.42 (8.72)	6.77 (5.69)	6.78 (6.74)

^a Obtained at 223 K with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. ^b For definitions cf. Table 3.

for 30 min. The solution was then reduced to dryness, leaving a red solid which was recrystallized by evaporation from a ca. 1:1 (v/v) mixture of acetone and toluene. The resulting black crystals were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 0.22 g (11%) of product. Absorption spectrum (MeCN): λ_{max} (ϵ_M) 534 (590), 586 (sh, 353) nm.

$(Bu_4N)_3[Re_6Se_7(SeH)I_6] \cdot 2Me_2CO$. The product recovered (1.957 g) from a reaction targeting $Cs_4Re_6Se_8I_6$ (as described above) was pulverized and stirred in 200 mL of 1 M aqueous HI for 2 h. The mixture was filtered to give a small amount of brown-black solid and a bright red filtrate. A 50-mL aliquot of 0.05 M aqueous $(Bu_4N)I$ was added to the stirred filtrate which turned colorless upon formation of a brown precipitate. The precipitate was collected by filtration and dissolved in 100 mL of acetonitrile to give a red-brown solution. Ten drops of $SOCl_2$ were added, and the solution was stirred for 15 min. The solution was then reduced to dryness, leaving a brown-black solid which was crystallized by evaporation from a ca. 1:1 (v/v) mixture of acetone and toluene. The resulting black, block-shaped crystals were washed with successive 30-mL aliquots of toluene, water, toluene, and pentane to afford 1.31 g (63%) of product. Absorption spectrum (MeCN): λ_{max} (ϵ_M) 477 (sh, 2060), 525 (sh, 1180), 609 (1190) nm. Anal. Calcd for $C_{48}H_{109}I_6N_3Se_8Re_6$: C, 17.72; H, 3.38; I, 23.43; N,

1.29; Re, 34.51; Se, 19.67. Found: C, 17.96; H, 3.42; I, 23.60; N, 1.26; Re, 34.32; Se, 19.36.

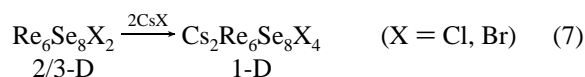
X-ray Data Collection and Reduction. Structures were determined for the compounds listed in Tables 3–5. Single crystals were picked from the reaction products, coated with Apiezon L grease, and attached to glass fibers. The crystals were then transferred to a Nicolet R3m/V diffractometer and cooled in a dinitrogen stream to -50 °C. Lattice parameters were obtained from least-squares analysis of more than 30 carefully centered reflections. Decay corrections were based on the measured intensities of reflections monitored periodically throughout the course of data collection; none of the crystals showed significant decay. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure factor amplitudes and their esd's using the program XDISK from the SHELXTL PLUS 4.21/V software package. An empirical absorption correction based on the observed variation in intensity of azimuthal (Ψ) scans was applied to each data set using the program XEMP. For $Cs_5Re_6S_8Br_7$, $Cs_6Re_6S_8I_8$, $Cs_2Re_6Se_8Br_4$, $CsRe_6Se_8I_3$, and $Cs_4Re_6Se_8I_6$, the absorption correction was improved by collecting excess data used to average equivalent reflections. Further details of the data collection are deposited as supporting information. Crystal data are collected in Tables 3–5.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for $\text{Tl}_2\text{Re}_6\text{S}_8\text{Cl}_4$, $\text{Tl}_2\text{Re}_6\text{Se}_8\text{Cl}_4$, and $\text{Cs}_2\text{Re}_6\text{Se}_8\text{Br}_4$

	$\text{Tl}_2\text{Re}_6\text{S}_8\text{Cl}_4^a$	$\text{Tl}_2\text{Re}_6\text{Se}_8\text{Cl}_4^a$	$\text{Cs}_2\text{Re}_6\text{Se}_8\text{Br}_4$
Re–Re	2.590(5)–2.634(5)	2.618(3)–2.666(3)	2.605(3)–2.662(3)
mean	2.603(11)	2.63(2)	2.62(2)
Re···Re ^b	3.216–3.259	3.407	3.370
mean	3.24(2)		
Re–Q ^c	2.35(3)–2.45(3)	2.500(7)–2.517(6)	2.506(6)–2.527(5)
mean	2.40(3)	2.510(5)	2.515(7)
Re–Q ^b	2.49(3)–2.56(2)	2.600(7)–2.633(5)	2.617(5)–2.638(6)
mean	2.51(3)	2.62(2)	2.63(1)
Re–X	2.38(2)–2.44(3)	2.411(12)–2.414(11)	2.543(7)–2.573(6)
mean	2.41(2)	2.413(2)	2.56(2)
Re–Re–Re ^d	59.5(1)–60.9(1)	59.4(1)–60.9(1)	59.3(1)–61.0(1)
Re–Re–Re ^e	89.4(2)–90.6(2)	89.3(1)–90.7(1)	89.4(1)–90.6(1)
Re–Re–X	133.2(6)–137.5(5)	134.1(4)–136.4(4)	131.2(2)–138.8(2)
mean	135(1)	135.2(7)	135(2)
Re–Q–Re ^c	63.7(5)–66.7(6)	61.2(1)–64.1(2)	62.1(1)–64.0(1)
mean	65(1)	63.0(8)	62.6(9)
Q–Re–Q ^b	99.6(7)–100.0(6)	98.7(2)	100.2(2)
mean	99.8(2)		
Q–Re–X	90.4(8)–95.6(8)	89.7(4)–93.4(4)	89.4(1)–95.2(2)
mean	93(2)	92.2(6)	92(2)

^a Reference 15. ^b Within core-linking Re_2Q_2 rhombs. ^c Excluding Re_2Q_2 rhombs. ^d Within triangular faces. ^e Within equatorial squares.

