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Chemistry of Hexanuclear Rhenium Chalcohalide Clusters

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I. Introduction

The synthesis of $\text{Re}_6\text{Q}_4\text{X}_{10}$ ($\text{Q} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}$)^{1,2} by Fedorov in 1971 and, 12 years later, the work of Leduc, Perrin and Sergent³ laid the foundation of an extensive high-temperature solid-state chemistry of hexanuclear rhenium chalcohalide clusters whose octahedral cores, $[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]^{(6-n)+}$ ($\text{Q} = \text{chalcogen}$, $\text{X} = \text{halogen}$, $n = 0–4$), are isostructural to the superconducting molybdenum chalcogenide analogues, the Chevrel–Sergent phases. The development of a molecular chemistry of their soluble cluster forms, whose inner core can only be prepared by high-temperature solid-state reactions, originates in the discovery, reported in 1987, of the solubility of $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ in ethanol.⁴

Today, the solution chemistry of hexanuclear rhenium chalcohalide clusters is in a stage of rapid development, an enhanced research activity driven by the opportunity to unravel the organic solution phase and redox chemistry of electron-rich mineral molecular forms and explore their substitution patterns and coordination chemistry which vary with the chalcogen/halogen ratio within the μ_3 -ligand shell surrounding the octahedral metal cluster core.

Sizing up and assessing this burgeoning field in the present review, we seek to provide a perspective on a fruitful symbiosis among solid-state chemistry, which focuses on structural aspects, the chemistry

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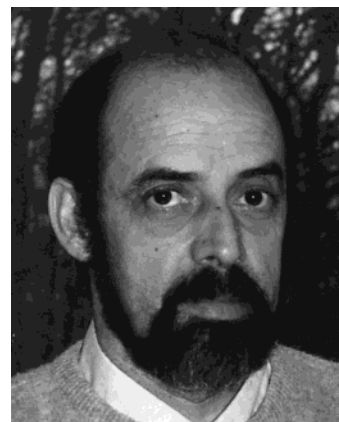
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Patrick Batail was born in 1947 and obtained his Doctorat d'Etat (Inorganic Chemistry) at the University of Rennes I in 1976 where he became Assistant-Délégué (1973–1977) and then Chargé de Recherche CNRS from 1977 to 1985. He was an IBM postdoctoral fellow from 1978 to 1980 at the IBM Research Laboratory in San Jose, CA, where he worked with Jerry B. Tarrance and Jim J. Mayerle on the neutral-to-ionic transition in TTF–chloranil. In 1985 he moved to the Laboratoire de Physique des Solides at the University of Paris-Sud at Orsay, France, to become Directeur de Recherche CNRS and create a molecular solid state chemistry group. In 1990 he also became Professeur Chargé de Cours at the Ecole Polytechnique in Palaiseau, France. In 1995 he moved to the Institut des Matériaux de Nantes, became its Director in 1998, and, following Jean Rouxel's sudden passing, went on to create a new CNRS Laboratory in 2000 (FRE 2068). His research interests concern the chemistry of molecular materials, especially long-range ordered hybrid solids whose collective conducting, magnetic, and optomagnetic properties are controlled by the nature of their organic–inorganic interface, the chemistry of organic solution soluble minerals, and lyotropic complex fluids with a mineral core. He has held visiting positions at the IBM Almaden Research Laboratory (1983), the Tokyo Institute of Technology (1989), and the Materials Research Laboratory at UCSB in 1996.



Jean-Christophe P. Gabriel was born in Saint Nazaire, France. He is a graduate of the Ecole Normale Supérieure (Paris) and of the University of Paris Sud (Orsay, France). He received his Ph.D. degree in 1993 under the supervision of P. Batail. His doctoral work dealt with the molecular chemistry of octahedral rhenium and their association within organic–inorganic materials, as well as with the study of some lyotropic liquid crystals with a mineral core. After a first postdoctoral stay supported by an E.U. Human Capital and Mobility fellowship at the Risø National Laboratory (Denmark) with Professor K. Bechgaard, he was awarded a Lavoisier postdoctoral fellowship from the French Foreign Office and spend two years at the Materials Research Laboratory of the University of California, Santa Barbara, CA, with Professor Anthony K. Cheetham. In 1996, he was appointed in the position of “Chargé de Recherche” from the Centre National de la Recherche Scientifique at the Institut des Matériaux de Nantes, Nantes, France. His current research interests are in the study of complex fluids with a mineral core and to their use in the synthesis of nanocomposite materials.



Kamal Boubekeur was born in Algiers, Algeria. He is a chemist engineer of the Ecole Supérieure de Chimie (Algiers) and a graduate of the University of Algiers (Doctorat 3ème cycle). His work dealt with the crystallographic studies of compounds of pharmaceutical interest. He served (1973–1985) at the University of Algiers as Assistant, then Maître-Assistant, and then Chargé de Cours. Simultaneously, he served (1985) as part time Chargé de Cours at the Ecole Nationale Polytechnique (Algiers). In 1985, he came in France and obtained a Ph.D. degree in 1989 from University of Rennes I where he has been also appointed guest Assistant Professor. His doctoral work with Patrick Batail shifted toward the synthesis, the crystal chemistry, and the electronic properties of radical cation salts of chalcogenide rhenium clusters. He then obtained a tenure position as Maître de Conférences in 1989 at the University of Paris XI, Orsay, France, where he joined the research group of Dr. Patrick Batail at the Laboratoire de Physique des Solides. After one year (1995) spent as Research Associate at the Centre National de la Recherche Scientifique, he moved to the Institut des Matériaux de Nantes at the University of Nantes where he is currently Maître de Conférences. His research interests include hybrid organic–inorganic materials, with focus on synthetic and structural chemistry of transition metal molecular ions and redox-active molecules based materials exhibiting electrical and magnetic properties.



Santiago Uriel was born in Madrid, Spain. He received his Ph.D. in 1992 from Zaragoza University, where he studied the synthesis of new (aminomethyl)tetrathiafulvalenes derivatives, under the direction of Dr. J. Garín. He spent two years (1993–1994) as a postdoctoral fellow with Dr. P. Batail under the E.U. Human Capital and Mobility Program at Laboratoire de Physique des Solides of the University of Paris XI (Orsay, France) and followed the group as Research Associate (1995) at the Centre National de la Recherche Scientifique at the Institut des Matériaux de Nantes. He worked in molecular chemistry of octahedral rhenium clusters and their association within organic–inorganic hybrid materials. He joined the research group of Dr. R. Llusa in 1997 at the Inorganic–Organic Chemistry Department at the University of Castellón. His research interest involve heterometallic clusters synthesis, optical and electrochemical properties, and hybrid organic–inorganic materials with electrical and magnetic properties.

of organic solution soluble minerals,⁵ and synthetic methodologies and concepts of molecular inorganic chemistry, which altogether blend into one single chemistry at the organic–inorganic, solid-state–solution interface.

Part II travels through the entangled issues of phase formulations and structural principles, a journey guided by the concept of dimensionality in solid-state synthesis. Part III considers the cluster reactivity and molecular properties in organic solutions, and part IV singles out several current themes and serves to provide a perspective on promising area where developments are likely to continue to appear at a vigorous pace.

This review do not treat Bronger's seminal early work⁶ and does not seek to encompass the all of rhenium sulfide chemistry, where trinuclear and tetranuclear clusters are also found and which was surveyed in recent papers by Saito⁷ and others.⁸ Some of the early developments of the high-temperature cluster chemistry of octahedral chalcosalides of molybdenum(II) and rhenium(III) were reviewed in 1988 by Perrin and Sergent.⁹

II. Cluster Core Synthesis

A. First Insight

The first synthesis of a series of hexanuclear rhenium chalcosalide cluster compounds, formulated $\text{Re}_3\text{Q}_2\text{X}_5$ ($\text{Q} = \text{Se}, \text{X} = \text{Cl}, \text{Br}; \text{Q} = \text{Te}, \text{X} = \text{Br}$), was reported by Opalovskii and Fedorov et al.^{1,2} in 1971. The composition of these compounds was obtained by chemical analysis. Two synthetic pathways were explored which both involved the reduction of Re(IV) or Re(V) chalcogenides, either by gaseous halides ($\text{ReSe}_2 + \text{Cl}_2$ at 480°C ;¹⁰ $\text{ReSe}_2 + \text{Br}_2$, starting reaction temperature 580°C ; $\text{Re}_2\text{Te}_5 + \text{Br}_2$, starting reaction temperature as low as 70°C) or upon a redox reaction of Re(IV) diselenide with ReCl_3 or ReBr_3 at $700\text{--}720^\circ\text{C}$.

B. A Chalcosalide with an Octahedral 24-Electron Re_6 Cluster Core

The 24-electron octahedral cluster core was first identified in chalcosalide hexarhenium compounds in 1983 by Leduc, Perrin, and Sergent within $\text{Re}_6\text{Se}_8\text{Cl}_2$ (Figure 1).^{11,12} By this time, the success of partial substitution of molybdenum for rhenium atoms in Mo_6Q_8 ,¹³ as well as the discovery by Bronger of metal chalcogenides with an octahedral rhenium cluster, such as $\text{Na}_4\text{Re}_6\text{S}_{12}$,¹⁴ had led Sergent's group to search for chalcosalides with this hexanuclear core, hence Leduc's seminal thesis work defended in 1983 at the University of Rennes I.^{3,15,16} The latter reports a large number of the known structural types of chalcosalides with an octahedral rhenium cluster, all of which obtained by high-temperature solid-state redox reaction between Re^0 and Re^{V} . Typically, a mixture of stoichiometric amounts of Re powder, ReCl_5 , and Se (with a 10% excess of ReCl_5) is pressed into a pellet, sealed in a silica tube under ca. 10^{-5}

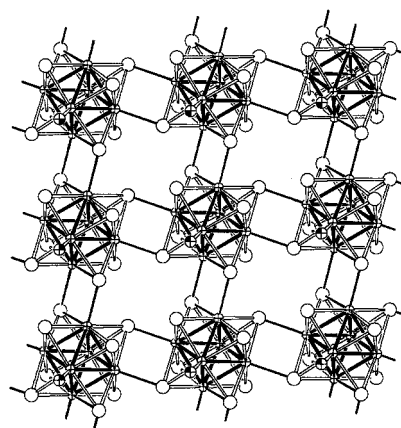


Figure 1. Projection of the 2-dimensional isomer of $\text{Re}_6\text{Se}_8\text{Cl}_2$, where a chalcosalide octahedral rhenium cluster was first revealed. Crossed, black-filled octant, and empty spheres represent Re , Cl , and Se atoms, respectively. The octahedral rhenium cluster as well as inter- $[\text{Re}_6\text{Se}_8]^{2+}$ core bonds are represented filled in black.

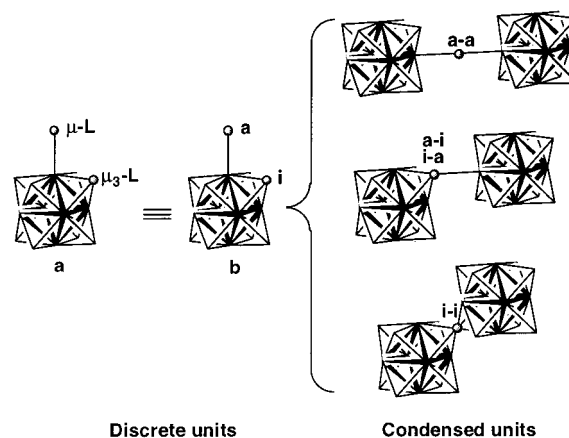


Figure 2. In Schäfer and von Schnering's notation, brackets designate the cluster core made out of 6 metal atoms forming the octahedral cluster and 8 inner ligands (μ_3) (the latter can be described as situated on the apex of a cube centered on the octahedral metal cluster), therefore labeled with a superscript "i". The outer/apical (*ausser* in German) ligands (μ) are not part of the core but are directly bonded to the metal atoms and, therefore, are listed outside the brackets and labeled with the superscript "a". Inner ligands that are also inner (μ_3 -) or outer (μ -) ligands for a neighboring core are indexed with a superscript "i-i" or "i-a", respectively. Outer ligands that are also inner or outer ligands for a neighboring core are indexed with the superscript "a-i" or "a-a", respectively.

Torr of residual pure argon, and then heated to 1300 K for 24 h.

Within the two-dimensional polymer, $\text{Re}_6\text{Se}_8\text{Cl}_2$, the monomeric unit is readily apparent and underlined using Schäfer and von Schnering's nomenclature (Figure 2),¹⁷ $[\text{Re}_6\text{Se}_4^{i-a}\text{Se}_{4/2}^{i-a}]\text{Cl}_2^a\text{Se}_{4/2}^{a-i}$. Thus, within the solid, $[\text{Re}_6\text{Se}_8]^{2+}$ cluster cores are linked by sharing four selenium ligands. The $\text{Re}\text{--}\text{Re}$ distances, which range from 2.727 to 2.665 Å , have been associated with a 24-electron cluster core consisting of $d^4\text{ Re(III)}$. Conductivity measurements performed on $\text{Re}_6\text{Se}_8\text{Cl}_2$, $\text{Re}_6\text{Se}_{8-x}\text{Te}_x\text{Cl}_2$ ($0 \leq x \leq 1$) and $\text{Re}_6\text{Se}_{8-x}\text{S}_x\text{Cl}_2$ ($0 \leq x \leq 1$) qualified these compounds as semiconductors.^{16,18}

C. A $[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]^{(6-n)+}$ Core with a Tunable Charge

In addition to the former 2D polymer, Leduc synthesized a series of compounds whose inner core may be formulated, $[\text{Re}_6\text{Se}_{4+n}\text{Cl}_{4-n}]^{(6-n)+}$, where halide ligands substitute for a fraction of the eight inner chalcogen atoms. All these compounds have an isostructural 24-electron Re_6 cluster core, but as a consequence of the exchange of a divalent chalcogen atom by a monovalent halide, their core charge may vary between $6+$ ($n = 0$) and $2+$ ($n = 4$). In the solid state one finds these motifs either isolated in discrete molecular forms, where each rhenium is capped by an apical, μ -ligand, or condensed into one-, two-, or three-dimensional polymers, where the motifs share one or several halogen and/or chalcogen "bridging" ligands, labeled "i-i", "a-a", "a-i", or "i-a", as exemplified in Figure 2.

D. Molecular Forms

1. Neutral

The single-crystal X-ray structure determination of $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ ^{3,15,19}—published in 1983 together with the unit cell of the isostructural phase $\text{Re}_6\text{S}_4\text{Br}_{10}$ —revealed the molecular structure of the group of compounds previously synthesized and formulated $\text{Re}_3\text{Q}_2\text{X}_5$ by Opalovskii, Fedorov, and co-workers. The structure of $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ at 153 K was also published independently by Fedorov and co-workers in 1984.^{20,21} Other members of the series, namely $\text{Re}_6\text{S}_4\text{Cl}_{10}$,^{22,23} $\text{Re}_6\text{Te}_4\text{Cl}_{10}$,²⁴ and $\text{Re}_6\text{Q}_4\text{Br}_{10}$ ($\text{Q} = \text{Se}, \text{Te}$),^{1,25} have since been reported. All these triclinic compounds are isostructural with two geometrically similar, independent molecules per unit cell (Figure 3a). As expected for compounds with discrete, noninteracting molecular motifs, $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ and $\text{Re}_6\text{S}_4\text{Br}_{10}$ are insulators.^{16,19} However, an unusual voltage-dependent phase transition was observed in the study of their dielectric constant versus temperature. In addition, Opalovskii and co-workers demonstrated that some of these phases react with hot 50% potassium hydroxide solution.² No further studies on these solutions have since been performed.

Another neutral molecular chalcogen halide with an octahedral rhenium cluster, namely, $[\text{Re}_6\text{Te}_6\text{Cl}_2]\text{Cl}_4^{2-}$ (TeCl_2)₂^a (Figure 3b), has been reported recently by Ibers and co-workers.²⁶ The set of six outer ligands includes 4 chlorine atoms and 2 TeCl_2 groups, the latter being linked to the rhenium atoms through the Te atom. It should be noted that tellurohalide TeX_2 ligands were known only in the gas phase as unstable species^{27,28} until Strähle ($\text{X} = \text{Br}$),²⁹ then Ibers' group ($\text{X} = \text{Cl}$),^{26,30} and Fedin and co-workers ($\text{X} = \text{I}$)³¹ were able to stabilize them on Re_4 cubane or Re_6 clusters. Another striking feature of this compound is that the six face-capping tellurium and two chlorine atoms are neatly ordered on the pseudocube surrounding the octahedral rhenium cluster. This unprecedented, precise registry of the eight mixed μ_3 -ligands is likely to be favored by the large difference in size of the halide and tellurium atoms.