Toward this end, attempts were made at utilizing the cesium halides as dimensional reduction agents.⁴² Uptake of cesium chloride and cesium bromide is limited to a single step:



The structure of $\text{Cs}_2\text{Re}_6\text{Se}_8\text{Br}_4$ (isomorphous with $\text{Cs}_2\text{Re}_6\text{Se}_8\text{Cl}_4$)¹³ exhibits one-dimensional chains composed of $[\text{Re}_6\text{Se}_8]^{2+}$ cores linked by Re_2Se_2 rhombs at *trans* rhenium apices, as shown in Figure 6. The chains are sheathed with terminal bromides, which ligate the remaining four rhenium atoms of each cluster core to afford the connectivity $\text{Cs}_2[\text{Re}_6\text{Se}_6\text{Se}^{i-2/2}]\text{Se}^{a-i/2}\text{Br}^a$. Nearly identical chains are present in the $\text{Re}_6\text{Se}_8\text{Br}_2$ parent (isotypic with $\text{Re}_6\text{S}_8\text{Cl}_2$, Figure 4) wherein each is linked to four neighboring chains via bridging bromide atoms. Thus, the inclusion of CsBr terminates all of the bromide bridges, and opens up the structure by inserting Cs^+ cations⁴³ between chains, effectively reducing the framework connectedness to four and the dimensionality to one. Interatomic distances and angles for the chains in $\text{Cs}_2\text{Re}_6\text{Se}_8\text{Br}_4$ are summarized in Table 6, and except for marginally shorter Re–Br distances, bear no significant differences from those in $\text{Re}_6\text{Se}_8\text{Br}_2$.^{10a} In both structures, the $[\text{Re}_6\text{Se}_8]^{2+}$ core consists of a regular Re_6 octahedron concentric with an Se_8 cube; the regularity of the latter is disrupted somewhat by the slightly (*ca.* 0.1 Å) longer Re–Se bonds within core-linking Re_2Se_2 rhombs. This last observation holds true for all frameworks featuring $[\text{Re}_6\text{Q}_8]^{2+}$ (Q = S, Se) cores linked in such a manner. Despite containing frameworks with a connectedness of just four, the compactness of their Re_2Se_2 core-linking interactions prevents $\text{Cs}_2\text{Re}_6\text{Se}_8\text{X}_4$ (X = Cl, Br) from breaking up into discrete clusters under standard excision conditions.⁴⁴ Interestingly, none of the above $\text{M}_2\text{Re}_6\text{Se}_8\text{X}_4$ phases assume the isomeric two-dimensional cluster framework of Figure 1, as adopted by $\text{Re}_6\text{Se}_6\text{Cl}_6$.³

(42) Halides of the smaller alkali metals were found to be considerably less effective in this role.

(43) The Cs^+ cations in all of the new phases display a complex coordination environment (with coordination number ≥ 7 , and a geometry often defying simple description) involving both chalcogenide and halide atoms.

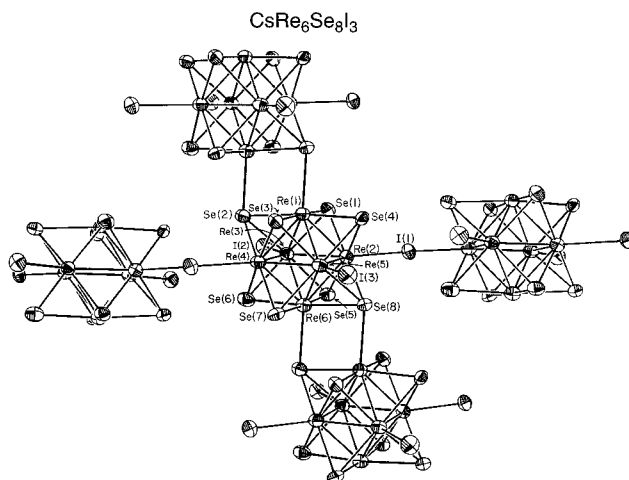
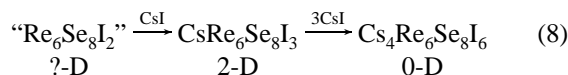


Figure 7. Local cluster environment in the structure of two-dimensional $\text{CsRe}_6\text{Se}_8\text{I}_3$ ($=\text{Cs}[\text{Re}_6\text{Se}_6\text{Se}^{i-2/2}]\text{Se}^{a-i/2}\text{I}^a$); ellipsoids are drawn at the 50% probability level. Selected mean interatomic distances (Å) and angles (deg) are as follows: Re–Re 2.63(2), non-rhomb Re–Se 2.51(1), bridging Re–I 2.819(1), terminal Re–I 2.757(3), Re–Re–Re 60.0(6) and 90.0(6), Re–Re–I 135(2), Re–Seⁱ–Re 62.9(8), Re–I–Re 119.1; within Re_2Se_2 rhombs Re–Se 2.603(2), Re···Re 3.390, Se–Re–Se 98.7.

Dimensional reduction of the fictitious $\text{Re}_6\text{Se}_8\text{I}_2$ parent solid with CsI proceeds in two steps:



The structure of the two-dimensional phase $\text{CsRe}_6\text{Se}_8\text{I}_3$ (Figure 7) is built up from $[\text{Re}_6\text{Se}_8]^{2+}$ cores linked in one dimension via *trans* rhombic Re_2Se_2 interactions and in another through *trans* bridging iodide ligands, with the remaining two apices capped by terminal iodides. The resulting six-connected sheet is readily obtained from the $\text{Re}_6\text{S}_8\text{Cl}_2$ structure (Figure 4) by terminating halide bridges in one dimension. Interatomic

(44) Given the apparent rigidity of the chains in these compounds, an intriguing alternative to excision is direct dissolution of entire one-dimensional $[\text{Re}_6\text{Se}_8\text{X}_4]^{2-}$ chains. Precedence for such a seemingly improbable occurrence has been established with the $[\text{Mo}_6\text{Q}_6]^{2-}$ (Q = Se, Te) chains in $\text{A}_2\text{Mo}_6\text{Q}_6$ (A = Li, K), which dissolve intact in highly polar solvents like DMSO: Tarascon, J. M.; DiSalvo, F. J.; Chen, C. H.; Carroll, P. J.; Walsh, M.; Rupp, L. *J. Solid State Chem.* **1985**, 58, 290.

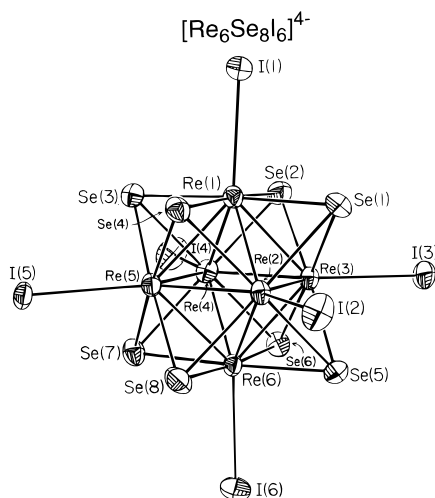
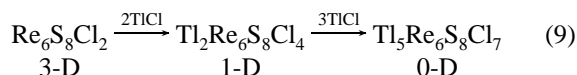


Figure 8. Structure of the discrete $[\text{Re}_6\text{Se}_8\text{I}_6]^{4-}$ clusters in $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$ (60% probability ellipsoids).