2. Monoanions

The synthesis and first single-crystal X-ray structure determination of a molecular monoanion, $[\text{Re}_6\text{Q}_5\text{X}_9]^-$, was achieved by Leduc with $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ ^{3,15,32} (Figure 3c). The unit cell parameters of a series of $(\text{M}^+)[\text{Re}_6\text{Q}_5\text{X}_9]^-$ salts, based on the assignment of X-ray powder diffraction patterns, were also reported (Table 1). All these compounds were found to crystallize in the cubic $Pn\bar{3}$ space group and to be isostructural with $\text{M}^{2+}[\text{Mo}_6\text{X}_{14}]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$).³³ The structure is of the NaCl type with the Re_6 cluster anions located at the vertexes and at the center of the faces and the cations at both the center of the cell and the middle of the edges in the octahedral environment of the apical chlorine atoms of the six neighboring clusters. For a 1:1 stoichiometry, none of the accessible tetrahedral sites are occupied, as expected. A monoclinic distortion of this cubic structure has been identified from single-crystal X-ray diffraction data for $\text{Rb}[\text{Re}_6\text{S}_5\text{Cl}_9]$ ²³ (Figure 3d), $\text{K}[\text{Re}_6\text{S}_5\text{Br}_9]$,³⁴ and $\text{Rb}[\text{Re}_6\text{Se}_5\text{Cl}_9]$,³⁵ although $\text{Rb}[\text{Re}_6\text{S}_5\text{Cl}_9]$ and $\text{Rb}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ were first reported as being cubic from an analysis of the powder X-ray diffraction patterns.^{3,15,32} As expected, and similarly to $\text{Re}_6\text{Se}_4\text{Cl}_{10}$, $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ has been shown to be an electric insulator.¹⁶

Access to the organic solution chemistry of such mineral salts was demonstrated for the first time when $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ was found to be soluble in ethanol,⁴ leaving the all-inorganic molecular anion intact (cf. section III). Cation exchange with tetrabutylammonium chloride yields $(\text{Bu}_4\text{N}^+)[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$, which, in turn, is soluble in polar organic solvents. This prompted the synthesis of $\text{Rb}[\text{Re}_6\text{S}_5\text{Cl}_9]$ in order to prepare a soluble salt in the (Re, S, Cl) system.^{23,36}

3. Dianions

An increase by 1 equiv of chalcogen in the synthesis of the monoanionic cluster salts, together with the use of a divalent cation, led to a series of compounds formulated $(\text{M}^{2+})\{[\text{Re}_6\text{Q}_6\text{X}_2]\text{X}_6\}$ (Table 1). These compounds, first synthesized and reported by Leduc and co-workers ($\text{M} = \text{Cd}, \text{Pb}$; $\text{Q} = \text{Se}$; $\text{X} = \text{Cl}$)^{3,15} are isostructural to the cubic monoanion salts described above. Recently, it was reported that this structure is also obtained with other dications such as Zn^{2+} , Ca^{2+} , and Mg^{2+} in the (S, Cl) and (Se, Cl) systems.³⁷ A monoclinic distortion of the cubic structure, similar to the one described in the case of $(\text{M}^+)[\text{Re}_6\text{Q}_5\text{X}_9]^-$, is not observed for any of these hexanuclear rhenium clusters salts with dicationic metals.

Interestingly, these isostructural compounds present contrasted solubility properties. While a solvent able to dissolve the Cd^{2+} , Pb^{2+} , and Zn^{2+} salts has not been found, the Ca^{2+} and Mg^{2+} salts, which indeed were synthesized for that purpose, are readily soluble in a variety of organic solvents.³⁷ Thus, $[\text{Ca}(\text{H}_2\text{O})_7][\text{Re}_6\text{Q}_6\text{Cl}_8] \cdot 3\text{H}_2\text{O}$ ($\text{Q} = \text{S}, \text{Se}$), $[\text{Ca}(\text{H}_2\text{O})_8][\text{Re}_6\text{S}_6\text{Cl}_8]$, and $\text{Mg}(\text{H}_2\text{O})_6[\text{Re}_6\text{S}_6\text{Cl}_8] \cdot 2\text{H}_2\text{O}$ readily crystallize out of the organic phase containing even minute amounts of water and are found to be in turn soluble in water.³⁷

One should note that $\text{Cs}_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$ has been reported³ to crystallize in the hexagonal system and

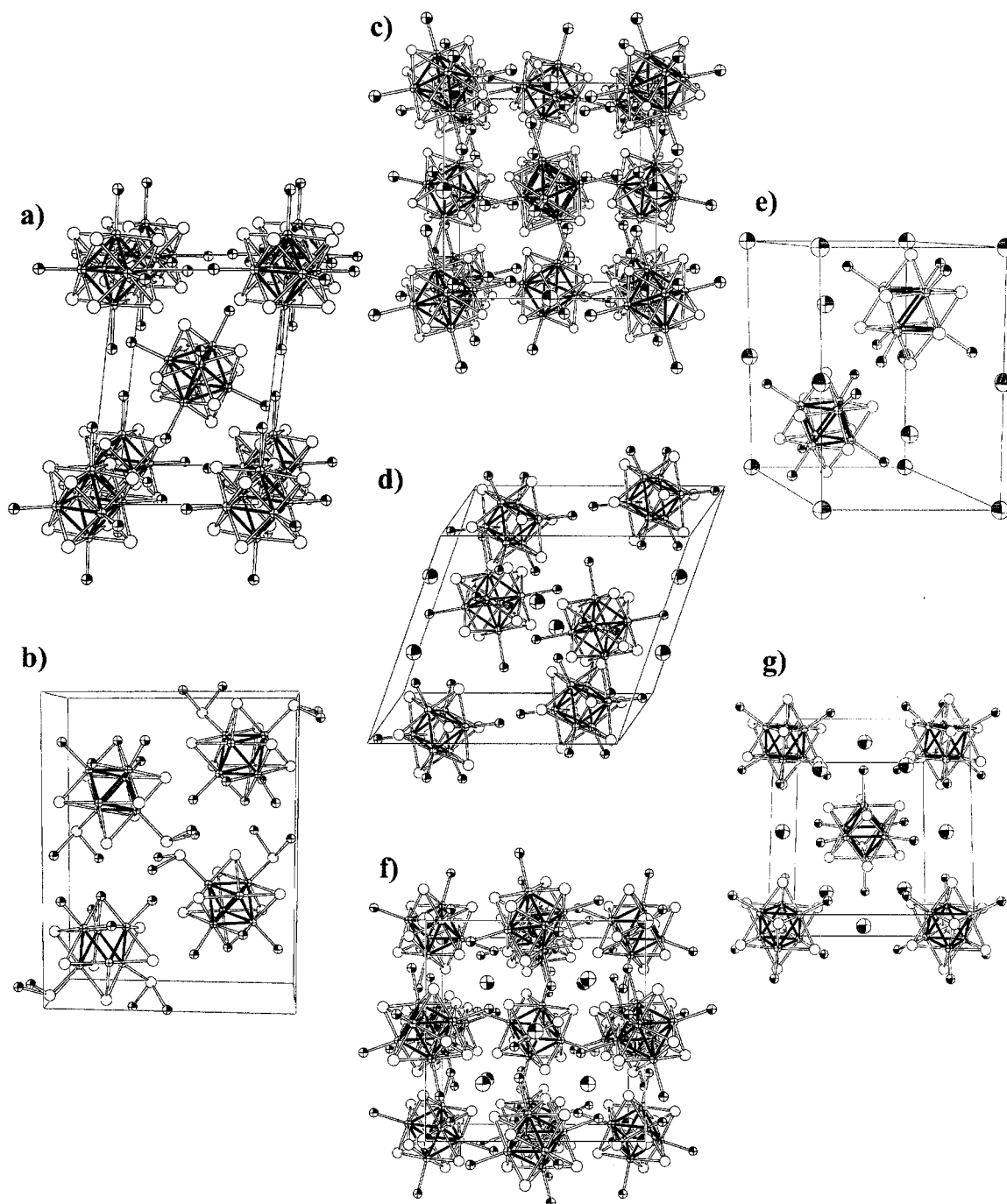


Figure 3. Unit cell content for the following compounds, all with discrete cluster motifs. (Empty and crossed atoms represent inner chalcogen or disordered chalcogen/halogen ligands and Re atoms, respectively; black-filled octant spheres represent apical or ordered inner halogen atoms as well as alkali-metal cations when present.). Key: (a) $\text{Re}_6\text{S}_4\text{Cl}_{10}$; (b) $\text{Re}_6\text{Te}_6\text{Cl}_6(\text{TeCl}_2)_2$; (c) $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$; (d) $\text{Rb}[\text{Re}_6\text{S}_5\text{Cl}_9]$; (e) $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$; (f) $\text{Rb}_5[\text{Re}_6\text{S}_6\text{Cl}_8][\text{Re}_6\text{S}_7\text{Cl}_7]$; (g) $\text{Cs}_3[\text{Re}_6\text{S}_7\text{Cl}_7]$.

to be isostructural to $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$ ³⁸ (Figure 3e) although the structure was never fully reported. In addition, the hypothetical phase $\text{K}_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ was postulated to have been formed as a soluble salt by reacting a mixture of Re_3Br_9 , PbS , and KBr at 550 °C.³⁹ The formula of this salt was proposed on the basis that $[\text{PPh}_4^+]_2[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ is obtained upon cation exchange with tetraphenylphosphonium halide. However, the authors did not rule out that the soluble inorganic salt could have been $\text{Pb}[\text{Re}_6\text{Se}_6\text{Br}_8]$. In that respect, a comparison of the X-ray powder pattern of the former raw material with that of $\text{K}_2[\text{Re}_6\text{S}_6\text{Br}_8]$, recently synthesized and characterized

by single-crystal X-ray diffraction,⁴⁰ could help clarify the present uncertainty.

Both the dianionic and trianionic molecular forms $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$ and $[\text{Re}_6\text{S}_7\text{Cl}_7]^{3-}$ were found to coexist in a 1:1 ratio in $\text{Rb}_5[\text{Re}_6\text{S}_6\text{Cl}_8][\text{Re}_6\text{S}_7\text{Cl}_7]$.²³ This was the first example in this chemistry of a ternary, mixed-cluster salt. This salt crystallizes in the cubic system $Pn\bar{3}$ with an arrangement similar to the cubic structure obtained for $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$, except that only the octahedral sites are filled in the latter whereas all octahedral as well as $3/4$ of the tetrahedral sites are occupied in $\text{Rb}_5[\text{Re}_6\text{S}_6\text{Cl}_8][\text{Re}_6\text{S}_7\text{Cl}_7]$ (Figure 3f). Thus, using Rb^+ , a fraction of the tetrahedral sites

Table 1. Molecular, Inorganic, Hexanuclear Rhenium Chalcogenide Clusters Obtained by High-Temperature Reactions

charge	compd	Schäfer's notation	structure determination	refs
4−	$M^I_4[Re_6Q_8Cl_6] \cdot M^I Cl$ ($M^I = Ti, Y = S, Se$; $M^I = Cs, Q = S$) $Cs_4[Re_6S_8Br_6] \cdot CsBr$ $Cs_4[Re_6S_8I_6] \cdot Cs_2I_2$ $Cs_4[Re_6Se_8I_6]$ $Cs_{2.87}K_{1.13}[Re_6S_8Cl_6]$	$n = 4: \{[Re_6Q_8^I]X_6^a\}^{4-}$	single crystal	45
	$Cs_3[Re_6S_7Cl_7]$		single crystal	46
	$Rb_3[Re_6S_7Br_7]$		single crystal	46
	$Rb_5[Re_6S_6Cl_8][Re_6S_7Cl_7]$		single crystal	46
3−	$Cs_2[Re_6Se_6Cl_8]$	$n = 3: \{[Re_6Q_7^I]X_6^a\}^{3-}$	single crystal	47
	$K_2[Re_6S_6Br_8]$		single crystal	43
	$Cd[Re_6Se_6Cl_8]$		single crystal	44a
2− and 3−	$Pb[Re_6Se_6Cl_8]$	$n = 2$ and 3	single crystal	23
2−	$M^{II}[Re_6Q_6Cl_6]$ ($M = Ca, Mg; Q = S, Se$)	$n = 2: \{[Re_6Q_6^I]X_6^a\}^{2-}$	not specified	3
	$Zn[Re_6S_6Cl_8]$		single crystal	40
	$K[Re_6Se_5Cl_9]$		powder	3
	$M^I[Re_6Se_5Cl_9]$ ($M = Li, Na, Rb, Cu, Ag$)		single crystal	15
	$Rb[Re_6Se_5Cl_9]$		single crystal	37
	$M^I[Re_6S_5X_9]$ ($M = Ag, X = Cl, Br$; $M = Rb, X = Cl$)	$n = 1: [Re_6Q_5^I]X_6^a\}^{-}$	single crystal	37
1−	$K[Re_6S_5Br_9]$		single crystal	15, 16, 32
	$Rb[Re_6S_5Cl_9]$		single crystal	3
	" $Re_3Se_2Br_5$ "		powder	3
	" $Re_3Se_2Cl_5$ "		single crystal	35
	" $Re_3Te_2Br_5$ "		powder	15
neutral	$Re_6S_4Cl_{10}$	$n = 0: [Re_6Q_4^I]X_6^a\}$	single crystal	34
	$Re_6Se_4Cl_{10}$		single crystal	23
	$Re_6Te_4Cl_{10}$		none	1, 2
	$Re_6S_4Br_{10}$		none	2
	$Re_6Q_4Br_{10}$ ($Q = S, Se, Te$)		none	2
	$[Re_6Te_6Cl_2][Cl_4(TeCl_2)_2]$		single crystal	23
	$[Re_6Te_8(TeBr_2)_6]Br_2$	$n = 2: [Re_6Q_6^I]X_6^a\}$	single crystal	15, 16, 19, 21
	$[Re_6Te_8(TeI_2)_6]I_2$	$n = 4: \{[Re_6Q_8^I] Z_6^a\}^a$	single crystal	24
2+			powder	15, 16, 19
			powder and single crystal	25
			single crystal	26
			single crystal	26
			single crystal	31

^a Z represents neutral ligands.

of the prototype cubic phase $K[Re_6Se_5Cl_9]$ must then be occupied or else the structure would collapse into the denser monoclinic arrangement described for $Rb[Re_6S_5Cl_9]$. Solid solutions, $M^{+}_{1+x}Re_6S_{4+x}Br_{10-2x}$ have been developed in the $M-Re-S-Br$ ($M = Na, K, Rb, Cs$) system.⁴¹

4. Trianions

The series of compounds¹⁵ with the formula $(M^{3+})_3\{[Re_6Q_7X]X_6\}^{3-}$ ($M = Cr, Mn, Fe, Co, Eu; Q = Se; X = Cl$) has been synthesized by Leduc, who did not ultimately ruled out an ambiguity in the oxidation state of the cation. This can be understood as Re metal is used in the synthesis, inducing a reductive atmosphere, prone to eventually reduce less electro-positive metal cations along the course of the reaction. Indeed, most characterization results obtained in our group on compounds obtained by this route point toward the occurrence of mixtures of M^{2+} and M^{3+} cluster salts in the final product.⁴² Hence, on the basis of the successful synthesis of $Cs_2[Re_6Se_6Cl_8]$,³ the use of a monocation in the synthesis was subsequently favored. The viability of this alternative route was sustained by the fact that $(Bu_4N)_3[Re_6S_7Cl_7]$ was found to crystallize out of the aqueous mother liquor obtained from the washing of the reaction products of a typical $Rb[Re_6S_5Cl_9]$ synthesis,²³ thereby indicating that some amounts of $Rb_3[Re_6S_7Cl_7]$ are formed. The main problem with this "monocation" pathway is to avoid the synthesis of lower charged anion salts such as those described previously. This can be

significantly overcome by optimizing the starting composition. Thus, a first attempt led us to synthesize the mixed-anion salt $Rb_5[Re_6S_6Cl_8][Re_6S_7Cl_7]$, described above, in which $[Re_6S_7Cl_7]^{3-}$ was unambiguously characterized for the first time in a mineral salt. Another indication that some amounts of $(M^+)_3[Re_6Y_7X_7]^{3-}$ might have actually been formed is that $(PPh_4)_3[Re_6S_7Br_7]$ could be recrystallized in low yield after reacting $Re_6S_4Br_{10}$ with KSCN at 550 °C, extraction in CH_3CN , and addition of PPh_4Br .³⁹ Further attempts, using Cs^+ instead of Rb^+ or K^+ , resulted in the synthesis in good yield of the novel phase $Cs_3[Re_6S_7Cl_7]$ (Figure 3g).⁴³ This deep red colored salt has a novel monoclinic structure (space group $P2_1/c$). As expected, it is found to be highly soluble in water where cation exchange with tetrabutylammonium chloride affords pristine $(Bu_4N^+)_3[Re_6S_7Cl_7]^{3-}$, which in turn is soluble in numerous polar organic solvents.

One may have expected that $(M^+)_3[Re_6S_7Cl_7]^{3-}$ would have adopted the cubic structure of, with all the tetrahedral sites now fully occupied. A close look at two vacant tetrahedral sites in $Rb_5[Re_6S_6Cl_8][Re_6S_7Cl_7]$ reveals however that they are too small to allow for insertion of an additional cation as large as Cs^+ but may possibly allow for some amounts of Li^+ instead. This would lead to the yet unknown cubic phase $Rb_{2.5}Li_{0.5}[Re_6S_7Cl_7]$.