distances and angles are summarized in the legend of Figure 7; again, there is some variation in the Re–Se and Re–I bond lengths, depending upon whether or not the Se or I atom is involved in intercore bonding. Note that the $\text{CsRe}_6\text{Se}_8\text{I}_3$ structure is an isomeric alternative to the $\text{TIRe}_6\text{Se}_8\text{Cl}_3$ structure described above. A soluble molecular form of the $[\text{Re}_6\text{Se}_8]^{2+}$ core is realized with incorporation of four total equivalents of CsI in the phase $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$. Here, all of the linkages between clusters have been replaced by terminal iodide atoms, resulting in completely isolated $[\text{Re}_6\text{Se}_8\text{I}_6]^{4-}$ clusters, as shown in Figure 8. Relevant distances and angles are listed in Table 7. The absence of any Re_2Se_2 core-linking interactions enables the cluster core to relax into a more uniform geometry, closely approaching O_h symmetry. However, this symmetry is somewhat disrupted by the terminal iodide ligands, which lie slightly and irregularly displaced from their ideal positions along the 4-fold rotational axes (as is apparent in Figure 8). The mean Re–Re distance of 2.625(5) Å is comparable to that observed in the other $[\text{Re}_6\text{Se}_8]^{2+}$ core-containing phases, and corresponds to a Re–Re single bond, as expected for an M_6Q_8 cluster with an ideal configuration of 24 metal-based electrons.⁴⁵ Comparison with the $[\text{Re}_6\text{Se}_8\text{Cl}_6]^{4-}$ cluster in $\text{TI}_5\text{Re}_6\text{Se}_8\text{Cl}_7$ (Table 7) exposes no obvious core differences.

Dimensional Reduction of $\text{Re}_6\text{S}_8\text{X}_2$ (X = Cl, Br, “I”). Dimensional reduction of the three-dimensional parent phase $\text{Re}_6\text{S}_8\text{Cl}_2$ (Figure 4) with TICl has been demonstrated to progress in two steps:¹³

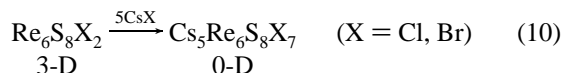


Obtained in near quantitative yields, the dimensionally-reduced phases are structurally analogous to their Se-containing counterparts, $\text{TI}_2\text{Re}_6\text{Se}_8\text{Cl}_4$ and $\text{TI}_5\text{Re}_6\text{Se}_8\text{Cl}_7$, described above. Geometric parameters for $\text{TI}_2\text{Re}_6\text{S}_8\text{Cl}_4$ and $\text{TI}_5\text{Re}_6\text{S}_8\text{Cl}_7$ are collected in Table 6 for comparison. The only remarkable differences between the two structures arise as a result of the shorter Re–S bonds (mean of 2.40(3) Å versus 2.510(5) Å for Re–Se), which induce contraction of both core S_8 cubes and Re_2S_2 rhombs, bringing cluster cores within chains closer together.

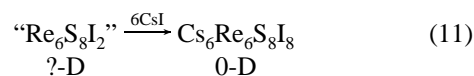
Again, cesium halides are the reagents of choice for directly preparing soluble molecular $[\text{Re}_6\text{S}_8]^{2+}$ core-containing phases

(45) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990; pp 286–290 and references therein.

via dimensional reduction. The three-dimensional $\text{Re}_6\text{S}_8\text{X}_2$ (X = Cl, Br) parent frameworks are completely dismantled with incorporation of 5 equiv of CsX ; no intermediate phases with fewer equivalents of CsX were targeted or encountered.



The structure of the discrete $[\text{Re}_6\text{S}_8\text{Br}_6]^{4-}$ cluster in $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ is depicted in Figure 9. Both $\text{Cs}_5\text{Re}_6\text{S}_8\text{Cl}_7$ and $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ are isotopic with $\text{TI}_5\text{Re}_6\text{Q}_8\text{Cl}_7$ (Q = S, Se). The extra equivalent of M^1X in these $\text{M}^1_5\text{Re}_6\text{Q}_8\text{X}_7$ ($=\text{M}^1_4[\text{Re}_6\text{Q}_8\text{X}_6]\cdot\text{M}^1\text{X}$) phases presumably facilitates the packing of clusters in the crystal lattice. Dimensional reduction of the fictitious parent $\text{Re}_6\text{S}_8\text{I}_2$ also terminates with a molecular product; insoluble intermediate phases were possibly observed by XRPD (*vide supra*), but could not be structurally characterized.



Two adventitious equivalents of CsI are present in $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$ ($=\text{Cs}_4[\text{Re}_6\text{S}_8\text{I}_6]\cdot 2\text{CsI}$) which crystallizes in the cubic space group $Fm\bar{3}m$. Pleasingly, the symmetry of the crystal lends itself to the cluster imposing it with perfect O_h symmetry. Interatomic distances and angles for the molecular $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ (X = Cl, Br, I) clusters in these Cs-containing phases are summarized in Table 8. Other than the expected increase in Re–X bond distance with increasing halide radius, the clusters do not exhibit any statistically meaningful geometric differences. A comparison of $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ and $[\text{Re}_6\text{Se}_8\text{X}_6]^{4-}$ (X = Cl, I; Tables 7 and 8) reveals that the expected differences due to the longer Re–Se bonds are accompanied by a subtle isotropic expansion of the Re_6 octahedron.

Enumeration of $[\text{M}_6\text{Q}_8]$ Framework Connectivities. The $\text{Re}_6\text{Q}_8\text{Cl}_2$ (Q = S, Se) parent frameworks and their dimensionally reduced offspring all share a number of defining attributes. All are composed of $[\text{Re}_6\text{Q}_8]^{2+}$ core units with six Re apices capped by one of three different types of outer ligands: a Q atom internal to a neighboring core ($\text{Q}^{\text{a-1}}$), a bridging halide atom linking it to the apex of a neighboring core ($\text{X}^{\text{a-2}}$), or a terminal halide atom (X^{a}). Furthermore, in a given framework, all cores display an identical coordination environment. Under these constraints, it is a simple matter to enumerate the possible framework connectivities. A compilation of the 28 possibilities for general $[\text{M}_6\text{Q}_8]$ cluster frameworks is set forth in Table 9, along with some structurally proven examples.^{3,6,8,10,13,36,37,46–49} As one scans the table from top to bottom, the connectedness of the framework decreases from a maximum of 12 (with each core engaged in six rhombic M_2Q_2 linkages) down to 0. The

(46) (a) Potel, M.; Gougeon, P.; Chevrel, R.; Sergent, M. *Rev. Chim. Mineral.* **1984**, *21*, 509. (b) Bars, O.; Guillevic, J.; Grandjean, D. *J. Solid State Chem.* **1973**, *6*, 48. (c) Guillevic, J.; Lestrat, H.; Grandjean, D. *Acta Crystallogr.* **1976**, *B32*, 1342. (d) Perrin, C.; Chevrel, R.; Sergent, M. *Mater. Res. Bull.* **1979**, *14*, 1505.