Finally, recent novel developments include the synthesis by direct high-temperature route of $Rb_3[Re_6Se_7Br_7]$, together with its recrystallized tetrahy-

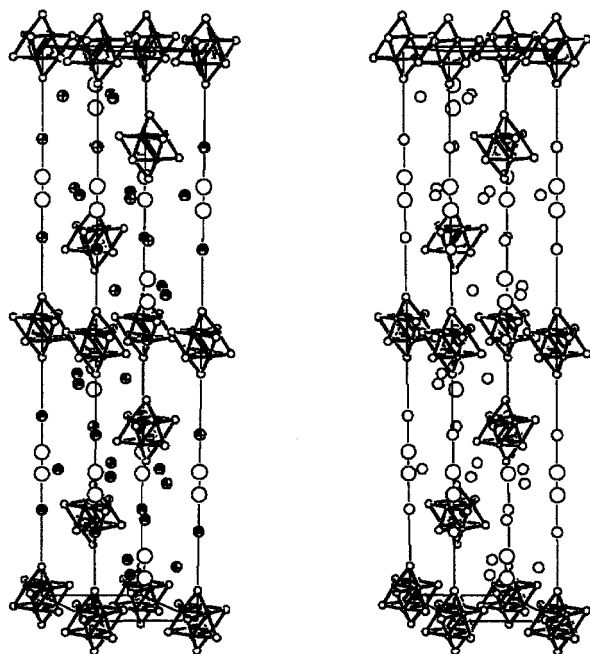


Figure 4. Stereoview of the unit cell content for $\text{Cs}_4[\text{Re}_6\text{S}_8\text{Cl}_6]\cdot\text{CsCl}$. Isolated empty and black-filled octahedra represent isolated chlorine and cesium atoms, respectively. To clarify this complex structure, apical halogen atoms have been removed.

hydrate $\text{Rb}_3[\text{Re}_6\text{Se}_7\text{Br}_7]\cdot 4\text{H}_2\text{O}$,^{44a} and the synthesis of the hydrate $\text{Rb}_3[\text{Re}_6\text{Se}_7\text{Br}_7]\cdot\text{H}_2\text{O}$.^{44b}

5. Tetraanions

Using a large excess of TiCl_4 or CsCl in the initial pressed pellet mixture, Holm and co-workers succeeded in obtaining the first mineral salts containing the tetravalent molecular anion clusters ($n = 4$) in the $[\text{Re}_6\text{Q}_{4+n}\text{X}_{10-n}]^{n-}$ series, namely $\text{M}^{\text{I}}_4[\text{Re}_6\text{Q}_8\text{Cl}_6]\cdot\text{M}^{\text{I}}\text{Cl}$ ($\text{M}^{\text{I}} = \text{Ti}$, $\text{Q} = \text{S}$, Se ; $\text{M}^{\text{I}} = \text{Cs}$, $\text{Q} = \text{S}$) (Figure 4).⁴⁵ Further investigations led the same authors to the synthesis of other molecular salts containing an $[\text{Re}_6\text{Q}_8]^{2+}$ core, namely, $\text{Cs}_4[\text{Re}_6\text{S}_8\text{Br}_6]\cdot\text{CsBr}$ (hexagonal), $\text{Cs}_4[\text{Re}_6\text{S}_8\text{I}_6]\cdot 2\text{CsI}$ (cubic), and $\text{Cs}_4[\text{Re}_6\text{Se}_8\text{I}_6]$ (monoclinic).⁴⁶ Most of these salts are soluble in water, and ion exchange of the alkali metal cation by an alkylammonium cation affords salts soluble in common polar solvents (Table 1).

Note that a water-soluble potassium salt has recently been synthesized by Fedin et al.⁴⁷ by reaction of Re , S , S_2Cl_2 , and KCl at 850°C . Although this potassium salt has not been characterized yet, addition of CsCl to an aqueous solution of this water-soluble phase led the authors to isolate a crystalline product whose formulation, $\text{Cs}_{2.87}\text{K}_{1.13}[\text{Re}_6\text{S}_8\text{Cl}_6]$, was based on a single-crystal X-ray structure determination.

6. Dication

In addition to the synthesis of the neutral cluster $\{[\text{Re}_6\text{Te}_6\text{Cl}_2]\text{Cl}_4(\text{TeCl}_2)_2\}$ discussed in paragraph II.D.1, molecular compounds containing a $[\text{Re}_6\text{Te}_8]^{2+}$ core have also been prepared by high-temperature reactions ($400\text{--}450^\circ\text{C}$). Thus, a dicationic cluster formulated $\{[\text{Re}_6\text{Te}_8](\text{TeBr}_2)_6\}\text{Br}_2$ (Figure 5)²⁶ was synthesized in which each rhenium atom of the $[\text{Re}_6\text{Te}_8]^{2+}$

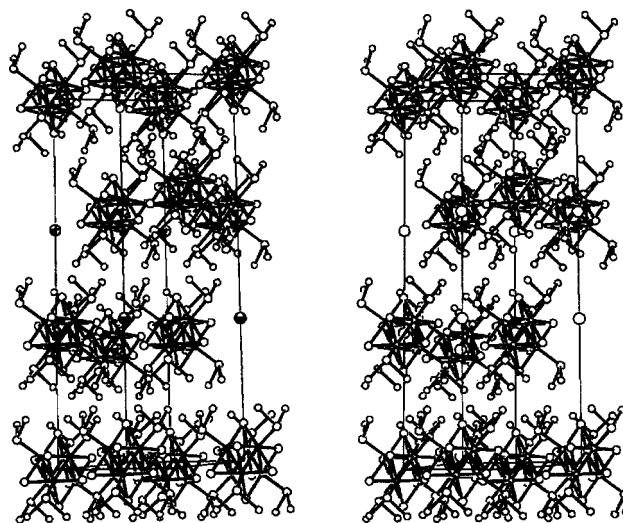


Figure 5. Stereoview of the unit cell content for $\{[\text{Re}_6\text{Te}_8](\text{TeBr}_2)_6\}\text{Br}_2$. (Isolated black-filled octahedra represent bromine atoms.)

core is ligated by a TeBr_2 neutral group. This compound crystallized in the trigonal system.

Its iodine analogue, $\{[\text{Re}_6\text{Te}_8](\text{TeI}_2)_6\}\text{I}_2$,³¹ has also been synthesized. It is not isostructural to the bromine compound, crystallizes in the triclinic system, and appears to be diamagnetic as well as insoluble in usual solvents.

E. Polymeric Compounds

When $[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]^{(6-n)+}$ cores share any of the six outer or eight inner, halogen and/or chalcogen ligands, a wealth of polymeric cluster phases with all possible dimensionalities is generated (Table 2).

1. One-Dimensional

Thus, the structure of $\text{Re}_6\text{Se}_5\text{Cl}_8$ (Figure 6a)^{3,15} reveals⁴⁸ that the compound contains a $[\text{Re}_6\text{Se}_5\text{Cl}_3]^{5+}$ core motif, identical to that identified within the molecular monoanion $[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$. Two trans apical chlorine atoms are shared between neighboring cores, forming a neutral zigzag chain, hence, the compound formulation in Schäfer's nomenclature, $[\text{Re}_6\text{Se}_5\text{Cl}_3]^{1-}\text{Cl}_4^{\text{a}}\text{Cl}_{2/2}^{\text{a-a}}$. $\text{Re}_6\text{S}_5\text{Cl}_8$ was later reported to be isostructural to its selenium analogue.²³ In both cases, the polymeric chains break into their neutral monomer components $\{[\text{Re}_6\text{Q}_5\text{Cl}_3]^{1-}\text{Cl}_5^{\text{a}}(\text{solvent})^{\text{i}}\}$ in polar coordinating solvents such as acetonitrile,^{23,49} as discussed in section III.A.2.

Negatively charged polymeric chains such as $\text{Ag}\{[\text{Re}_6\text{Se}_6\text{Cl}_2]^{1-}\text{Cl}_4^{\text{a}}\text{Cl}_{2/2}^{\text{a-a}}\}$ and $\text{Zn}\{[\text{Re}_6\text{Se}_7\text{Cl}]^{1-}\text{Cl}_4^{\text{a}}\text{Cl}_{2/2}^{\text{a-a}}\}$, isostructural with $\text{Na}[\text{Mo}_6\text{Cl}_{13}]$ (Figure 6b),⁵⁰ have been reported (p 78 of ref 15).

A strikingly different mode of linkage is that revealed by Holm and co-workers in the series $\text{M}^{\text{I}}_2\text{--}[\text{Re}_6\text{Q}_8\text{X}_4]$ ($\text{M}^{\text{I}} = \text{Ti}$, $\text{Q} = \text{S}$, Se , $\text{X} = \text{Cl}$; $\text{M}^{\text{I}} = \text{Cs}$, $\text{Q} = \text{Se}$, $\text{X} = \text{Br}$),^{45,46} where the $[\text{Re}_6\text{Q}_8]^{2+}$ cores are linked via inner chalcogen atoms in a symmetrical linkage mode; i.e., the outer ligand of a rhenium atom is one of the inner chalcogen of the adjacent cluster core and vice versa (Figure 6c,d). All these structures exhibit one-dimensional arrangements, whose explicit Schäfer formulation reads $\text{M}^{\text{I}}_2\{[\text{Re}_6\text{Q}_6^{\text{i}}\text{Q}_{2/2}^{\text{i-a}}]\text{X}_4^{\text{a}}\text{Q}_{2/2}^{\text{a-i}}\}$

Table 2. Inorganic Hexanuclear Rhenium Chalcohalide Cluster Polymers Obtained by High-Temperature Reactions

	compd	Schäfer's notation	(<i>n</i> , <i>m</i> , <i>l</i>) indices	refs
1D	Re ₆ Se ₅ Cl ₈	{[Re ₆ Se ₅ ⁱ Cl ₃ ⁱ]Cl ₄ ^a Cl _{2/2} ^{a-a} }	(1, 0, 2)	15, 16, 48
	Re ₆ S ₅ Cl ₈	{[Re ₆ S ₅ ⁱ Cl ₃ ⁱ]Cl ₄ ^a Cl _{2/2} ^{a-a} }	(1, 0, 2)	22
	Ag[Re ₆ Se ₆ Cl ₇]	{[Re ₆ Se ₆ ⁱ Cl ₂ ⁱ]Cl ₄ ^a Cl _{2/2} ^{a-a} } ⁻	(2, 0, 2)	15
	Zn[Re ₆ Se ₇ Cl ₆]	{[Re ₆ Se ₇ ⁱ Cl ⁱ]Cl ₄ ^a Cl _{2/2} ^{a-a} } ²⁻	(3, 0, 2)	15
	M ⁱ ₂ [Re ₆ Q ₈ Cl ₄] (M ⁱ = Tl, Q = S, Se; M ⁱ = Cs, Q = S)	{[Re ₆ Q ₆ ⁱ Q _{2/2} ^{i-a}]Cl ₄ ^a Q _{2/2} ^{a-i} } ²⁻	(4, 2, 0)	45
2D	Cs ₂ [Re ₆ Se ₈ Br ₄]	{[Re ₆ Se ₆ ⁱ Se _{2/2} ^{i-a}]Br ₄ ^a Se _{2/2} ^{a-i} } ²⁻	(4, 2, 0)	46
	Re ₆ Se ₈ Cl ₂	{[Re ₆ Se ₄ ⁱ Se _{4/4} ^{i-a}]Cl ₂ ^a Se _{4/2} ^{a-i} }	(4, 4, 0)	11, 15, 18, 53, 55
	Re ₆ Se ₆ Cl ₆	{[Re ₆ Se ₆ ⁱ Cl ₂ ⁱ]Cl ₂ ^a Cl _{4/2} ^{a-a} }	(2, 0, 4)	15, 48
	Re ₆ Te ₁₆ Cl ₆	{[Re ₆ Te ₈ ⁱ](TeCl ₃) ₂ ^a (Te ₆) _{4/4} ^{a-a} }	(4, 0, 4) [*]	56
	Tl[Re ₆ Se ₈ Cl ₃]	{[Re ₆ Se ₅ ⁱ Se _{3/2} ^{i-a}]Cl ₃ ^a Se _{3/2} ^{a-i} } ⁻	(4, 3, 0)	45
3D	Cs[Re ₆ Se ₈ I ₃]	{[Re ₆ Se ₆ ⁱ Se _{2/2} ^{i-a}]Cl ₂ ^a Cl _{2/2} ^{a-a} Se _{2/2} ^{a-i} } ⁻	(4, 2, 2)	46
	Re ₆ S ₇ Br ₄	{[Re ₆ S ₇ ⁱ Br ⁱ]Br _{6/2} ^{a-a} }	(3, 0, 6)	15, 48
	Re ₆ Se ₇ Br ₄	{[Re ₆ Se ₇ ⁱ Br ⁱ]Br _{6/2} ^{a-a} }	(3, 0, 6)	15, 48, 57
	Re ₆ Q ₈ Br ₂ (Q = S, Se)	{[Re ₆ Q ₆ ⁱ Q _{2/2} ^{i-a}]Br ₄ ^a Q _{2/2} ^{a-i} } ⁻	(4, 2, 4)	25, 58
	Re ₆ S ₈ Cl ₂	{[Re ₆ S ₆ ⁱ S _{2/2} ^{i-a}]Cl ₄ ^a S _{2/2} ^{a-i} }	(4, 2, 4)	60
	Re ₆ Te ₁₆ Cl ₁₈	{[Re ₆ Te ₈ ⁱ](Te ₈ Cl ₁₈) _{6/6} ^{a-a} }	(4, 0, 6) ^a	56

^a Here, because the apical ligands are different, the net charge of the cluster motif reads (*m* - *n* + *l*/2).

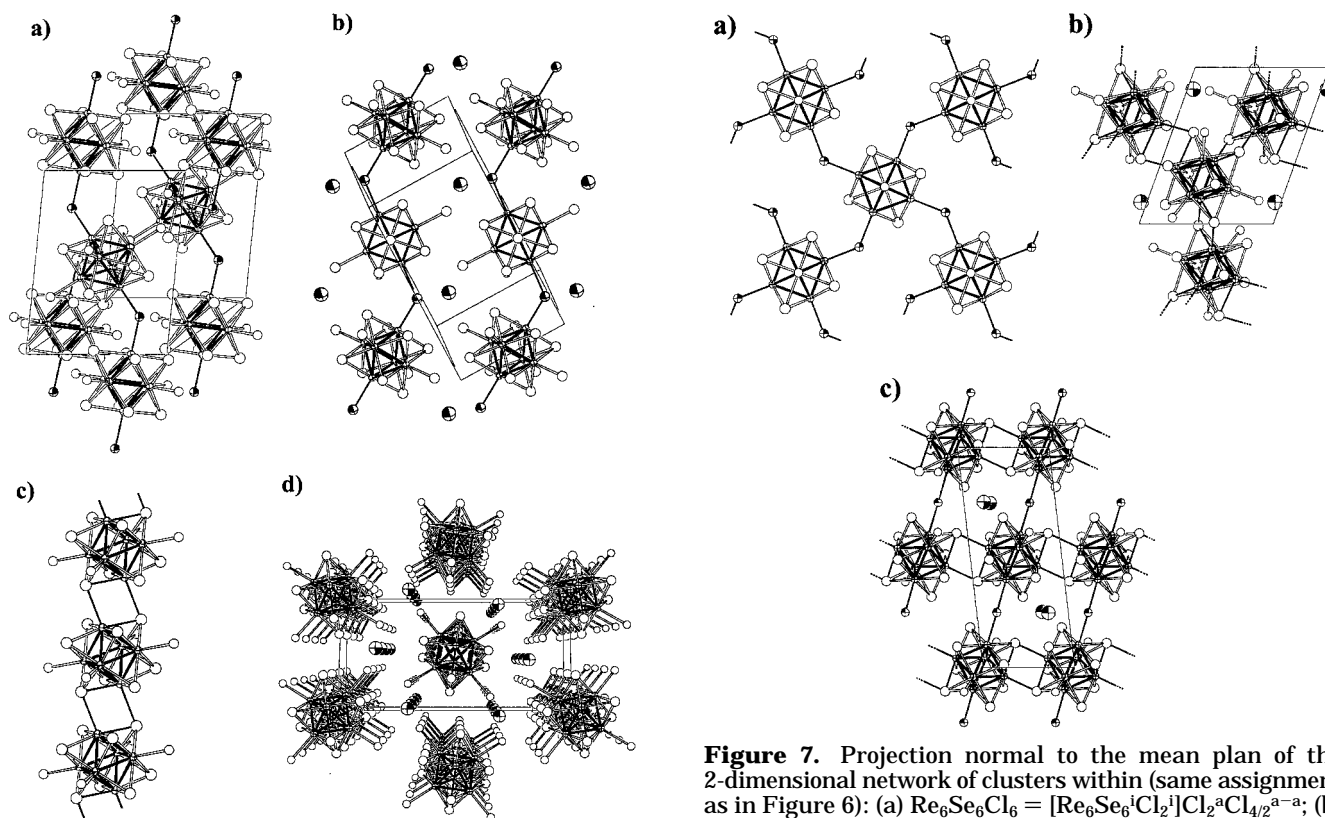


Figure 6. Variety of chains within the one-dimensional compound series. (Empty spheres represent inner μ_3 -chalcogen or μ_3 -halogen ligands or nonbridging apical μ -halogen atoms; crossed spheres represent metal atoms; black-filled octant spheres represent apical bridging "a-a" (μ_2) halogen as well as alkali-metal atoms; metal-metal as well as bridging bonds are filled in black.) One type is illustrated by (a) Re₆S₅Cl₈ = [Re₆Se₅ⁱCl₃ⁱ]Cl₄^aCl_{2/2}^{a-a} and (b) Na[Mo₆Cl₁₃] = Na{[Mo₆Cl₈ⁱ]Cl₄^aCl_{2/2}^{a-a}}. Another type of chain can be observed within M₂[Re₆Q₈Cl₄] = M₂ⁱ{[Re₆Q₆ⁱQ_{2/2}^{i-a}]Cl₄^aQ_{2/2}^{a-i}} (Mⁱ = Tl, Q = S, Se, X = Cl; Mⁱ = Cs, Q = S, X = Br); (c) presents detail of this chain, and (d) shows a perspective representation of the structure viewed along the chain axis.

and where the lack of X^{a-a} (μ_2 -) halogen bridges brings the [Re₆Q₈]²⁺ cores closer to each other than within the chains in Re₆Q₅Cl₈. One consequence is

Figure 7. Projection normal to the mean plan of the 2-dimensional network of clusters within (same assignment as in Figure 6): (a) Re₆Se₆Cl₆ = [Re₆Se₆ⁱCl₂ⁱ]Cl₂^aCl_{4/2}^{a-a}; (b) the triclinic structure, Tl[Re₆Se₈Cl₃] = Tl₃{[Re₆Se₅ⁱSe_{3/2}^{i-a}]Cl₃^aSe_{3/2}^{a-i}}⁻; (c) the monoclinic structure, Cs[Re₆Se₈I₃] = Cs{[Re₆Se₆ⁱSe_{2/2}^{i-a}]I₂^aI_{2/2}^{a-a}Se_{2/2}^{a-i}}⁻.

that such chains can neither be dissolved in usual solvents nor dissociated into their monomeric components.