(47) (a) Perrin, C.; Sergent, M.; Le Traon, F.; Le Traon, A. *J. Solid State Chem.* **1978**, *25*, 197. (b) Bateman, I. R.; Blount, J. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1082. (c) Simon, A.; von Schnering, H. G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1967**, *355*, 295. (d) Imoto, H.; Corbett, J. D. *Inorg. Chem.* **1980**, *19*, 1241.

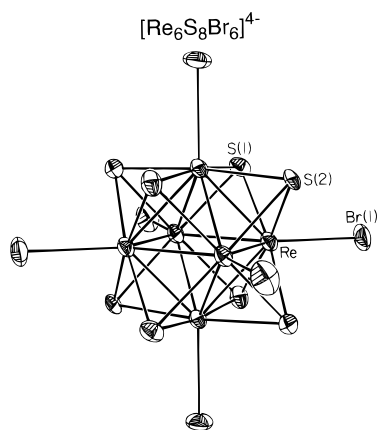
(48) Franolic, J. D.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 8139.

(49) (a) Perrin, A.; Leduc, L.; Potel, M.; Sergent, M. *Mater. Res. Bull.* **1990**, *25*, 1227. (b) Fedorov, V. E.; Mishchenko, A. V.; Kolesov, B. A.; Gubin, S. P.; Slovokhotov, Y. L.; Struckhov, Y. T. *Soviet. J. Coord. Chem.* **1985**, *11*, 980. (c) Leduc, L.; Perrin, A.; Sergent, M.; Le Traon, F.; Pilet, J. C.; Le Traon, A. *Mater. Lett.* **1985**, *3*, 209.

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for $\text{Tl}_5\text{Re}_6\text{Se}_8\text{Cl}_7$, $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$, and $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ ^b

	$\text{Tl}_5\text{Re}_6\text{Se}_8\text{Cl}_7^a$	$\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$	$[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ ^b
Re–Re	2.609(2)–2.619(2)	2.617(4)–2.635(4)	2.616(2)–2.632(2)
mean	2.614(5)	2.625(5)	2.624(6)
Re–Se	2.520(4)–2.526(3)	2.505(6)–2.534(7)	2.494(3)–2.515(3)
mean	2.523(3)	2.519(7)	2.506(5)
Re–X	2.431(8)	2.779(5)–2.801(5)	2.768(3)–2.777(3)
mean		2.793(8)	2.773(4)
Re–Re–Re ^c	59.7(1)–60.1(1)	59.7(1)–60.4(1)	59.7(1)–60.3(1)
mean	60.0(2)	60.0(2)	60.0(2)
Re–Re–Re ^d	90.0(1)	89.7(1)–90.2(1)	89.5(1)–90.5(1)
mean		90.0(2)	90.0(4)
Re–Re–Se	58.7(1)–59.0(1)	58.1(2)–58.9(2)	58.0(1)–58.8(1)
mean	58.8(1)	58.6(2)	58.4(2)
Re–Re–X	133.4(2)–136.6(2)	131.1(1)–139.0(1)	133.6(1)–136.8(1)
mean	135(1)	135(2)	135(1)
Re–Se–Re	62.3(1)–62.5(1)	62.4(2)–63.1(2)	62.9(1)–63.5(1)
mean	62.4(1)	62.8(2)	63.1(2)
Se–Re–Se	89.7(1)–90.2(1)	89.1(2)–90.8(2)	89.4(1)–90.5(1)
mean	90.0(2)	89.9(5)	89.9(3)
Se–Re–X	90.7(2)–92.8(2)	87.1(2)–96.2(2)	90.1(1)–93.7(1)
mean	91(1)	92(2)	92(1)

^a Reference 13. ^b From $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]\cdot 2\text{Me}_2\text{CO}$. ^c Within triangular faces. ^d Within equatorial squares.

**Figure 9.** Structure of the discrete $[\text{Re}_6\text{S}_8\text{Br}_6]^{4-}$ cluster in $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$ (50% probability ellipsoids). The cluster resides on a $\bar{3}$ symmetry site, with atom S(2) on the 3-fold rotation axis.**Table 8.** Selected Interatomic Distances (Å) and Angles (deg) for $\text{Cs}_5\text{Re}_6\text{S}_8\text{Cl}_7$, $\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$, and $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$

	$\text{Cs}_5\text{Re}_6\text{S}_8\text{Cl}_7$	$\text{Cs}_5\text{Re}_6\text{S}_8\text{Br}_7$	$\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$
Re–Re	2.594(2)–2.559(2)	2.593(3)–2.599(2)	2.607(3)
mean	2.597(3)	2.596(3)	
Re–S	2.395(6)–2.404(10)	2.380(12)–2.407(13)	2.408(11)
mean	2.399(3)	2.397(10)	
Re–X	2.421(10)	2.596(6)	2.780(5)
Re–Re–Re ^a	59.9(1)–60.1(1)	59.9(1)–60.1(1)	60.0(1)
mean	60.0(1)	60.0(1)	
Re–Re–Re ^b	90.0(1)	90.0(1)	90.0(1)
Re–Re–S	57.1(2)–57.3(1)	56.7(3)–57.6(2)	57.2(2)
mean	57.2(1)	57.2(3)	
Re–Re–X	133.8(2)–136.2(2)	133.5(2)–136.5(1)	135.0(1)
mean	135.0(9)	135(1)	
Re–S–Re	63.3(3)–65.7(2)	65.3(4)–65.8(3)	65.6(4)
mean	65.5(1)	65.6(2)	
S–Re–S	89.7(2)–89.9(2)	89.4(3)–90.2(3)	89.8(1)
mean	89.8(1)	89.8(3)	
S–Re–X	92.3(3)–94.6(2)	92.1(3)–94.8(2)	93.4(2)
mean	93.4(9)	93(1)	

^a Within triangular faces. ^b Within equatorial squares.

corresponding trend in the dimensionality of structured examples is much less unwavering.⁵⁰

(50) Note that, for reasons analogous to those explained above for simple metal–anion frameworks, the connectivity formulation dictates the connectedness, but *not* the dimensionality, of the cluster framework.

Excluding the two end points M_6Q_8 and $\text{M}_6\text{Q}_8\text{X}_6$, all of the stoichiometries in Table 9 have at least two possible connectivity formulations available. From the list of examples, we see that in three cases ($\text{M}_6\text{Q}_8\text{X}_2$, $\text{M}_6\text{Q}_8\text{X}_3$, and $\text{M}_6\text{Q}_8\text{X}_4$) more than one of these structural isomers has been realized experimentally. What drives a cluster framework to choose one connectivity over another? The present work may help shed some light on this difficult issue. Cluster systems in which all eight of the core Q atoms are chalcogenides display a pronounced tendency to form rhombic M_2Q_2 connections directly between cores. On the other hand, systems with eight halide atoms in the core never employ this connectivity mode, relying strictly upon outer halide bridges.⁵¹ Apparently, the negative charge of a chalcogenide atom is sufficient (or even prefers) to support a μ_4 bridging environment with four surrounding, positively-charged metal centers, whereas the lesser negative charge of a halide atom is not. The absence of direct core linkages in mixed-core phases of the type $\text{Re}_6\text{Q}_{8-n}\text{X}_{2+2n}$ (Q = S, Se; X = Cl, Br; $n = 1, 2, 3, 4$) is perhaps attributable to the ease of disorder of the core anions, due to their similarity in size. Finally, among phases of the type $\text{M}'_n\text{Re}_6\text{Q}_8\text{X}_{2+n}$ ($\text{M}' = \text{Cs}, \text{Tl}$; Q = S, Se; X = Cl, Br, I; $n = 0, 1, 2, 4, 5, 6$), there exists an occasional preference of the softer halides for bridging ($\text{X}^{\text{a-a}}$) over terminal (X^{a}) ligand roles. Instances of such behavior are evident in the structures of $\text{Re}_6\text{Se}_8\text{Cl}_2$ and $\text{Re}_6\text{Q}_8\text{Br}_2$, as well as $\text{TlRe}_6\text{Se}_8\text{Cl}_3$ and $\text{CsRe}_6\text{Se}_8\text{I}_3$.

Solution Chemistry. Successful demonstration of the dimensional reduction of $\text{Re}_6\text{S}_8\text{Cl}_2$ and $\text{Re}_6\text{Se}_8\text{Cl}_2$ type frameworks is punctuated by the establishment of their solution-phase analogues. The compounds $\text{Cs}_5\text{Re}_6\text{S}_8\text{X}_7$ (X = Cl, Br) and $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$ readily dissolve in aqueous acid to give a bright yellow or yellow-orange solution. The solutions are made alkaline to prevent core protonation (*vide infra*), and the clusters precipitated by addition of excess $(\text{Bu}_4\text{N})\text{X}$ (X = Cl, Br, I). The solids, which are highly soluble in acetonitrile and dichloromethane, are collected from the filtration apparatus by dissolution in acetonitrile and reduction to dryness. Recrystallization from a mixture of acetone and toluene affords the soluble molecular products $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$, $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Br}_6]\cdot\text{H}_2\text{O}$, and $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{I}_6]\cdot\text{H}_2\text{O}$. The crystal structures of these products confirm retention of the $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ cluster in solution.

(51) This observation is true only of $[\text{M}_6\text{X}_8]$ cluster frameworks, and does not extend to $[\text{M}_6\text{X}_{12}]$ cluster systems in which the core halides are edge-bridging (μ_2).

Table 9. Possible Connectivities for [M₆Q₈] Cluster Frameworks and Some Structurally Proven Examples

formula	framework connectivity	conn ^a	examples ^b	ref
M ₆ Q ₈	[M ₆ Q ₂ Q ^{i-a} _{6/2}]Q ^{a-i} _{6/2}	12	Mo ₆ Q ₈ , PbMo ₆ Se ₈ , Mo ₆ S ₆ Br ₂ (3-D)	46
M ₁₂ Q ₁₆ X	[M ₆ Q ₃ Q ^{i-a} _{5/2}]Q ^{a-i} _{5/2} X ^{a-a} _{1/2}	11		
M ₆ Q ₈ X	[M ₆ Q ₃ Q ^{i-a} _{5/2}]Q ^{a-i} _{5/2} X ^a	10		
	[M ₆ Q ₄ Q ^{i-a} _{4/2}]Q ^{a-i} _{4/2} X ^{a-a} _{2/2}	10		
M ₁₂ Q ₁₆ X ₃	[M ₆ Q ₄ Q ^{i-a} _{4/2}]Q ^{a-i} _{4/2} X ^a X ^{a-a} _{1/2}	9		
	[M ₆ Q ₅ Q ^{i-a} _{3/2}]Q ^{a-i} _{3/2} X ^{a-a} _{3/2}	9		
M ₆ Q ₈ X ₂	[M ₆ Q ₄ Q ^{i-a} _{4/2}]Q ^{a-i} _{4/2} X ^{a2}	8	Re ₆ Se ₈ Cl ₂ (2-D)	6
	[M ₆ Q ₅ Q ^{i-a} _{3/2}]Q ^{a-i} _{3/2} X ^{a-a} _{2/2}	8		
	[M ₆ Q ₆ Q ^{i-a} _{2/2}]Q ^{a-i} _{2/2} X ^{a-a} _{4/2}	8	Re ₆ S ₈ X ₂ , Re ₆ Se ₈ Br ₂ (3-D)	10
M ₁₂ Q ₁₆ X ₅	[M ₆ Q ₅ Q ^{i-a} _{3/2}]Q ^{a-i} _{3/2} X ^a X ^{a-a} _{1/2}	7		
	[M ₆ Q ₆ Q ^{i-a} _{2/2}]Q ^{a-i} _{2/2} X ^a X ^{a-a} _{3/2}	7		
	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^{a-a} _{5/2}	7		
M ₆ Q ₈ X ₃	[M ₆ Q ₅ Q ^{i-a} _{3/2}]Q ^{a-i} _{3/2} X ^{a3}	6	TlRe ₆ Se ₈ Cl ₃ (2-D)	13
	[M ₆ Q ₆ Q ^{i-a} _{2/2}]Q ^{a-i} _{2/2} X ^{a2} X ^{a-a} _{2/2}	6	CsRe ₆ Se ₈ I ₃ (2-D)	
	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^a X ^{a-a} _{4/2}	6		
	[M ₆ Q ₈]X ^{a-a} _{6/2}	6	Li ₄ Re ₆ S ₁₁ , Re ₆ Q ₇ Br ₄ , ^c Mo ₆ SeCl ₁₀ , Nb ₆ I ₁₁ , CsNb ₆ I ₁₁ (3-D)	3, 37a, 47
M ₁₂ Q ₁₆ X ₇	[M ₆ Q ₆ Q ^{i-a} _{2/2}]Q ^{a-i} _{2/2} X ^{a3} X ^{a-a} _{1/2}	5		
	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^{a2} X ^{a-a} _{3/2}	5		
	[M ₆ Q ₈]X ^a X ^{a-a} _{5/2}	5		
M ₆ Q ₈ X ₄	[M ₆ Q ₆ Q ^{i-a} _{2/2}]Q ^{a-i} _{2/2} X ^{a4}	4	Tl ₂ Re ₆ Q ₈ Cl ₄ , Cs ₂ Re ₆ Se ₈ X ₄ (1-D)	13
	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^{a3} X ^{a-a} _{2/2}	4		
	[M ₆ Q ₈]X ^{a2} X ^{a-a} _{4/2}	4	Re ₆ Se ₆ Cl ₆ , Mo ₆ Cl ₁₂ , W ₆ I ₁₂ (2-D)	3, 36a, 48
M ₁₂ Q ₁₆ X ₉	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^{a4} X ^{a-a} _{1/2}	3		
	[M ₆ Q ₈]X ^{a3} X ^{a-a} _{3/2}	3		
M ₆ Q ₈ X ₅	[M ₆ Q ₇ Q ^{i-a} _{1/2}]Q ^{a-i} _{1/2} X ^{a5}	2		
	[M ₆ Q ₈]X ^{a4} X ^{a-a} _{2/2}	2	Re ₆ S ₅ Cl ₈ , NaMo ₆ Cl ₁₃ (1-D)	8a, 36b
M ₁₂ Q ₁₆ X ₁₁	[M ₆ Q ₈]X ^{a5} X ^{a-a} _{1/2}	1		
M ₆ Q ₈ X ₆	[M ₆ Q _b]X ^{a6}	0	Tl ₅ Re ₆ Q ₈ Cl ₇ , Cs ₅ Re ₆ S ₈ X ₇ , Cs ₆ Re ₆ S ₈ I ₈ , Cs ₄ Re ₆ Se ₈ I ₆ , Re ₆ Q ₄ Cl ₁₀ , KRe ₆ Se ₅ Cl ₉ , RbRe ₆ S ₅ Cl ₉ , A ₁₀ M ₆ S ₁₄ , ^d PbMo ₆ X ₁₄ ^e (0-D)	8b, 13, 36c, 37b, 49