2. Two-Dimensional

Re₆Se₆Cl₆ is the prototypical two-dimensional polymer. It is characterized by its distinctive, four coplanar μ_2 -chloride ligands as shown (Figure 7a).^{3,15,16} Its Schäfer-von Schnering formulation reads [Re₆Se₆ⁱCl₂ⁱ]Cl₂^aCl_{4/2}^{a-a}, and it is isostructural to MoCl₂.⁵¹ Just as the latter, this 24-electron cluster phase is

insulating¹⁶ and, as shown for MoCl_2 by Sheldon in 1960,⁵² it can be dismantled in polar solvents.⁴⁹

Another pattern of two-dimensional association is revealed in $\text{Re}_6\text{Se}_8\text{Cl}_2$ where any given core is now linked to four adjacent neighbors via symmetrical linkage modes (Figure 1). Here, Se inner atoms of any cluster serve as outer ligands for neighboring clusters. Thus, face-capped octahedral $[\text{Re}_6\text{Se}_8]$ clusters, each with two trans terminal Cl ligands, are directly linked through intercluster Re–Se bonds to form eight connected sheets (see Figure 1). Photoelectrochemical investigations of $\text{Re}_6\text{Se}_8\text{Cl}_2$ single crystals have shown that it is an n-type semiconductor with a direct optical transition and a band gap of 1.42 eV.⁵³ Its electronic structure has been investigated and discussed (see section IV.G) with an emphasis on the structural relationship to the Chevrel–Sergent supraconducting phases^{16,18} and because semiconducting behavior had been predicted for Chevrel–Sergent phases with 24 electrons/cluster unit.^{54,55}

A remarkable example of framework isomerism in inorganic solid-state chemistry has been reported by Holm and co-workers while comparing the structures of the two-dimensional compounds $(\text{Ti}^+)[\text{Re}_6\text{Se}_8\text{Cl}_3]^-$ ⁴⁵ and $(\text{Cs}^+)[\text{Re}_6\text{Se}_8\text{I}_3]^-$.⁴⁶ Thus, as exemplified in Figure 7b, any $[\text{Re}_6\text{Se}_8]^{2+}$ core within $\text{Ti}[\text{Re}_6\text{Se}_8\text{Cl}_3]$ is linked to *three* neighboring $[\text{Re}_6\text{Se}_8]^{2+}$ cores via three symmetrical linkage modes. Therefore, $[\text{Re}_6\text{Se}_8\text{Cl}_3]^-$ reads $\{[\text{Re}_6\text{Se}_5^i\text{Se}_{3/2}^{i-a}]\text{Cl}_3^a\text{Se}_{3/2}^{a-i}\}^-$. Now, for $\text{Cs}[\text{Re}_6\text{Se}_8\text{I}_3]$, each $[\text{Re}_6\text{Se}_8]^{2+}$ core is linked to *four* neighboring $[\text{Re}_6\text{Se}_8]^{2+}$ cores but via only two symmetrical linkage modes and two additional bridging apical chlorine atoms (Figure 7c). Hence the novel formulation now reads $\{[\text{Re}_6\text{Se}_6^i\text{Se}_{2/2}^{i-a}]\text{I}_2^a\text{I}_{2/2}^{a-a}\text{Se}_{2/2}^{a-i}\}^-$. As we shall see in section 3, structural isomers have been previously reported for hexarhenium chalcohalide clusters in the neutral $\text{Re}_6\text{Q}_8\text{X}_2$ series.

Finally, in their recent investigation of the Re–X–Te system, Ibers and co-workers obtained a two-dimensional phase, $\text{Re}_6\text{Te}_{16}\text{Cl}_6$ (Figure 8a),⁵⁶ in which two Re atoms at opposite vertexes of the Re_6 octahedron are capped by $[\text{TeCl}_3]^-$ ligands. The four remaining coplanar Re atoms are capped with neutral Te_6 ligands, any single Te_6 ligand being linked to four different $[\text{Re}_6\text{Te}_8]^{2+}$ cores, hence, the “4/4” indices in Schäfer’s notation, $[\text{Re}_6\text{Te}_8^i](\text{Te}_6)_{4/4}^{a-a}(\text{TeCl}_3)_2^a$. In the latter, one chlorine atom has a longer Te–Cl bond (2.817(9) Å in comparison to 2.387(8) and 2.433(8) Å for the two others) and is in fact interacting with the Te^{2+} center of a $[\text{TeCl}_3]^-$ ligand belonging to an adjacent layer ($\text{Cl}_3\text{Te}\cdots\text{Cl}$ 3.028(9) Å), and the Te^{2+} ion adopts a square-planar coordination pattern (Figure 8b). Therefore, and even though no covalent bonding can be found between $[\text{TeCl}_3]^-$ ligands, it is suggested that the two-dimensional motifs are strongly interacting. Further theoretical work is necessary in order to evaluate the actual dimensionality of the chemical bonding in this system.

3. Three-Dimensional

The structure of $\text{Re}_6\text{Q}_7\text{Br}_4$ (Q = S, Se), initially reported by Leduc,^{15,3} has been made available in full

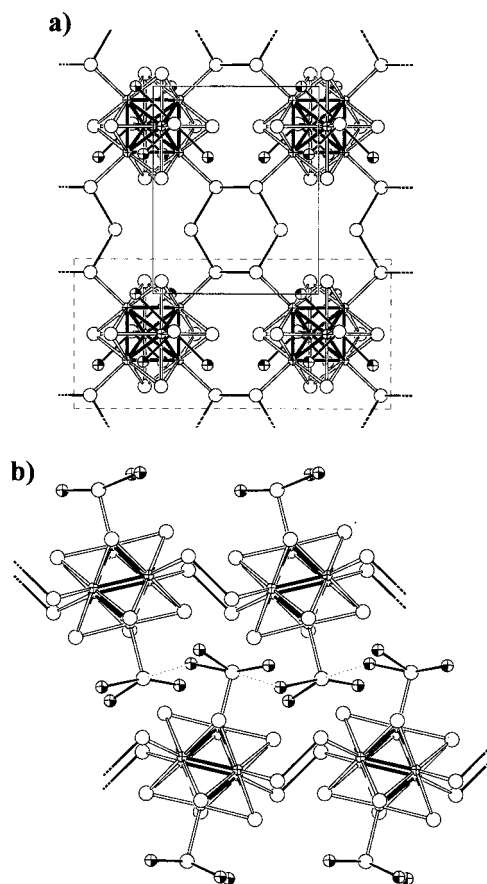


Figure 8. (a) Projection of the 2-dimensional network of clusters within $[\text{Re}_6\text{Te}_8](\text{Te}_6)_{4/4}^{a-a}(\text{TeCl}_3)_2^a$ perpendicular to the mean plan of the sheet (same assignment as in Figure 6; Re–Re, Te–Te, and short Te–Cl bonds are filled in black). The area delimited by the dashed rectangle is shown in (b) in a perpendicular orientation involving two successive layers (the long Te–Cl contact is indicated here by a dotted line).

details only recently (Figure 9a).⁵⁷ It is to be considered as the prototypical, three-dimensional (dimensionality $d = 3$) halogen-bridged octahedral rhenium cluster architecture of general formula $\text{Re}_6\text{Q}_{4+d}\text{X}_{10-2d}$. Within the rhombohedral ($R\bar{3}c$) structure, each $[\text{Re}_6\text{Se}_7\text{Br}]^{3+}$ core is linked via halogen-bridged atoms to six $[\text{Re}_6\text{Se}_7\text{Br}]^{3+}$ neighboring cores located at the apex of an octahedron. The synthesis of $\text{Re}_6\text{Se}_7\text{Cl}_4$ has also been reported,^{15,48} but systematic twinning precluded the structure determination. These three-dimensional phases, formulated $[\text{Re}_6\text{Q}^i7\text{X}^i]\text{X}_{6/3}^{a-a}$, proved to be insoluble.⁴⁹

The mixed, intercluster core, three-dimensional bridging mode, in which both halogen bridges and symmetrical linkage modes coexist, is exemplified in $\text{Re}_6\text{Q}_8\text{X}_2$ (X = Cl, Q = S; X = Br, Q = S, Se) (Figure 9b).^{58,59,60} A striking point is that these compounds have the same formulation as the two-dimensional prototype, $\text{Re}_6\text{Se}_8\text{Cl}_2$. In the present three-dimensional isomer, formulated $[\text{Re}_6\text{Q}_6^i\text{Q}_{2/2}^{i-a}]\text{Q}_{2/2}^{a-i}\text{X}_{4/2}^{a-a}$, one identifies infinite symmetrical linkage modes generating chains similar to the one observed in $\text{M}^1_2\text{Re}_6\text{Q}_8\text{Cl}_4$ (Figure 6c). The four remaining rhenium atoms, located in planes perpendicular to the chain axis, are linked to the adjacent chains via halogen bridges.

Table 3. Schäfer–von Schnering's Notation of All Known (*n*, *l*) Hexanuclear Rhenium Chalcogenide Clusters

<i>l</i>	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4
0 molecular, <i>d</i> = 0	{[Re ₆ Q ₄ ⁱ X ₄ ⁱ]X ₆ ^a }	{[Re ₆ Q ₅ ⁱ X ₃ ⁱ]X ₆ ^a } [−]	{[Re ₆ Q ₆ ⁱ X ₂ ⁱ]X ₆ ^a } ^{2−}	{[Re ₆ Q ₇ ⁱ X ⁱ]X ₆ ^a } ^{3−}	{[Re ₆ Q ₈ ⁱ]X ₆ ^a } ^{4−}
2 1D, <i>d</i> = 1		{[Re ₆ Q ₅ ⁱ X ₃ ⁱ]X ₄ ^a X _{2/2} ^{a−a} }	{[Re ₆ Q ₆ ⁱ X ₂ ⁱ]X ₄ ^a X _{2/2} ^{a−a} } [−]	{[Re ₆ Q ₇ ⁱ X ⁱ]X ₄ ^a X _{2/2} ^{a−a} } ^{2−}	
4 2D, <i>d</i> = 2			{[Re ₆ Q ₆ ⁱ X ₂ ⁱ]X ₂ ^a X _{4/2} ^{a−a} }		
6 3D, <i>d</i> = 3				{[Re ₆ Q ₇ ⁱ X ⁱ]X _{6/2} ^{a−a} }	

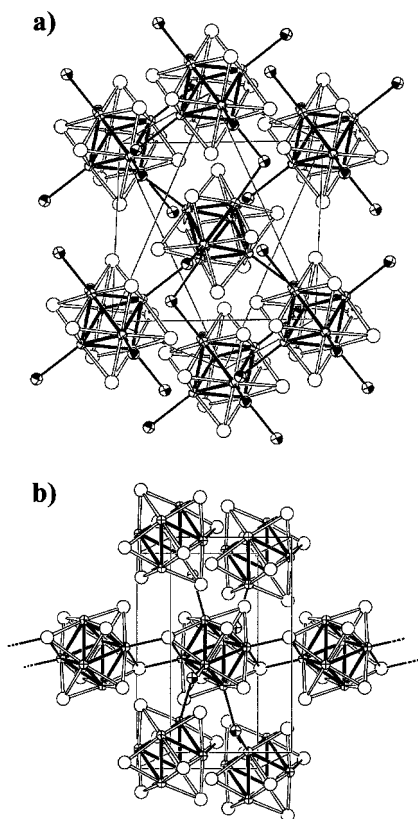


Figure 9. Prototypical structure for the 3-dimensional compounds (same assignment as in Figure 6; to simplify this complex structure, only the central cluster motif is shown complete with all bonds drawn) shown here in projection: (a) Re₆Q₇Br₄ = [Re₆Qⁱ7Brⁱ]Br_{6/3}^{a−a} (Q = S, Se); (b) Re₆Q₈X₂ = [Re₆QⁱQ_{2/2}^{i−a}]Q_{2/2}^{a−i}X_{4/2}^{a−a} (X = Cl, Q = S; X = Br, Q = S, Se).

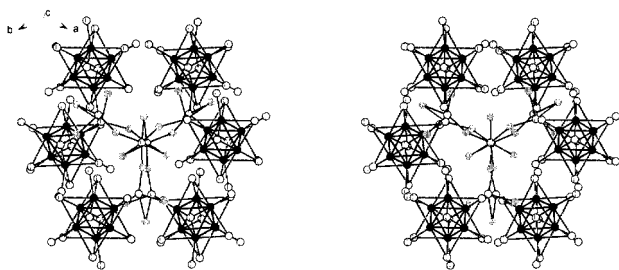


Figure 10. Stereoview of the [Te₈Cl₁₈]^{2−} ligand environment in Re₆Te₁₆Cl₁₈ = [Re₆Te₈]ⁱ(Te₈Cl₁₈)_{6/6}^{a−a}. Each ligand chelates six [Re₆Te₈]²⁺ cluster cores (Re, Te, and Cl atoms are drawn as black, crossed white, and gray hollow spheres, respectively).

The singularity of tellurium in these systems is again exemplified in the three-dimensional series by Re₆Te₁₆Cl₁₈ (Figure 10).⁵⁶ In this compound, one identifies [Re₆Te₈]²⁺ cores, now bridged by a complex [Te₈Cl₁₈]^{2−} apical ligand linking six cores together in a three-dimensional fashion, as shown by the formulation [Re₆Te₈]ⁱ(Te₈Cl₁₈)_{6/6}^{a−a}. Thus, clusters cores and ligands are arranged in a rock-salt fashion.

F. Construction of a Virtual Library Spanning the Re–Q–X System

An analysis of the modes of linkages via apical chloride bridges for 1-, 2-, or 3-D networks within the five known types of molecular forms based on octahedral rhenium cluster cores formulated [Re₆Q_{4+n}ⁱX_{4−n}ⁱ]^{(6−n)+} led to the general formulation

$$\{[\text{Re}_6\text{Q}_{4+n}^i\text{X}_{4-n}^i]\text{X}_{6-l}^a\text{X}_{l/2}^{a-a}\}^{(l/2-n)} \quad (1)$$

where *l* is the number of bridging, outer halogen atoms and may take any value from 0 to 6 (*n* = 0–4). With this formula, the three polymers Re₆Q₅X₈, Re₆Q₆X₆, and Re₆Q₇X₄ are represented by the couple (*n*, *l*) of indices (1, 2), (2, 4), and (3, 6), respectively. Note that the dimensionality of these phases is given by *d* = *l*/2.

Once put aside cationic phases,⁶¹ 14 different compounds can be formulated whose charges range from neutral to tetraanionic and dimensionality from 0- (molecular forms) to 3-dimensional (Table 3). Only in the Re–S–Cl system have all the molecular forms (first line of Table 3) now been synthesized. The *n* = 3 phase is still missing in the Re–Se–Cl system, and other systems have not been explored to any extent yet, not to mention their solubility properties. Besides, all halogen-bridged neutral polymers (main diagonal of Table 3) were fully characterized,¹⁵ although essentially in the Re–Se–Cl system. If one considers halogen-bridged anionic polymers, apart from a brief mention of Ag{[Re₆Se₆ⁱCl₂ⁱ]Cl₄^aCl_{2/2}^{a−a}} (*n* = 2, *l* = 2) and Zn{[Re₆Se₇ⁱClⁱ]Cl₄^aCl_{2/2}^{a−a}} (*n* = 3, *l* = 2),⁶² many new compounds await to be synthesized.