^a Framework connectedness. ^b Q = S, Se; X = Cl, Br. ^c Complete structural details have not been published. ^d A = Rb, Cs; M = Tc, Re. ^e X = Cl, Br, I.

Table 10. Selected Interatomic Distances (Å) and Angles (deg) for [Re₆S₈X₆]⁴⁻ (X = Cl, Br, I)

	[Re ₆ S ₈ Cl ₆] ⁴⁻ ^a	[Re ₆ S ₈ Br ₆] ⁴⁻ ^b	[Re ₆ S ₈ I ₆] ⁴⁻ ^c
Re—Re	2.597(2)—2.609(2)	2.583(3)—2.608(3)	2.592(4)—2.608(3)
mean	2.601(4)	2.594(7)	2.599(5)
Re—S	2.387(8)—2.418(8)	2.368(15)—2.421(13)	2.369(16)—2.432(14)
mean	2.403(9)	2.396(12)	2.40(2)
Re—X	2.448(10)—2.457(9)	2.579(6)—2.606(6)	2.781(5)—2.790(6)
mean	2.451(4)	2.595(10)	2.786(3)
Re—Re—Re ^d	59.8(1)—60.2(1)	59.6(1)—60.4(1)	59.8(1)—60.3(1)
mean	60.0(1)	60.0(2)	60.0(1)
Re—Re—Re ^e	89.9(1)—90.1(1)	89.8(1)—90.2(1)	89.9(1)—90.1(1)
mean	90.0(1)	90.0(1)	90.0(1)
Re—Re—S	56.9(2)—57.6(2)	56.5(4)—58.1(3)	56.4(4)—58.1(3)
mean	57.2(2)	57.2(4)	57.3(4)
Re—Re—X	132.8(2)—137.1(2)	132.3(2)—137.6(2)	133.0(1)—136.8(2)
mean	135(1)	135(1)	135(1)
Re—S—Re	65.2(2)—65.9(2)	64.9(3)—66.1(4)	64.7(4)—66.4(3)
mean	65.5(2)	65.5(3)	65.5(4)
S—Re—S	89.2(3)—90.2(3)	88.8(5)—90.6(5)	88.5(6)—90.9(5)
mean	89.8(3)	89.8(5)	89.8(6)
S—Re—X	91.7(3)—95.2(3)	91.4(4)—95.5(3)	91.2—95.2
mean	93(1)	93(1)	93(1)

^a From (Bu₄N)₄[Re₆S₈Cl₆]. ^b From (Bu₄N)₄[Re₆S₈Br₆]·H₂O. ^c From (Bu₄N)₄[Re₆S₈I₆]·H₂O. ^d Within triangular faces. ^e Within equatorial squares.

Interatomic distances and angles are summarized in Table 10; comparison with their solid-state precursors (Table 8) does not reveal any meaningful differences in cluster geometry. Cs₄-Re₆Se₈I₆ dissolves in aqueous HI to yield a bright red solution. Basifying the solution with KOH results in a color change to yellow. Preliminary experimentation suggests that the change is due to a complete exchange of OH⁻ for terminal I⁻ ligands, to give the cluster [Re₆Se₈(OH)₆]⁴⁻. Although the exchange curtails a direct preparation of [Re₆Se₈I₆]⁴⁻, this species should be readily accessible by reaction of its protonated form ([Re₆Se₇(SeH)I₆]³⁻, described below) with an appropriate sterically hindered base. No evidence of a similar ligand substitution was observed for the [Re₆S₈X₆]⁴⁻ (X = Cl, Br) cluster

analogues; however, such an exchange might partially account for the low yields attained in preparing (Bu₄N)₄[Re₆S₈I₆]·H₂O.

Treatment of [Re₆S₈X₆]⁴⁻ (X = Cl, Br, I) with acid in a nonaqueous solvent such as acetonitrile reversibly protonates the cluster cores in accordance with the following formal reaction.



The protonation, which may be accomplished using HX, as well as a variety of other anhydrous acids, induces an immediate color change to red (X = Cl, Br) or red-brown (X = I). The color change is never observed in aqueous solutions, implying

Table 11. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{Re}_6\text{S}_7(\text{SH})\text{X}_6]^{3-}$ (X = Cl, Br, I)

	$[\text{Re}_6\text{S}_7(\text{SH})\text{Cl}_6]^{3-}$ ^a	$[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6]^{3-}$ ^b	$[\text{Re}_6\text{S}_7(\text{SH})\text{I}_6]^{3-}$ ^c
Re—Re	2.591(2)–2.608(2)	2.593(2)–2.606(2)	2.597(3)–2.612(3)
mean	2.599(5)	2.600(4)	2.604(5)
Re—S	2.377(7)–2.424(6)	2.381(10)–2.248(9)	2.378(13)–2.412(10)
mean	2.407(11)	2.403(10)	2.398(9)
Re—X	2.413(6)–2.429(8)	2.554(4)–2.577(4)	2.753(4)–2.763(3)
mean	2.419(6)	2.568(9)	2.759(4)
Re—Re—Re ^d	59.7(1)–60.3(1)	59.8(1)–60.3(1)	59.8(1)–60.3(1)
mean	60.0(2)	60.0(1)	60.0(2)
Re—Re—Re ^e	89.7(1)–90.3(1)	89.6(1)–90.4(1)	89.5(1)–90.5(1)
mean	90.0(2)	90.0(2)	90.0(4)
Re—Re—S	56.5(2)–57.9(1)	56.7(2)–57.9(2)	56.6(3)–57.7(3)
mean	57.3(3)	57.3(3)	57.1(3)
Re—Re—X	133.2(1)–136.8(2)	132.6(1)–137.4(1)	133.0(1)–136.8(1)
mean	135(1)	135(1)	135(1)
Re—S—Re	64.7(2)–66.0(2)	64.9(2)–65.9(2)	65.4(3)–66.1(3)
mean	65.4(3)	65.5(2)	65.7(3)
S—Re—S	89.1(2)–90.4(2)	88.7(3)–90.5(3)	89.1(4)–90.4(4)
mean	89.8(4)	89.8(4)	89.8(4)
S—Re—X	91.4(2)–95.4(2)	90.9(3)–95.6(3)	91.7–95.5
mean	93.3(9)	93(1)	94(1)

^a From $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Cl}_6]$. ^b From $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6] \cdot 2\text{Me}_2\text{CO}$. ^c From $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{I}_6] \cdot 2\text{Me}_2\text{CO}$. ^d Within triangular faces. ^e Within equatorial squares.

that $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ is a weaker base than H_2O . The reagents SOX_2 (X = Cl, Br) provide a useful means of generating HX while simultaneously removing any unwanted water. The presence of three $(\text{Bu}_4\text{N})^+$ cations in the crystal structures of the protonated products $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Cl}_6]$, $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6] \cdot 2\text{Me}_2\text{CO}$, and $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{I}_6] \cdot 2\text{Me}_2\text{CO}$ indicates that just one proton is associated with each cluster. The geometric details from these structures are reported in Table 11. Comparison with the unprotonated cluster (Table 10) exposes a slight shortening in the Re—X bond lengths—consistent with the increase in overall core charge—as the only noteworthy difference.⁵² When precipitated with $(\text{Bu}_4\text{N})\text{I}$ from an acidic aqueous solution of $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$, the $[\text{Re}_6\text{Se}_8\text{I}_6]^{4-}$ cluster protonates under similar conditions, ultimately affording crystalline black $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6] \cdot 2\text{Me}_2\text{CO}$. Interatomic distances and angles for the structure of the latter are included in Table 7.

In solution, electronic absorption spectra (Figure 10) provide a clear means of distinguishing the protonated and unprotonated cluster species. Note the correspondence between peaks in the spectra of the chloride- and bromide-ligated clusters: the positions of the latter are slightly red-shifted from those of the former. Although the peaks are not as well resolved, this trend in band shifts may be extrapolated to the iodide-ligated clusters (*e.g.*, $\lambda_{\text{max}} = 434, 443,$ and 507 nm for $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ with X = Cl, Br, and I, respectively), indicating that the bands are likely due to halide ligand-to-metal charge transfer. A spectrophotometric titration of $[\text{Re}_6\text{S}_8\text{Br}_6]^{4-}$ with anhydrous perchloric acid in acetonitrile confirmed the uptake of no more than one proton per cluster. Further, titration of $[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6]^{3-}$ with triethylamine in acetonitrile allowed its $\text{p}K_{\text{a}}$ to be estimated at 20 (the $\text{p}K_{\text{a}}$ of Et_3NH^+ in acetonitrile is 18.5).⁵³ Thus, consistent with their high negative charge, these clusters exhibit considerable basicity in aprotic solvents such as acetonitrile. Indeed, yellow acetonitrile or dichloromethane solutions of $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ (X = Cl, Br) gradually turn red over the course of 1 or 2 days when exposed to air (H_2O and CO_2). In water, on the other hand, the clusters are not demonstrably basic (presumably due to the inability of a protonated cluster to act as a hydrogen-bond

(52) The absence of any metric differences in S atom coordination is not surprising, since the core proton could not be located in any of these structures and is almost certainly disordered over all eight possible sites.

(53) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005.

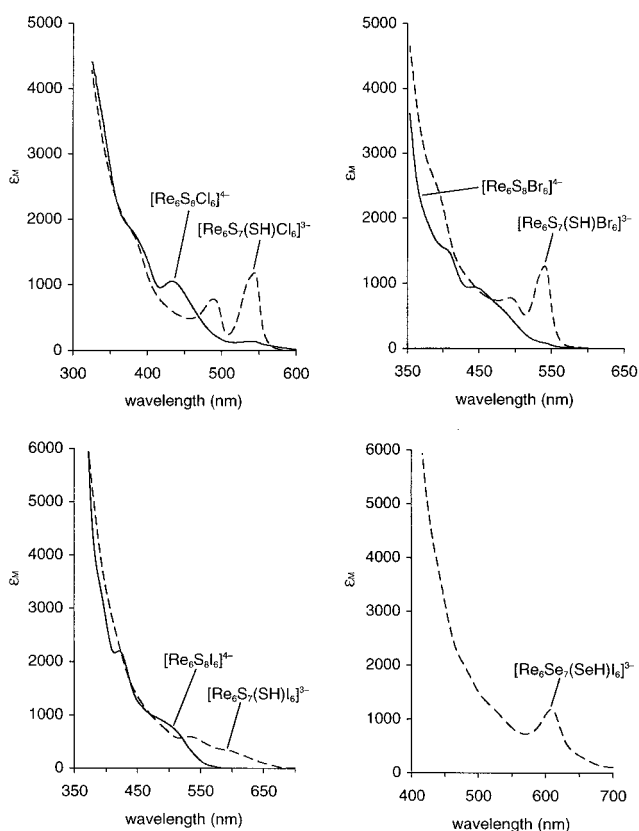


Figure 10. Absorption spectra for acetonitrile solutions of $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ (solid line) compared with $[\text{Re}_6\text{S}_7(\text{SH})\text{X}_6]^{3-}$ (dashed line) and $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$.

donor), and their solutions remain yellow in air for periods of >3 months. The cyclic voltammetry of the $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ (X = Cl, Br) clusters in acetonitrile reveals a reversible one-electron oxidation wave at $E_{1/2} = +0.27$ and $+0.31$ V, respectively, and remarkably similar voltammograms are observed for solutions of their protonated analogues. Direct characterization of the SH moiety in $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7(\text{SH})\text{Br}_6] \cdot 2\text{Me}_2\text{CO}$ could not be elicited from either its ^1H NMR (CD_3CN ; no evidence for paramagnetism) or infrared (KBr) spectra.