A more general formulation encompasses those phases, like Re₆Se₈Cl₂,^{15,16} in which intercluster bonds are created by linking *m* inner ligands via symmetrical linkage modes:

$$\{[\text{Re}_6\text{Q}_{4+n-m}^i\text{Q}_{m/2}^{i-a}\text{X}_{4-n}^i] \times \text{X}_{6-m-l}^a\text{X}_{l/2}^{a-a}\text{Q}_{m/2}^{a-i}\}^{(m-n+l/2)} \quad (2)$$

Note that the following restrictions apply: 0 ≤ *n* ≤ 4; *m* and *l* are positive integers with *m* + *l* ≤ 6 and *m* − *n* + *l*/2 ≤ 0, if one put aside cationic phases. The value of the (*n*, *m*, *l*) triplet for each known polymer type is given in Table 2. Thus, if one looks for neutral compounds (*m* − *n* + *l*/2 = 0) with a [Re₆Q₈]²⁺ core (*n* = 4), and given the above restrictions, one ends up with only three possible (*n*, *m*, *l*) triplets of indices: (4, 4, 0); (4, 3, 2); (4, 2, 4). The first and latter correspond to the two known structural isomers of Re₆Q₈X₂, [Re₆Se₄ⁱSe_{4/2}^{i−a}]Cl₂^aSe_{4/2}^{a−i}, and [Re₆Q₆ⁱQ_{2/2}^{i−a}]Br_{4/2}^aQ_{2/2}^{a−i} (Q = S, Se), respectively. Other known structural isomers are Tl[Re₆–Se₈Cl₃] and Cs[Re₆Se₈I₃], with triplets indices of (4,

Table 4. Virtual Library of All Possible Hexarhenium Chalcogenide Clusters and Their Associated (*n, m, l*) Triplets, Compiled with Their Schäfer–von Schnering's Formulation

<i>n</i> = 4, <i>m</i> = 0			
charge = 4– (<i>n, m, l</i>) = (4, 0, 0) formulation: [Re ₆ Q ₈ X ₆] ^{4–} {[Re ₆ Q ₈ ^l X ₆ ^a] ^{4–} }	charge = 4– (<i>n, m, l</i>) = (4, 0, 1) formulation: [Re ₆ Q ₈ X ₆] ^{4–} {[Re ₆ Q ₈ ^l X ₅ ^a X _{1/2} ^{a–a}] ^{4–} }	charge = 3– (<i>n, m, l</i>) = (4, 0, 2) formulation: [Re ₆ Q ₈ X ₅] ^{3–} {[Re ₆ Q ₈ ^l X ₄ ^a X _{2/2} ^{a–a}] ^{3–} }	charge = 3– (<i>n, m, l</i>) = (4, 0, 3) formulation: [Re ₆ Q ₈ X ₅] ^{3–} {[Re ₆ Q ₈ ^l X ₃ ^a X _{3/2} ^{a–a}] ^{3–} }
charge = 2– (<i>n, m, l</i>) = (4, 0, 4) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₈ ^l X ₂ ^a X _{4/2} ^{a–a}] ^{2–} }	charge = 2– (<i>n, m, l</i>) = (4, 0, 5) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₈ ^l X ^a X _{5/2} ^{a–a}] ^{2–} }	charge = 1– (<i>n, m, l</i>) = (4, 0, 6) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₈ ^l X _{6/2} ^{a–a}] [–] }	
<i>m</i> = 1			
charge = 3– (<i>n, m, l</i>) = (4, 1, 0) formulation: [Re ₆ Q ₈ X ₅] ^{3–} {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] ^{3–} X ₅ ^a X _{1/2} ^{a–a}] ^{3–} }	charge = 3– (<i>n, m, l</i>) = (4, 1, 1) formulation: [Re ₆ Q ₈ X ₅] ^{3–} {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] ^{3–} X ₄ ^a X _{1/2} ^{a–a} Q _{1/2} ^{a–i}] ^{3–} }	charge = 2– (<i>n, m, l</i>) = (4, 1, 2) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] ^{2–} X ₃ ^a X _{2/2} ^{a–a} Q _{1/2} ^{a–i}] ^{2–} }	charge = 2– (<i>n, m, l</i>) = (4, 1, 3) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] ^{2–} X ₂ ^a X _{3/2} ^{a–a} Q _{1/2} ^{a–i}] ^{2–} }
charge = 1– (<i>n, m, l</i>) = (4, 1, 4) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] [–] X ^a X _{4/2} ^{a–a} Q _{1/2} ^{a–i}] [–] }	charge = 1– (<i>n, m, l</i>) = (4, 1, 5) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₇ ^l Q _{1/2} ^{l–a}] [–] X _{5/2} ^{a–a} Q _{1/2} ^{a–i}] [–] }		
<i>m</i> = 2			
charge = 2– (<i>n, m, l</i>) = (4, 2, 0) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₆ ^l Q _{2/2} ^{l–a}] ^{2–} X ₄ ^a Q _{2/2} ^{a–i}] ^{2–} }	charge = 2– (<i>n, m, l</i>) = (4, 2, 1) formulation: [Re ₆ Q ₈ X ₄] ^{2–} {[Re ₆ Q ₆ ^l Q _{2/2} ^{l–a}] ^{2–} X ₃ ^a X _{1/2} ^{a–a} Q _{2/2} ^{a–i}] ^{2–} }	charge = 1– (<i>n, m, l</i>) = (4, 2, 2) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₆ ^l Q _{2/2} ^{l–a}] [–] X ₂ ^a X _{2/2} ^{a–a} Q _{2/2} ^{a–i}] [–] }	charge = 1– (<i>n, m, l</i>) = (4, 2, 3) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₆ ^l Q _{2/2} ^{l–a}] [–] X ^a X _{3/2} ^{a–a} Q _{2/2} ^{a–i}] [–] }
charge = 0 (<i>n, m, l</i>) = (4, 2, 4) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₆ ^l Q _{2/2} ^{l–a}] ⁰ X _{4/2} ^{a–a} Q _{2/2} ^{a–i}] ⁰ }			
<i>m</i> = 3			
charge = 1– (<i>n, m, l</i>) = (4, 3, 0) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₅ ^l Q _{3/2} ^{l–a}] [–] X ₃ ^a Q _{3/2} ^{a–i}] [–] }	charge = 1– (<i>n, m, l</i>) = (4, 3, 1) formulation: [Re ₆ Q ₈ X ₃] [–] {[Re ₆ Q ₅ ^l Q _{3/2} ^{l–a}] [–] X ₂ ^a X _{1/2} ^{a–a} Q _{3/2} ^{a–i}] [–] }	charge = 0 (<i>n, m, l</i>) = (4, 3, 2) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₅ ^l Q _{3/2} ^{l–a}] ⁰ X ^a X _{2/2} ^{a–a} Q _{3/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (4, 3, 3) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₅ ^l Q _{3/2} ^{l–a}] ⁰ X _{3/2} ^{a–a} Q _{3/2} ^{a–i}] ⁰ }
<i>m</i> = 4			
charge = 0 (<i>n, m, l</i>) = (4, 4, 0) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₄ ^l Q _{4/2} ^{l–a}] ⁰ X ₂ ^a Q _{4/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (4, 4, 1) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₄ ^l Q _{4/2} ^{l–a}] ⁰ X ^a X _{1/2} ^{a–a} Q _{4/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (4, 4, 0) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₄ ^l Q _{4/2} ^{l–a}] ⁰ X ₂ ^a Q _{4/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (4, 4, 1) formulation: [Re ₆ Q ₈ X ₂] ⁰ {[Re ₆ Q ₄ ^l Q _{4/2} ^{l–a}] ⁰ X ^a X _{1/2} ^{a–a} Q _{4/2} ^{a–i}] ⁰ }
<i>m</i> = 5, <i>m</i> = 6			
<i>n</i> = 3, <i>m</i> = 0			
charge = 3– (<i>n, m, l</i>) = (3, 0, 0) formulation: [Re ₆ Q ₇ X ₇] ^{3–} {[Re ₆ Q ₇ ^l X ^l X ₆ ^a] ^{3–} }	charge = 3– (<i>n, m, l</i>) = (3, 0, 1) formulation: [Re ₆ Q ₇ X ₇] ^{3–} {[Re ₆ Q ₇ ^l X ^l X ₅ ^a X _{1/2} ^{a–a}] ^{3–} }	charge = 2– (<i>n, m, l</i>) = (3, 0, 2) formulation: [Re ₆ Q ₇ X ₆] ^{2–} {[Re ₆ Q ₇ ^l X ^l X ₄ ^a X _{2/2} ^{a–a}] ^{2–} }	charge = 2– (<i>n, m, l</i>) = (3, 0, 3) formulation: [Re ₆ Q ₇ X ₆] ^{2–} {[Re ₆ Q ₇ ^l X ^l X ₃ ^a X _{3/2} ^{a–a}] ^{2–} }
charge = 1– (<i>n, m, l</i>) = (3, 0, 4) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₇ ^l X ^l X ₂ ^a X _{4/2} ^{a–a}] [–] }	charge = 1– (<i>n, m, l</i>) = (3, 0, 5) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₇ ^l X ^l X ^a X _{5/2} ^{a–a}] [–] }	charge = 0 (<i>n, m, l</i>) = (3, 0, 6) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₇ ^l X ^l X _{6/2} ^{a–a}] ⁰ }	
<i>m</i> = 1			
charge = 2– (<i>n, m, l</i>) = (3, 1, 0) formulation: [Re ₆ Q ₇ X ₆] ^{2–} {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] ^{2–} X ₄ ^a X _{1/2} ^{a–a} Q _{1/2} ^{a–i}] ^{2–} }	charge = 2– (<i>n, m, l</i>) = (3, 1, 1) formulation: [Re ₆ Q ₇ X ₆] ^{2–} {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] ^{2–} X ₃ ^a X _{1/2} ^{a–a} Q _{1/2} ^{a–i}] ^{2–} }	charge = 1– (<i>n, m, l</i>) = (3, 1, 2) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] [–] X ₃ ^a X _{2/2} ^{a–a} Q _{1/2} ^{a–i}] [–] }	charge = 1– (<i>n, m, l</i>) = (3, 1, 3) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] [–] X ₂ ^a X _{3/2} ^{a–a} Q _{1/2} ^{a–i}] [–] }
charge = 0 (<i>n, m, l</i>) = (3, 1, 4) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] ⁰ X ^a X _{4/2} ^{a–a} Q _{1/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (3, 1, 5) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₆ ^l Q _{1/2} ^{l–a} X ^l] ⁰ X _{5/2} ^{a–a} Q _{1/2} ^{a–i}] ⁰ }		
<i>m</i> = 2			
charge = 1– (<i>n, m, l</i>) = (3, 2, 0) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₅ ^l Q _{2/2} ^{l–a} X ^l] [–] X ₄ ^a Q _{2/2} ^{a–i}] [–] }	charge = 1– (<i>n, m, l</i>) = (3, 2, 1) formulation: [Re ₆ Q ₇ X ₅] [–] {[Re ₆ Q ₅ ^l Q _{2/2} ^{l–a} X ^l] [–] X ₃ ^a X _{1/2} ^{a–a} Q _{2/2} ^{a–i}] [–] }	charge = 0 (<i>n, m, l</i>) = (3, 2, 2) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₅ ^l Q _{2/2} ^{l–a} X ^l] ⁰ X ₂ ^a X _{2/2} ^{a–a} Q _{2/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (3, 2, 3) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₅ ^l Q _{2/2} ^{l–a} X ^l] ⁰ X ^a X _{3/2} ^{a–a} Q _{2/2} ^{a–i}] ⁰ }
<i>m</i> = 3			
charge = 0 (<i>n, m, l</i>) = (3, 3, 0) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₄ ^l Q _{3/2} ^{l–a} X ^l] ⁰ X ₂ ^a X _{1/2} ^{a–a} Q _{3/2} ^{a–i}] ⁰ }	charge = 0 (<i>n, m, l</i>) = (3, 3, 1) formulation: [Re ₆ Q ₇ X ₄] ⁰ {[Re ₆ Q ₄ ^l Q _{3/2} ^{l–a} X ^l] ⁰ X ₂ ^a X _{1/2} ^{a–a} Q _{3/2} ^{a–i}] ⁰ }		

Table 4 (Continued)

		$n = 2, m = 0$	
charge = 2− (n, m, l) = (2, 0, 0) formulation: $[\text{Re}_6\text{Q}_6\text{X}_8]^{2-}$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_6^a]^{2-}\}$	charge = 2− (n, m, l) = (2, 0, 1) formulation: $[\text{Re}_6\text{Q}_6\text{X}_8]^{2-}$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_5^a\text{X}_{1/2}^{a-a}]^{2-}\}$	charge = 1− (n, m, l) = (2, 0, 2) formulation: $[\text{Re}_6\text{Q}_6\text{X}_7]^-$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_4^a\text{X}_{2/2}^{a-a}]^- \}$	charge = 1− (n, m, l) = (2, 0, 3) formulation: $[\text{Re}_6\text{Q}_6\text{X}_7]^-$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_3^a\text{X}_{3/2}^{a-a}]^- \}$
charge = 0 (n, m, l) = (2, 0, 4) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_2^a\text{X}_{4/2}^{a-a}] \}$	charge = 0 (n, m, l) = (2, 0, 5) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_6^i\text{X}_2^i\text{X}_5^a\text{X}_{5/2}^{a-a}] \}$		
		$m = 1$	
charge = 1− (n, m, l) = (2, 1, 0) formulation: $[\text{Re}_6\text{Q}_6\text{X}_7]^-$ $\{\text{[Re}_6\text{Q}_5^i\text{Q}_{1/2}^{1-a}\text{X}_2^i\text{X}_5^a\text{Q}_{1/2}^{a-1}]^- \}$	charge = 1− (n, m, l) = (2, 1, 1) formulation: $[\text{Re}_6\text{Q}_6\text{X}_7]^-$ $\{\text{[Re}_6\text{Q}_5^i\text{Q}_{1/2}^{1-a}\text{X}_2^i\text{X}_4^a\text{X}_{1/2}^{a-a}\text{Q}_{1/2}^{a-1}]^- \}$	charge = 0 (n, m, l) = (2, 1, 2) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_5^i\text{Q}_{1/2}^{1-a}\text{X}_2^i\text{X}_3^a\text{X}_{2/2}^{a-a}\text{Q}_{1/2}^{a-1}] \}$	charge = 0 (n, m, l) = (2, 1, 3) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_5^i\text{Q}_{1/2}^{1-a}\text{X}_2^i\text{X}_2^a\text{X}_{3/2}^{a-a}\text{Q}_{1/2}^{a-1}] \}$
		$m = 2$	
charge = 0 (n, m, l) = (2, 2, 0) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{2/2}^{1-a}\text{X}_2^i\text{X}_4^a\text{Q}_{2/2}^{a-1}] \}$	charge = 0 (n, m, l) = (2, 2, 1) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{2/2}^{1-a}\text{X}_2^i\text{X}_3^a\text{X}_{1/2}^{a-a}\text{Q}_{2/2}^{a-1}] \}$	charge = 0 (n, m, l) = (2, 2, 0) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{2/2}^{1-a}\text{X}_2^i\text{X}_4^a\text{Q}_{2/2}^{a-1}] \}$	charge = 0 (n, m, l) = (2, 2, 1) formulation: $[\text{Re}_6\text{Q}_6\text{X}_6]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{2/2}^{1-a}\text{X}_2^i\text{X}_3^a\text{X}_{1/2}^{a-a}\text{Q}_{2/2}^{a-1}] \}$
		$m = 3-6$	
		$n = 1, m = 0$	
charge = 1− (n, m, l) = (1, 0, 0) formulation: $[\text{Re}_6\text{Q}_5\text{X}_9]^-$ $\{\text{[Re}_6\text{Q}_5^i\text{X}_3^i\text{X}_6^a]^- \}$	charge = 1− (n, m, l) = (1, 0, 1) formulation: $[\text{Re}_6\text{Q}_5\text{X}_9]^-$ $\{\text{[Re}_6\text{Q}_5^i\text{X}_3^i\text{X}_5^a\text{X}_{1/2}^{a-a}]^- \}$	charge = 0 (n, m, l) = (1, 0, 2) formulation: $[\text{Re}_6\text{Q}_5\text{X}_8]$ $\{\text{[Re}_6\text{Q}_5^i\text{X}_3^i\text{X}_4^a\text{X}_{2/2}^{a-a}] \}$	charge = 0 (n, m, l) = (1, 0, 3) formulation: $[\text{Re}_6\text{Q}_5\text{X}_8]$ $\{\text{[Re}_6\text{Q}_5^i\text{X}_3^i\text{X}_3^a\text{X}_{3/2}^{a-a}] \}$
		$m = 1$	
charge = 0 (n, m, l) = (1, 1, 0) formulation: $[\text{Re}_6\text{Q}_5\text{X}_8]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{1/2}^{1-a}\text{X}_3^i\text{X}_5^a\text{Q}_{1/2}^{a-1}] \}$	charge = 0 (n, m, l) = (1, 1, 1) formulation: $[\text{Re}_6\text{Q}_5\text{X}_8]$ $\{\text{[Re}_6\text{Q}_4^i\text{Q}_{1/2}^{1-a}\text{X}_3^i\text{X}_4^a\text{X}_{1/2}^{a-a}\text{Q}_{1/2}^{a-1}] \}$		
		$m = 2-6$	
		$n = 0, m = 0$	
charge = 0 (n, m, l) = (0, 0, 0) formulation: $[\text{Re}_6\text{Q}_4\text{X}_{10}]$ $\{\text{[Re}_6\text{Q}_4^i\text{X}_4^i\text{X}_6^a] \}$	charge = 0 (n, m, l) = (0, 0, 1) formulation: $[\text{Re}_6\text{Q}_4\text{X}_{10}]$ $\{\text{[Re}_6\text{Q}_4^i\text{X}_4^i\text{X}_5^a\text{X}_{1/2}^{a-a}] \}$		
		$m = 1-6$	

3, 0) and (4, 2, 2), respectively. Again, cationic phases not withstanding, 64 structurally different compounds, many of them still unknown, can be enumerated (Table 4), which decompose into 24, 19, 13, 6, and 2 for $n = 4,^{46}$ 3, 2, 1, and 0, respectively.

Furthermore, this formula remains valid for other $\text{M}-\text{Q}-\text{X}$ systems where $\text{M}_6\text{Q}_n\text{X}_{8-n}$ cluster cores exist, for example the $\text{Mo}-\text{Q}-\text{X}$ system, although the overall charge will depend on the nature of the metal and/or its oxidation state. A consequence is that changing the metal or its oxidation state allows for novel triplets that were explicitly excluded in the Re-(III) series because they would have led to cationic species. This is the case, for example, of the triplet (4, 6, 0) which describes the Chevrel–Sergent phases. Such triplets can also be used in the case of apical bridging chalcogen instead of halogen. Once again, only the overall charge will change in the formula. Thus, $[\text{Re}_6\text{S}_{11}]^{4-}$ or $\{\text{[Re}_6\text{S}_8^i\text{S}_{6/2}^{a-a}]^{4-}\}$ would be represented by the triplet (4, 0, 6),⁶³ and the Siamese twin cluster, $\{\text{[Re}_6\text{S}_5\text{OCl}_7]_2\text{O}\}^{4-}$ (section III.A.1), by the triplet (2, 0, 1).⁶⁴

G. Manipulating the Dimensionality of Solid-State Structures

Conceptually, one recognizes how the 1-, 2-, and 3-dimensional, outer halide-bridged frameworks dis-

cussed above (section II.E) might be broken into small pieces by incorporating additional, bridge-terminating halide ligands in the structure. Here, one perceives a means of disrupting intercluster bonds through the insertion of intervening outer ligands. In a more or less implicit formulation, this strategy has prevailed for the syntheses designed by solid-state chemists of virtually all molecular anion cluster forms starting from $\{\text{[Re}_6\text{Q}_{4+n}\text{X}_{4-n}^i\text{X}_6^a\text{X}_{2/2}^{a-a}]^{(2-n)-}\}$. Thus, from $\text{Re}_6\text{Q}_8\text{X}_2$, the cesium salts of discrete, molecular motifs, $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ ($\text{Q} = \text{S, Se; X} = \text{Cl, Br, I}$), and a set of compounds of intermediate dimensionalities (see Table 2) have been prepared by Holm and co-workers using this principle, formulated dimensional reduction.^{45,46} Tulsy and Long recently proposed a practical formalism for the manipulation of the structures of solids using the dimensional reduction concept, very much in the spirit of the retrosynthesis paradigm.⁶⁵

H. Practical Procedures for High-Temperature Solid-State Synthesis

All synthetic routes to octahedral chalcogenide rhenium clusters require high-temperature reactions. Most starting chemicals are given in Table 5. The synthesis usually starts either directly from the

Table 5. Starting Chemicals Used for the High-Temperature Synthesis of Hexanuclear Rhenium Chalcogenide Clusters

	Re	Q (S, Se, Te)	X (Cl, Br, I)
Re	Re powder	ReS ₂ , ReSe ₂ "Re ₂ Te ₅ " = Re ₆ Te ₁₅	"ReCl ₃ " = Re ₃ Cl ₉ , "ReBr ₃ " = Re ₃ Br ₉ "ReCl ₅ " = Re ₂ Cl ₁₀ , "ReBr ₅ " = Re ₂ Br ₁₀
Q (S, Se, Te)		S, Se, Te powder KSCN	S ₂ Cl ₂
X (Cl, Br, I)	Re ₆ S ₄ Br ₁₀		ICl ₃ , Cl ₂ , Br ₂ , I ₂

elements or from binary phases. Only rarely has a ternary phase been used as a starting material.³⁹

Given the complexity of the phase diagrams with the inherent close proximity of many different phases, it is of paramount importance to properly report⁶⁶ the following set of experimental data:

(i) The temperature, typically 800 to 850 °C, is obviously the most important parameter because small differences can lead to different ending products.²³

(ii) The oven gradient should be registered, reported, and related to the position of the crystal growth when needed.

(iii) The actual thermal cycle²³ affects the crystalline quality of the products and may also influence the formulation of the final product. For example, two compounds being in equilibrium, a short thermal cycle would select the kinetic compound when a longer one yields the thermodynamic phase.

(iv) Since volatile materials are often used, the reaction is achieved under gaseous pressure; this pressure will also be of strong influence on the ending product; therefore, all papers should not only give the stoichiometry of the reaction but also the exact amount of reactants as well as the volume of the tube once sealed. For the sake of reproducibility, volume used during the synthesis should be carefully logged and reported.

(v) A consequence of the previous point is that tubes might explode when heated if their thickness is too small, creating a hazard. Therefore this thickness should also be reported.

III. Solution Chemistry

The remarkable developments of the solid-state and crystal chemistry of octahedral rhenium chalcogenide clusters discussed in the preceding sections had effectively flooded the pool of discrete or polymeric precursors of molecular forms of such cluster compounds. Thus, when the need for a *monoanionic* cluster form isosteric and isostructural to [Mo₆Cl₁₄]²⁻ became necessary following our synthesis of (TMTTF⁺)₂[Mo₆Cl₁₄]²⁻,⁶⁷ we turned to (K⁺)[Re₆Se₅Cl₉]⁻, hence, our initial discovery of the solubility of K[Re₆Se₅Cl₉] in ethanol.⁴

A. From Soluble Mineral Cluster Compounds to a Large Series of Alkylammonium or Tetraphenylphosphonium Discrete Cluster Salts

1. Molecular Cluster Approach

All the salts collected in Table 1 have not been systematically tested for solubility yet. Instead, comparatively few have been reported to be soluble

(Table 6) and most are alkali-metal or alkaline-earth cation salts.⁴² The alkali-metal salts (Rb, K) of the monovalent cluster forms are soluble in ethanol, and although they are barely soluble in water, in the case of the potassium salt, the inner sphere, octacoordinated bis(aquo) potassium complex [K(H₂O)₂][Re₆Se₅Cl₉] is obtained after dispersion of the initial salt in water and overnight stirring.⁶⁸ Note that the cluster core remains intact in solution and that, contrary to an earlier indication, no substitution of an inner, μ_3 -core halogen ligand for OH⁻ occurs to yield K[Re₆Se₅(μ_3 -OH)₂Cl₇]·H₂O.^{69,70} The alkaline-earth salts of the divalent cluster forms are not soluble in water but are highly soluble in a variety of polar organic solvents such as alcohol, acetonitrile, tetrahydrofuran, dimethylformamide, dioxane, and acetone. In turn, the water-soluble, hydrated solid phases such as [Ca(H₂O)_n][Re₆Q₆Cl₈]·mH₂O crystallize out of the former organic phases containing even minute amounts of water (see section II.D.3).³⁷ It is only when the cluster anion charge reaches 3 and 4 that their alkali-metal salts become soluble in water. This is also true for the mixed cluster anion salt Rb₅[Re₆S₆Cl₈][Re₆S₇Cl₇].

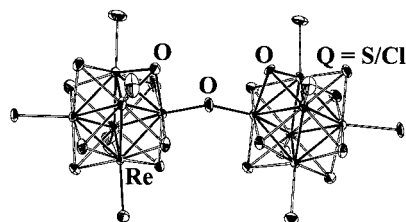
Cation exchange in alcohol or water with alkylammonium halides or tetraphenylphosphonium halides yields the extended series of organic solvent soluble salts of differently charged isosteric molecular cluster forms listed in Table 6. This route provides a ready access to the organic solution phase chemistry of a large set of molecular forms of mineral clusters.

Finally, by direct solid-state synthesis in the presence of minute amounts of water followed by cation exchange in ethanol, an oxo-bridged Siamese twin cluster of two dianion cluster units, (Bu₄N)₄[Re₆S₅OC₂Cl₅]₂O (Figure 11), the first (2, 0, 1) compound (section II.F), is obtained and recrystallized in acetonitrile.⁶⁴ Formally, a single μ -chloride is replaced by an oxo bridge across two identical cluster units; in addition, a single μ_3 -core ligand is substituted by an oxygen atom. The X-ray structure determination has demonstrated that the inner μ_3 -oxygen atom loci are perfectly defined and that no disorder with the other inner ligands can be observed. The chemistry of this oxo-bridged, twin cluster unit has not been explored to any extent yet. It is certainly conceivable, however, that it may in turn be subjected to reactions with water or with, for example, (Me₃Si)₂O (see section B.1). One appealing objective would be to construct out of this twin monomer unprecedented oxo-bridged extended networks of increasing dimensionalities, from chains and slabs eventually all the way to, for example, augmented CaB₆ nets, in the spirit of design principles described by O'Keeffe et al.⁷¹

Table 6. Molecular Forms of Hexanuclear Chalcogenide Rhenium Clusters Derived in Solution

ion	ref	ion	ref
(Bu ₄ N) ₄ {[Re ₆ S ₅ OC ₁₂]Cl ₅ } ₂ O	Tetraanion 64	(Bu ₄ N) ₄ [Re ₆ S ₈ X ₆]·H ₂ O (X = Br, I)	46
(Bu ₄ N) ₄ [Re ₆ S ₈ Cl ₆]	46		
(Bu ₄ N) ₃ {[Re ₆ S ₇ Cl]Cl ₆ }	Trianion 23	(Bu ₄ N) ₃ [Re ^{III} ₅ Re ^{IV} S ₈ Cl ₆]	112
(PPh ₄) ₃ {[Re ₆ S ₇ Br]Br ₆ }	39	Rb ₃ [Re ₆ S ₇ Br ₇]·4 H ₂ O	44a
(Bu ₄ N) ₃ {[Re ₆ Q ₈]Cl ₆ }	46,79	Cs ₃ [Re ₆ Se ₇ Br ₇]·H ₂ O	44b
(Bu ₄ N) ₃ {[Re ₆ Q ₈]X ₆ }·2Me ₂ CO" (Q = S, X = Br, I; Q = Se, X = I)	46,79		
(Bu ₄ N) ₂ {[Re ₆ S ₆ Cl ₂]Cl ₆ }	Dianion 23	[Mg(H ₂ O) ₆]{[Re ₆ S ₆ Cl ₂]Cl ₆ }·2H ₂ O	37
(R ₄ N) ₂ {[Re ₆ Se ₆ Cl ₂]Cl ₆ } (R = Et, Pr ⁿ , Bu ⁿ)	49, 68	(R ₄ N) ₂ {[Re ₆ Se ₆ Cl ₂]Cl ₆ } (R = Et, Pr, Bu)	49
(Bu ₄ N) ₂ {[Re ₆ Q ₅ EC ₁₂]Cl ₆ } (Q = S, E = O, S, Se; Q = Se, E = S, Se, Te)	74	(Pr ₄ N) ₂ {[α-Re ₆ Se ₄ O ₂ Cl ₂]Cl ₆ }·2DMF	49
(PPh ₄) ₂ {[Re ₆ S ₆ Br ₂]Br ₆ }·CH ₃ C ₆ H ₅	39	(Pr ₄ N) ₂ {[β-Re ₆ Se ₄ O ₂ Cl ₂]Cl ₆ }	49
(Bu ₄ N) ₂ {[Re ₆ Q ₅ (NR)Cl ₂]Cl ₆ } (Q = S, Se; R = Me, Bz)	75	(Bu ₄ N) ₂ [Re ₆ S ₈ (PET ₃) ₂ Br ₄]	80
(Bu ₄ N) ₂ {[Re ₆ Q ₅ (N ⁻ SiMe ₃)Cl ₂]Cl ₆ } (Q = S, Se)	75	(Bu ₄ N) ₂ [Re ₆ S ₈ Cl ₄ (L) ₂] (<i>cis</i> and <i>trans</i>); with L = py, pz, cpy, bpy, mpy, dmap) ^a	88, 111
(Bu ₄ N) ₂ {[Re ₆ Q ₅ (NH)Cl ₂]Cl ₆ } (Q = S, Se)	75	(Bu ₄ N) ₂ [Re ₆ Se ₈ (μ-dpph) ₄] ^a	85
[Ca(H ₂ O) ₇][Re ₆ Q ₆ Cl ₈]·3H ₂ O (Q = S, Se), [Ca(H ₂ O) ₈][Re ₆ S ₆ Cl ₈]	37		
(Bu ₄ N){[Re ₆ Se ₅ Cl ₃]Cl ₆ }	Monoanion 4	(Bu ₄ N)[Re ₆ S ₈ (PET ₃) ₃ Br ₃]	80
(Bu ₄ N){[Re ₆ S ₅ Cl ₃]Cl ₆ }	23	(Bu ₄ N)[<i>mer</i> -Re ₆ S ₈ Cl ₃ (py) ₃] ^a	83
K(H ₂ O) ₂ [Re ₆ Se ₅ Cl ₉]	68	(Bu ₄ N)[<i>trans</i> -Re ^{III} ₅ Re ^{IV} S ₈ Cl ₄ (L) ₂] ^a	88
(R ₄ N){[Re ₆ Se ₅ Cl ₃]Cl ₆ } (R = Et, Pr ⁿ , Bu ⁿ)	49	(L = py, py-CN) ^a	
(Bu ₄ N)[Re ₆ Se ₈ (PET ₃) ₃ I ₃]	82		
[Re ₆ Se ₈ (PET ₃) ₄ I ₂]·2CHCl ₃ (<i>trans</i> , <i>cis</i>)	82	[<i>mer</i> -Re ^{III} ₅ Re ^{IV} S ₈ Cl ₃ (py) ₃] ^a	83
[Re ₆ S ₈ (PET ₃) ₄ Br ₂]	80	(<i>cis</i> and <i>trans</i>)-[Re ₆ Se ₈ (μ-dpph) ₂ I ₂] ^a	85
[Re ₆ S ₆ E ₂ (PPr ⁿ) ₃] ₆ (E = As, P)	89		
[Re ₆ Se ₈ (PET ₃) ₅ I] ₂ ·2CH ₂ Cl ₂	Monocation 82	[Re ₆ S ₈ (PET ₃) ₅ Br]Br	80
[Re ₆ Se ₈ (PET ₃) _n (MeCN) _{6-n}] ₂ A ₂ (n = 0, 5, 6, A = BF ₄ ; n = 4, A = SbF ₆)	Dication 82	[Re ₆ S ₈ (H ₂ O) ₆] ²⁺	47
[Re ₆ Se ₈ (PET ₃) ₄ (solv) ₂](SbF ₆) ₂ (solv = Bu ⁿ CN, DMF, Me ₂ SO, py) ^a	83	Re ₆ Se ₈ (pyridyl functionality-bearing dendrons) ₆] ²⁺	81
<i>trans</i> -[Re ₆ Se ₈ (PET ₃) ₄ (solv) ₂](SbF ₆) ₂ (solv = MeCN, DMF, Me ₂ SO)	84	[Re ₆ Se ₈ (L) ₆] ²⁺ (L = py-R, py-OH) ^a	81, 82
[Re ₆ S ₈ (PET ₃) ₆]Br ₂	80	[Re ₆ Se ₈ (L) ₆](SbF ₆) ₂ (L = DMF, Me ₂ SO, py, bpy (<i>cis</i> , <i>trans</i>))	84
[Re ₆ S ₆ Y ₂ (PPr ⁿ) ₃] ₆ [Re ₆ S ₆ Cl ₈]·2CH ₃ CN (E = NH, O, S)	89	[Re ₆ Se ₈ (μ-dpph) ₃](SbF ₆) ₂ ^a	85
	Tetracation and Hexacation		
[Re ₁₂ Se ₁₆ (PET ₃) ₁₀](BF ₄) ₄ ·4CH ₂ Cl ₂	82	{[Re ₆ Se ₈ (PET ₃) ₅] ₂ (py ₂ C ₂ H ₄)}(SbF ₆) ₄ ^a	84
<i>trans</i> -[Re ₁₂ Se ₁₆ (PET ₃) ₈ (MeCN) ₂](SbF ₆) ₄ ·4 CH ₂ Cl ₂	83	{[Re ₆ Se ₈ (PET ₃) ₅] ₂ (py ₂ C ₂ H ₄)}(SbF ₆) ₄ ^a	84
{[Re ₆ Se ₈ (PET ₃) ₅] ₂ (bpy)}(SbF ₆) ₄ ^a	84	[Re ₁₈ Se ₂₄ (PET ₃) ₁₄ (bpy) ₂](SbF ₆) ₆ ^a	84

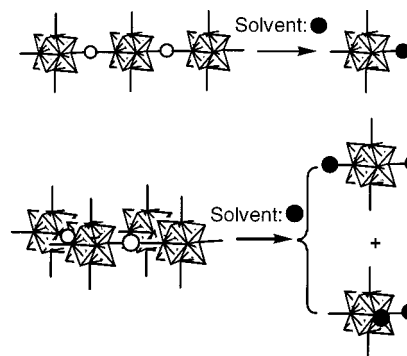
^a py = pyridine; pz = pyrazine; cpy = cyanopyridine; bpy = 4,4-bipyridine; mpy = 4-methylpyridine; dmap = (4-dimethyl-amino)pyridine; py-CN = 4-cyanopyridine; py-OH = 4-hydroxypyridine; py₂C₂H₄ = *trans*-1,2-bis(4-pyridyl)ethylene; py₂C₂H₄ = *trans*-1,2-bis(4-pyridyl)ethane; dpph = diphenylphosphine hexane.