There exists scant precedent in metal–chalcogenide cluster chemistry for core protonation reactions of the type established

here. The most closely related examples involve the reversible uptake of a single proton by the cubane clusters $[\text{Fe}_4\text{Q}_4(\text{Q}'\text{R})_4]^{2-}$ ($\text{Q}, \text{Q}' = \text{S}, \text{Se}$) in aqueous solution.⁵⁴ Fully protonated cubanes $[\text{M}_4(\text{SH})_4(\text{CO})_{12}]$ ($\text{M} = \text{Mn}, \text{Re}$) have also been reported, but were not demonstrated to undergo deprotonation.⁵⁵ Otherwise, there are only a few dinuclear examples of relevance, and in these cases, protonation is generally accompanied by some rather severe structural changes.⁵⁶ Given the current level of reliance upon single-crystal X-ray diffraction techniques for characterizing new cluster compounds, it seems probable that there are other examples in which the protonation of a highly-charged anionic metal–chalcogenide cluster may have gone undetected. For instance, in light of the above results (as well as the synthetic procedures and means of characterization employed), it appears plausible that the ruby red cluster previously identified as $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$ ^{8a} might actually correspond to $[\text{Re}_6\text{S}_6(\text{SH})\text{Cl}_7]^{2-}$ formed by protonation of $[\text{Re}_6\text{S}_7\text{Cl}_7]^{3-}$ in acetonitrile upon exposure to air.

Summary

Many transition metal clusters have been exclusively attained in solid phases as integral components of extended covalent frameworks that are not amenable to breakup by means of conventional cluster excision techniques. Dimensional reduction, a general approach for deconstructing extended solid frameworks, is described in detail, and its effectiveness in liberating clusters from such environs is demonstrated by application to a number of intractable $[\text{Re}_6\text{Q}_8]^{2+}$ ($\text{Q} = \text{S}, \text{Se}$) core-containing phases. The following are the principal results and conclusions from this endeavor.

(1) The concept of dimensional reduction is exemplified in Figure 3 with the stepwise dismantling of a simple three-dimensional framework, MX_3 . Each additional equivalent of X incorporated in the structure serves to terminate the bridges in one dimension, resulting in two-dimensional sheets, one-dimensional chains, and ultimately, discrete molecules. The charge built up in this process is compensated by the simultaneous incorporation of cations, A, residing external to the anionic framework. Thus, the connectedness (and, less rigorously, the dimensionality) of a solid framework can be predictably reduced with the controlled insertion of AX. This formalistic approach may be used for targeting solid-state reaction products featuring lower-dimensional, less tightly-bound frameworks. Further, by replacing metal centers M with multinuclear cluster cores $[\text{M}_m\text{Q}_q]$, it is readily extended to include cluster-containing frameworks.

(2) Equation 6 summarizes the dimensional reduction of $\text{Re}_6\text{Se}_8\text{Cl}_2$ (Figure 2; this two-dimensional structure features rhombic Re_2Se_2 linkages of the type common to many intractable cluster phases) via incorporation of TiCl . As expected, the new phases encountered exhibit cluster frameworks of reduced connectedness and dimensionality: two-dimensional $[\text{Re}_6\text{Se}_8\text{Cl}_3]^{1-}$

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sheets, one-dimensional $[\text{Re}_6\text{Se}_8\text{Cl}_4]^{2-}$ chains, and discrete $[\text{Re}_6\text{Se}_8\text{Cl}_6]^{4-}$ clusters. Frameworks of the latter two types are also observed in the dimensional reduction of three-dimensional $\text{Re}_6\text{S}_8\text{Cl}_2$ (Figure 4) with TiCl .

(3) In pursuit of a directly soluble form of the $[\text{Re}_6\text{Se}_8]^{2+}$ cluster core, cesium halides were employed as dimensional reduction agents (eqs 7 and 8). The insoluble one-dimensional chain phases $\text{Cs}_2\text{Re}_6\text{Se}_8\text{X}_4$ ($\text{X} = \text{Cl}, \text{Br}$; Figure 6) are the sole cluster products with use of CsCl and CsBr . However, reactions with CsI enable isolation of two-dimensional $\text{CsRe}_6\text{Se}_8\text{I}_3$ (Figure 7) and, finally, the soluble molecular phase $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$ (Figure 8). A similar strategy permits synthesis of soluble phases containing the $[\text{Re}_6\text{S}_8]^{2+}$ core: $\text{Cs}_5\text{Re}_6\text{S}_8\text{X}_7$ ($\text{X} = \text{Cl}, \text{Br}$; Figure 9) and $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$.

(4) The possible connectivities for frameworks featuring $[\text{M}_6\text{Q}_8]$ clusters are enumerated in Table 9. Of the 28 possibilities, 10 have been observed, and three are unique to novel $[\text{Re}_6\text{Q}_8]^{2+}$ ($\text{Q} = \text{S}, \text{Se}$) core-containing phases described herein.

(5) The compounds $\text{Cs}_5\text{Re}_6\text{S}_8\text{X}_7$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{Cs}_6\text{Re}_6\text{S}_8\text{I}_8$ dissolve in aqueous base to afford yellow solutions of their respective $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ clusters. Addition of $(\text{Bu}_4\text{N})\text{X}$ yields the $(\text{Bu}_4\text{N})^+$ salts of these molecular clusters in solid forms conveniently soluble in polar organic solvents; selected cluster interatomic distances and angles resulting from the single-crystal X-ray analysis of each salt are set out in Table 10 for comparison. Rapid substitution of hydroxide for the terminal iodide ligands on the cluster prevents isolation of an analogous species from basic solutions of $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$.

(6) Yellow acetonitrile solutions of $[\text{Re}_6\text{S}_8\text{X}_6]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) react with anhydrous HX to give red solutions of the singly protonated clusters $[\text{Re}_6\text{S}_7(\text{SH})\text{X}_6]^{3-}$, as evidenced by spectrophotometric titrations, single-crystal X-ray structure determinations, and elemental analyses. The red-brown species $[\text{Re}_6\text{S}_7(\text{SeH})\text{I}_6]^{3-}$ is also obtained with an analogous workup of red, acidic aqueous solutions of $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$.

Results (2), (3), and (5) above clearly demonstrate the utility of the dimensional reduction approach (1) in deconstructing tightly-bound cluster frameworks and accessing their core components in soluble molecular form. With entry to $[\text{Re}_6\text{Q}_8]^{2+}$ core-containing clusters, their molecular chemistry can now be disclosed. Studies directed toward this end are in progress.

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Supporting Information Available: X-ray structural information for the compounds in Tables 3–5, including tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles (101 pages). Ordering information is given on any current masthead page.

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