**Figure 11.** Oxo-bridged Siamese twin cluster in (Bu₄N)₄-[Re₆S₅OC₁₂]₂O.

2. Polymeric Clusters Approach

An alternative entry into the organic solution phase chemistry of the former monoanionic and dianionic molecular cluster forms starts from the corresponding neutral one- and two-dimensional, μ₂-halide-bridged polymers, Re₆Q₅Cl₈ and Re₆Q₆Cl₆

Scheme 1



(Scheme 1). In the presence of coordinating solvent molecules such as acetonitrile or dimethylformamide, and along the progress of the excision of their

solvated molecular forms, $\text{Re}_6\text{Q}_5\text{Cl}_8(\mu_1\text{-solvent})$ and $\text{Re}_6\text{Q}_6\text{Cl}_6(\mu_1\text{-solvent})_2$, the μ_2 -halide bridges are severed and yield μ -halide and μ -solvent ligand sites as shown in Scheme 1, prior to the reaction with appropriate alkylammonium halides.^{49,23} This process, analogous to Sheldon's dissociation of MoCl_2 and reminiscent of our own observation that $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_{14}]$ is readily obtained from $\text{Na}[\text{Mo}_6\text{Cl}_{13}]$ in polar solvents,⁷² has been recently developed in Holm's group.⁷³ In that respect, it would be of interest to explore the solubility properties of the one-dimensional anionic polymers $\{[\text{Re}_6\text{Se}_6^i\text{Cl}_2^i]\text{Cl}_4^a\text{Cl}_{2/2}^{a-a}\}^-$ and $\{[\text{Re}_6\text{Se}_6^i\text{Cl}^i]\text{Cl}_4^a\text{Cl}_{2/2}^{a-a}\}^{2-}$ (see section II.E.1) isostructural to $\text{Na}[\text{Mo}_6\text{Cl}_{13}]$.

Thus, the mono- and dianion molecular cluster salts are accessible from two different routes. However, the latter suffers from the inherent difficulty to prepare the neutral polymeric precursors as pure single phase materials because of their close proximity in the Re–Q–Cl phase diagram.¹⁵ By contrast, the solid-state synthesis of the alkali-metal and alkaline-earth cation salts of the discrete molecular cluster anion forms proved to yield compounds that can be purified because of their different solubility.^{23,37} Furthermore, the neutral polymeric clusters approach provides an access to solely the mono- and dianion cluster forms in solution since the neutral, halide-bridged three-dimensional polymers $\text{Re}_6\text{Q}_7\text{Cl}_4$ have so far proven to be insoluble.⁴⁹ In that respect, it is suggested that the yet unknown phases $\text{M}^+\{[\text{Re}_6\text{Q}_7\text{Cl}^i]\text{Cl}_2^a\text{Cl}_{4/2}^{a-a}\}^-$ and $\text{M}^{2+}\{[\text{Re}_6\text{Q}_8^i]\text{Cl}_2^a\text{Cl}_{4/2}^{a-a}\}^{2-}$, where negatively charged two-dimensional inorganic polymers are effectively screened by metal cations, would both prove to be easier to synthesize as single phase materials and be readily soluble in coordinating solvents, thereby extending the polymeric clusters approach to the synthesis of the tri- and tetranionic cluster forms in solution.

B. Core Reactivity and Core Coordination: Toward Molecular Hybrids

1. μ_3 -Functionalization

The first evidence of the lability of one face-capping, μ_3 -chloride can be traced to our discovery, back in 1985, that cation exchange with Bu_4NCl of warm, aged overnight solutions of $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ in ethanol yields $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$ while cold, aged solutions consistently proved to afford the unreacted cluster core, $(\text{Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$.³⁶ This was also consistent with a number of puzzling, essentially concomitant observations such as the diamagnetic character of single crystals of the putative mixed-valence cation radical salt $(\text{TMTTF})_2[\text{Re}_6\text{Se}_5\text{Cl}_9]$, obtained by slow oxidation over several days at a platinum wire electrode of TMTTF solutions in acetonitrile containing $(\text{Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$ as an electrolyte, and which proved to be $(\text{TMTTF})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$ instead.³⁶ Thus, evidence was accumulating that the monoanionic cluster forms were prone to substitution of one μ_3 -chloride by a chalcogenide element, both in the sulfur and selenium series.

This chemistry has been exemplified by Yaghi et al. with two sets of experiments (Figure 12).⁴⁹ First,

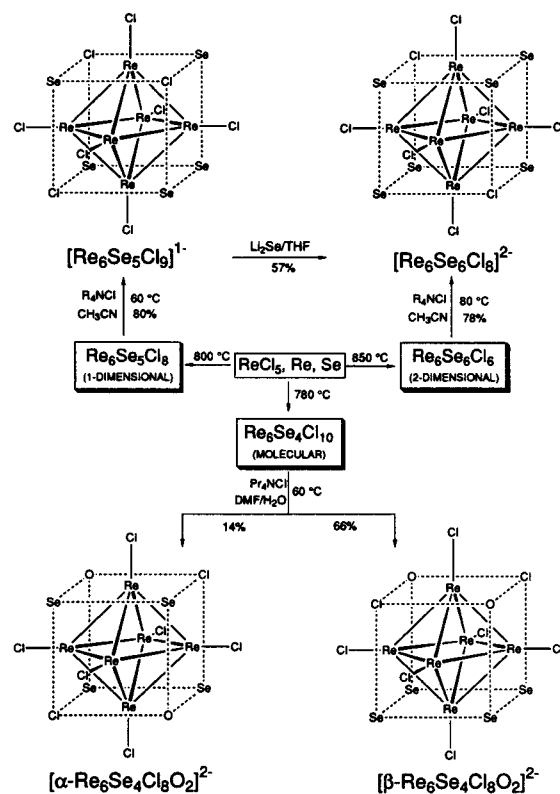


Figure 12. Reaction scheme illustrating the excision of clusters from the phase $\text{Re}_6\text{Se}_5\text{Cl}_8$ and $\text{Re}_6\text{Se}_6\text{Cl}_6$ and core conversion reactions in which chloride is substituted by selenide or oxide. For the sake of definiteness, core atom positions are specified, but some atoms are actually disordered. Reprinted from ref 49. Copyright 1992 American Chemical Society.

it was shown that the neutral molecular ($n = 0$) phase $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ reacts with water in a DMF solution of NPr^nCl at 60 °C to give $\{[\text{Re}_6\text{Se}_4\text{O}_2\text{Cl}_2^i]\text{Cl}_6^a\}^{2-}$, whose two isomers were isolated. Second, THF solutions of $[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$ react with Li_2Se to afford $[\text{Re}_6\text{Se}_6\text{Cl}_8]^{2-}$.

A neat demonstration of the $[\text{Re}_6\text{S}_5\text{Cl}_3]^{5+}$ core reactivity in solution is offered by a key electrochemical experiment which follows the core transformation upon reaction with $(\text{Me}_3\text{Si})_2\text{S}$, taking advantage that $[\text{Re}_6\text{S}_5\text{Cl}_9]^-$ and $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$ have markedly different redox behaviors (see section IV.B and Figure 13).

On the basis of these early results, the reaction in acetonitrile of silylated reagents $(\text{Me}_3\text{Si})_2\text{E}$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) with alkylammonium salts of the cluster monoanions forms has been explored and proved to provide a neat, efficient synthesis⁷⁴ of a series of alkylammonium salts of heterosubstituted cluster cores $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Q}_5\text{ECI}_8]$ ($\text{Q} = \text{S}, \text{E} = \text{O}, \text{S}, \text{Se}; \text{Q} = \text{Se}, \text{E} = \text{S}, \text{Se}, \text{Te}$) (Table 6), as shown in Scheme 2. Among the former, the oxo chalcogenide cluster, $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_5\text{OCl}_8]$, stands alone because its $[\text{Re}_6\text{S}_5\text{O}]^{2+}$ core is not disordered in the solid-state structure, a consequence of the ordering of the oxygen atom on one single μ_3 -site only. In addition, the ordered, noncentrosymmetrical cluster proved to be distorted as a result of a contraction of the Re_3 face capped by the oxygen atom.⁷⁴ Similar structural features are observed for the Siamese twin oxo cluster case reported in section A.1.

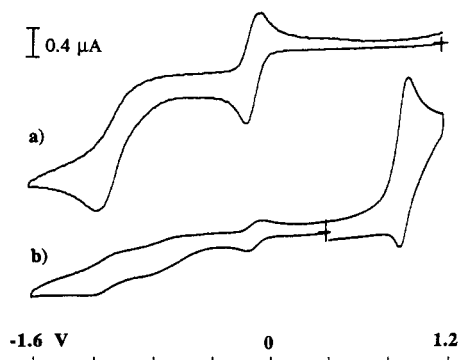
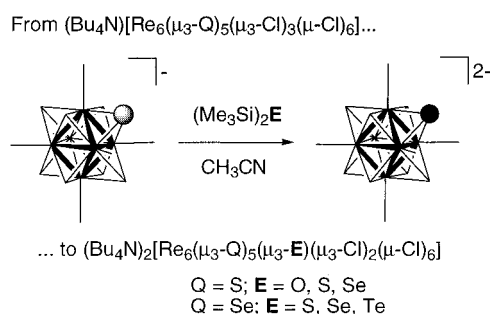


Figure 13. Cyclic voltammograms at a platinum electrode vs SCE in acetonitrile containing 0.1 M $(\text{Bu}_4\text{N})\text{PF}_6$ (scan rate 0.1 V s^{-1}) of $(\text{Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{Cl}_9]$ (a) before and (b) after addition of $(\text{Me}_3\text{Si})_2\text{S}$ and PPh_4Cl . Reprinted from ref 23. Copyright 1993 American Chemical Society.

Scheme 2



Among many attractive features⁷⁴ such as availability of large quantities in good yields, the latter silylated reagents route yields a wealth of novel compounds which include, for E = NR (R = H, Me, Bz), the μ_3 -imido-functionalized Chevrel–Sergent-type molecular clusters $\{[\text{Re}_6\text{Q}_5^{\text{I}}(\mu_3\text{-NR})^{\text{I}}\text{Cl}_2^{\text{I}}]\text{Cl}_6^{\text{a}}\}^{2-}$ ⁷⁵ and $\{[\text{Re}_6\text{Q}_5^{\text{I}}(\text{NSiMe}_3)^{\text{I}}\text{Cl}_2^{\text{I}}]\text{Cl}_6^{\text{a}}\}^{2-}$ (Q = S, Se) (Figure 14). The nucleophilic conversion of the cluster-supported NSiMe₃ group into NH by reaction with Bu_4NF and the demonstration that the imido-functionalized core in turn reacts with electrophiles (Figure 14) are important new synthetic methods to prepare inorganic–organic hybrid compounds starting from cluster compounds which can only be prepared by high-temperature solid-state reactions.⁷⁵

2. μ -Functionalization

$(\text{Bu}_4\text{N}^+)[\text{Re}_6\text{S}_5\text{Cl}_9]^-$ and $(\text{Bu}_4\text{N}^+)[\text{Re}_6\text{Se}_6\text{Cl}_9]^-$ do not react with AgBF_4 in refluxed acetonitrile,⁷⁶ indicating that the outer $\mu\text{-Cl}^-$ ligands held onto the hexarhenium chalcogenide cluster cores more strongly than in $[\text{Mo}_6\text{Cl}_{14}]^{2-}$.⁷⁷

Scheme 3

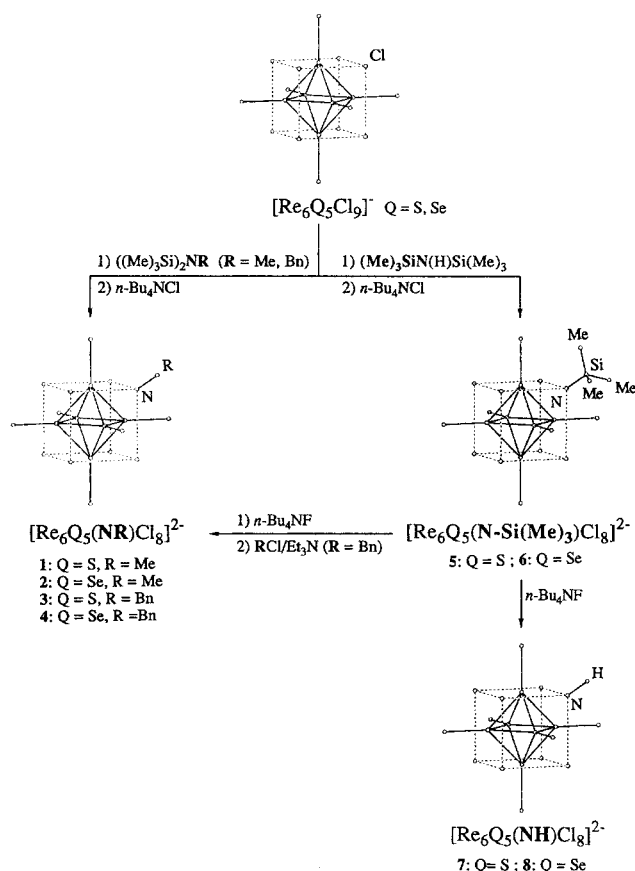
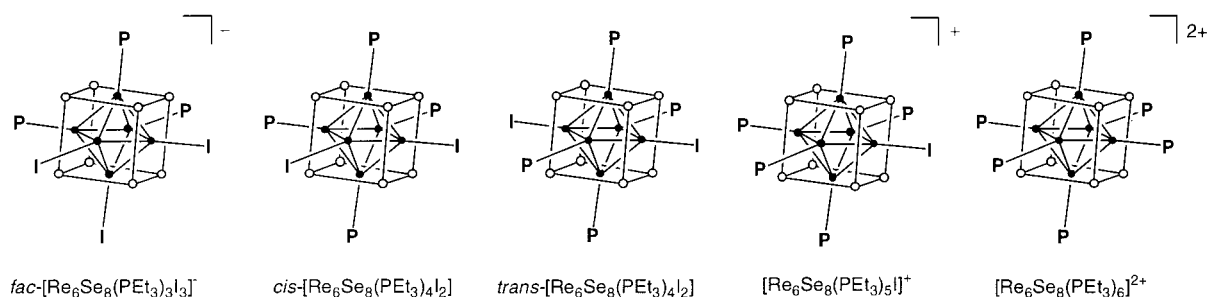
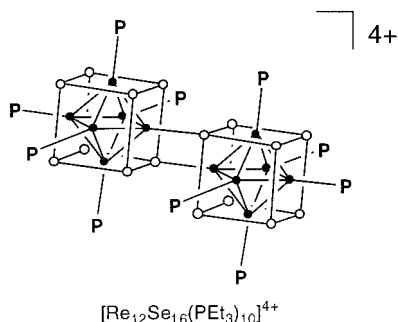


Figure 14. Reaction scheme for the preparation of compounds labeled here as 1–8. In each case the counterions of the anionic cluster are Bu_4N^+ ions. Bn = benzyl. Reprinted from ref 75. Copyright 1996 Wiley-VCH.

The lability of outer iodides has been demonstrated recently by Zheng et al. for $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]$,⁷⁸ actually the oxidized, paramagnetic species, $(\text{Bu}_4\text{N})_3[\text{Re}^{\text{III}}_5\text{Re}^{\text{IV}}\text{Se}_8\text{I}_6]$,⁷⁹ which is found to react with various amounts of PET_3 in refluxed acetonitrile or DMF, to afford $[\text{Re}_6\text{Se}_8(\text{PET}_3)_n\text{I}_{6-n}]^{(n-4)-}$, $n = 3\text{--}6$ (Scheme 3).⁸² This is not a simple μ -ligand exchange of $[\text{Re}_6\text{Se}_8\text{I}_6]^{3-}$ because simultaneous reductions of the 23-electron hexarhenium cores take place during the reaction.

The partially substituted clusters may be ultimately condensed upon thermolysis at 180°C into dicluster species, such as $[\text{Re}_{12}\text{Se}_{16}(\text{PET}_3)_{10}]^{4+}$ (Scheme 4).⁸² Likewise, $(\text{Bu}_4\text{N}^+)_3[\text{Re}_6\text{S}_8\text{Br}_6]^{3-}$ reacts with PET_3 to give $[\text{Re}_6\text{S}_8(\text{PET}_3)_n\text{Br}_{6-n}]^{(n-4)+}$ ($n = 2\text{--}6$).⁸⁰ Also, a fraction up to the totality of the μ -iodide ligands may be stripped off $(\text{Bu}_4\text{N}^+)_3[\text{Re}_6\text{S}_8\text{Br}_6]^{3-}$ upon reaction with AgBF_4 in acetonitrile (see Table 6),⁸² to yield

Scheme 4



$[\text{Re}_6\text{Se}_8(\text{MeCN})_6](\text{BF}_4)_2$. The latter solvated hexanuclear chalcogenide cluster core has been used recently to prepare pyridine- or 4-hydroxypyridine-ligated Re_6Se_8 complexes as well as the first dendrimers (Scheme 5) supported by a $[\text{Re}_6\text{Q}_8]^{2+}$ metal cluster core, based upon pyridyl functionality-bearing dendrons.^{81,82} When *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]$ is used as a starting material instead and dissolved in various solvents prior to the addition of AgSbF_6 , additional phases have been obtained,⁸³ namely *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{solvent})_2](\text{SbF}_6)_2$ (Table 6). It should be noted that the iodide to solvent molecule exchange here occurs in the absence of any oxidation of the $[\text{Re}_6\text{Se}_8]^{2+}$ core. Thermolysis of *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2](\text{SbF}_6)_2$ allowed another dicluster form, *trans*- $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}(\text{MeCN})_2]^{4+}$, to be isolated.

This work has been extended to the synthesis of the SbF_6^- salts of *trans*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2]^{2+}$, $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(4,4'\text{-bpy})]^{2+}$ (Scheme 6), and *trans*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(4,4'\text{-bpy})_2]^{2+}$ (Scheme 6) and of the bridged diclusters $\{[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5]_2(\text{L-L})\}^{4+}$ ($\text{L-L} = 4,4'\text{-bpy}$, 4,4'-bipyridine (Scheme 7), 4,4'- $\text{py}_2\text{C}_2\text{H}_2$, *trans*-1,2-bis(4-pyridyl)ethylene, and 4,4'- $\text{py}_2\text{C}_2\text{H}_4$, 1,2-bis(4-pyridyl)ethane) (Scheme 8)), up to the quasi-linear tricluster $\{[\text{Re}_{18}\text{Se}_{24}(\text{PEt}_3)_{14}(4,4'\text{-bpy})_2]\}^{6+}$.⁸⁴ Further

developments were recently disclosed where chelate embraces of the hexarhenium cluster core is achieved by the diphosphane 1,6-bis(diphenylphosphino)hexane (dpph) which substitutes for a fraction or the totality of μ -iodides in $(\text{Bu}_4\text{N}^+)_3[\text{Re}_6\text{Se}_8\text{I}_6]^{3-}$, to yield $[\text{Re}_6\text{Se}_8(\mu\text{-dpph})_n\text{I}_{6-2n}]^{2n-4}$ ($n = 1-3$), as shown in Scheme 9.⁸⁵

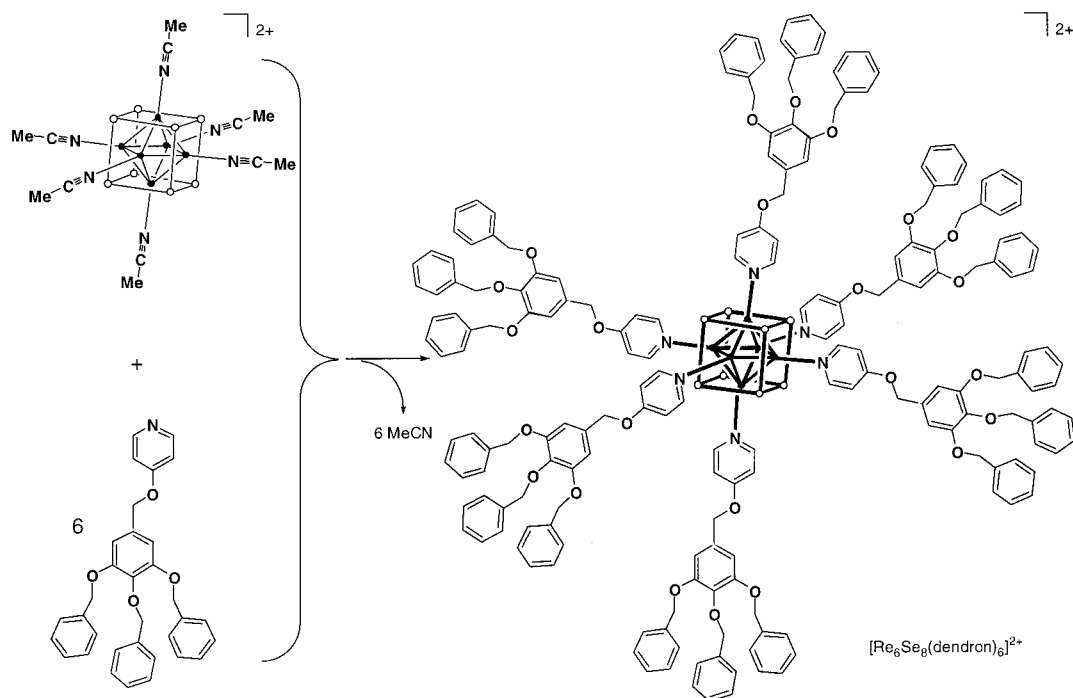
Recently, Holm and Zheng have reported⁸⁶ the syntheses and characterization of three molecular squares by reacting *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2](\text{SbF}_6)_2$ with ditopic ligands such as 4,4'-bipyridyl, 4,4'- $\text{py}_2\text{C}_2\text{H}_2$, and 4,4'- $\text{py}_2\text{C}_2\text{H}_4$.

The first aqua ion, $[\text{Re}_6\text{S}_8(\text{H}_2\text{O})_6]^{2+}$,⁴⁷ was obtained in a parallel work by Fedin et co-workers by addition of a silver salt to an aqueous solution of $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$. However, no structural characterization of this dication have yet confirmed this interesting result.

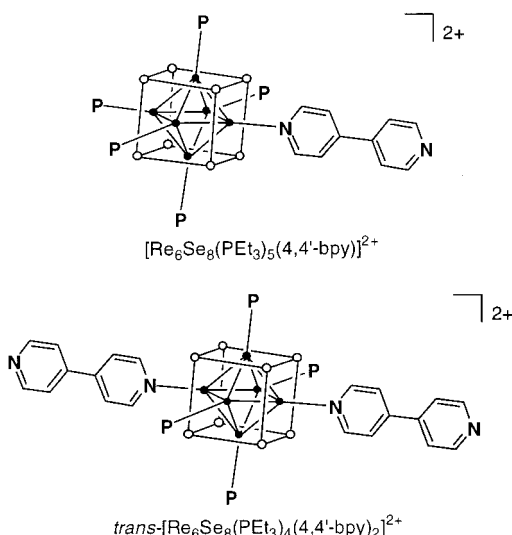
Novel substitutions of μ -chlorine ligands of the one-electron-oxidized species $(\text{Bu}_4\text{N})_3[\text{Re}^{\text{III}}_5\text{Re}^{\text{IV}}\text{S}_8\text{Cl}_6]$ have been reported recently by Sasaki and co-workers.⁸⁷ Thus, this paramagnetic 23-electron trianion reacts with pyridine (py) or 4-cyanopyridine (cpy) in DMF, leading, presumably upon an in-situ reduction, to a series of diamagnetic, 24-electron cluster salts, $(\text{Bu}_4\text{N})_{4-n}[\text{Re}^{\text{III}}_5\text{S}_8\text{Cl}_{6-n}(\text{py-R})_n]$ ($n = 2-3$, py-R = pyridine; $n = 2$, py-R = 4-cyanopyridine).⁸⁸ The attendant, one-electron-oxidized species have also been prepared upon electrochemical oxidation at constant potential, $(\text{Bu}_4\text{N})_{3-n}[\text{Re}^{\text{III}}_5\text{Re}^{\text{IV}}\text{S}_8\text{Cl}_{6-n}(\text{py-R})_n]$ ($n = 2-3$, py-R = pyridine; $n = 2$, py-R = 4-cyanopyridine).⁹³ The same authors have extended the series recently to include complexes with new N-heterocyclic ligands such as pyrazine (pz) (Scheme 10), 4,4'-bipyridine (bpy), 4-methylpyridine (mpy), and (4-dimethylamino)pyridine (dmap) (see Table 6 and section IV.C).

Finally, when the number of substitutions of μ -halogen ligands reaches 2–4, two different isomers

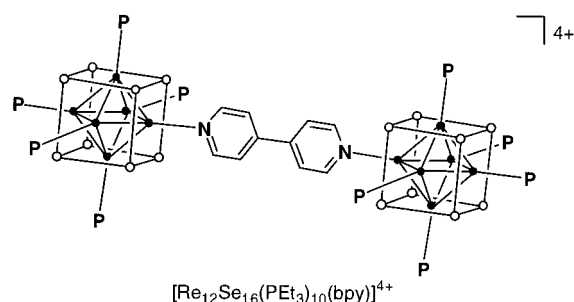
Scheme 5



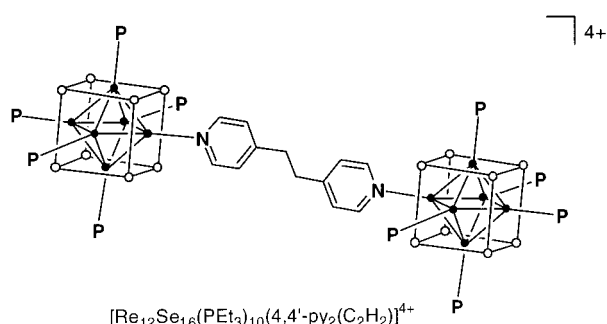
Scheme 6



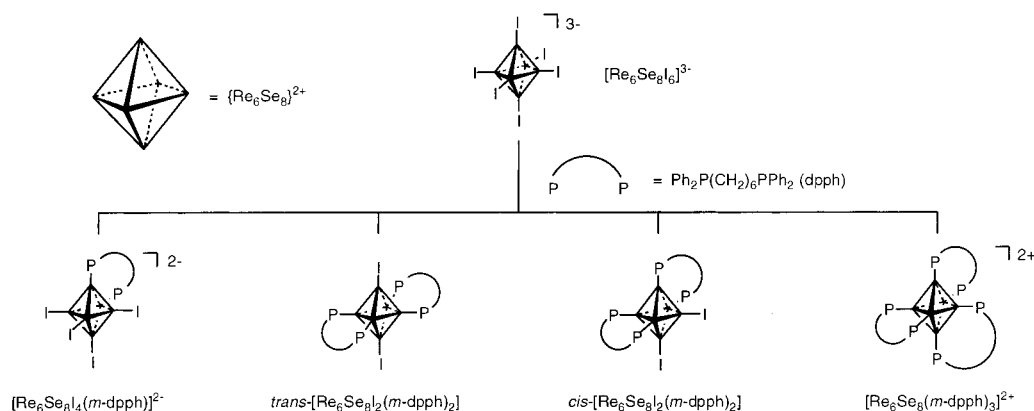
Scheme 7



Scheme 8



Scheme 9



(Adapted from ref. 89. Copyright 2001 from Wiley-VCH)

are possible in each case. Their separation was achieved both in the $[\text{Re}_6\text{Q}_8(\text{PEt}_3)_n\text{X}_{6-n}]^{n-4}$ ($n = 2-4$, $\text{X} = \text{Br}$, $\text{Q} = \text{Se}$; $n = 3-4$, $\text{X} = \text{I}$, $\text{Q} = \text{Se}$)⁸⁰ and $(\text{Bu}_4\text{N})_{4-n}[\text{Re}^{\text{III}}_6\text{S}_8\text{Cl}_{6-n}(\text{py-R})_n]$ ($n = 2-3$, $\text{py-R} = \text{pyridine}$; $n = 2$, $\text{py-R} = 4\text{-cyanopyridine}$)⁸⁸ series either by chromatography on silica/flash silica gel columns or by difference of solubility. The former proved to be most efficient for neutral and charged molecules alike, allowing for example to separate in good yield the cis and trans isomers of $[\text{Re}_6\text{Y}_8(\text{PEt}_3)_4\text{X}_2]$ as well as $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_8\text{Cl}_4(\text{py-R})_2]$.

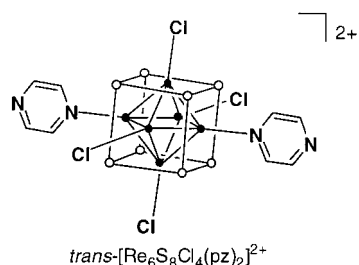
3. Concomitant μ - and μ_3 -Functionalization

Concomitant $\mu\text{-Cl}$ and $\mu_3\text{-Cl}$ displacement reactions have recently been achieved by reacting $\text{Ca}(\text{THF})_6\text{-}[\text{Re}_6\text{S}_6\text{Cl}_8]$,⁸⁹ instead of $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_6\text{Cl}_8]$,⁸³ with $(\text{Me}_3\text{Si})_2\text{E}$ ($\text{E} = \text{NH}$, O , S) or $(\text{Me}_3\text{Si})_3\text{E}'$ ($\text{E}' = \text{P}$, As) in the presence of PPr^n_3 . Thus, unprecedented neutral and dicationic hexanuclear rhenium phosphine clusters with respectively $\mu_3\text{-imido}$ or $\mu_3\text{-oxo-chalcogenide}$ heteroligand shells, $[\text{Re}_6\text{S}_6\text{E}_2(\text{PPr}^n_3)_6]^{2+}$ ($\text{E} = \text{NH}$, O , S), and $\mu_3\text{-phosphido-chalcogenide}$ or $\mu_3\text{-arsenido-chalcogenide}$, $[\text{Re}_6\text{S}_6\text{E}_2(\text{PPr}^n_3)_6]$ ($\text{E} = \text{As}$, P), are obtained in good yields (Table 6 and Figure 15).⁹⁴

4. Unsettled Mechanistic Issues

The cluster core inner and outer ligand-substitution chemistry in solution is still in its infancy, yet a number of key mechanistic questions may already be formulated and will have to be tackled by further reactivity and theoretical studies. One is the contrasted ease of μ - or μ_3 -substitution as it would appear to depend on the presence of any halogen atom onto the eight inner cluster core μ_3 -ligand sites within the $\{[\text{Re}_6(\mu_3\text{-Q})_{4+n}(\mu_3\text{-X})_{4-n}](\mu\text{-X})_6\}^{n-}$ series. An analysis of the reaction products listed in Table 6 for which μ -functionalization occurred reveals that none of the latter retain an inner halogen ligand in its cluster core. Furthermore, when reactions were performed starting with those cluster forms having two to four inner halogen ligands, no purely μ -functionalization has been achieved. Either, purely μ_3 -reactivity have been observed instead^{23,49,74,75} or else all μ_3 -halogen ligands were also substituted in the final compounds.⁸⁹

Scheme 10



It is perhaps too early to claim that the removal of all inner μ_3 -halogen ligands and their replacement by chalcogen or pnictogen atoms might be required in order to activate the reactivity of the apical μ -halogen atoms.⁹⁰ Two experimental findings correlate with this assumption and are reformulated now. First, whenever any number of μ_3 -halogen ligands are present onto the cluster core, the latter remains reluctant to oxidation, as discussed in section IV.C. Second, as reviewed in the preceding section (section III.B. 2), it is the oxidized, 23-electron forms, $[\text{Re}^{\text{III}}_5\text{Re}^{\text{IV}}\text{Q}_8\text{X}_6]^{3-}$ ($\text{Q} = \text{S}, \text{Se}; \text{X} = \text{Cl}, \text{Br}, \text{I}$), typically prepared by reacting the 24-electron precursors $[\text{Re}^{\text{III}}_6\text{Q}_8\text{X}_6]^{4-}$ with SOCl_2 or SOBr_2 , which are consistently engaged in the substitution reactions. Note that the latter are not simple μ -X substitution reactions of $[\text{Re}^{\text{III}}_5\text{Re}^{\text{IV}}\text{Q}_8\text{X}_6]^{3-}$ because simultaneous reduction of the hexarhenium cores takes place

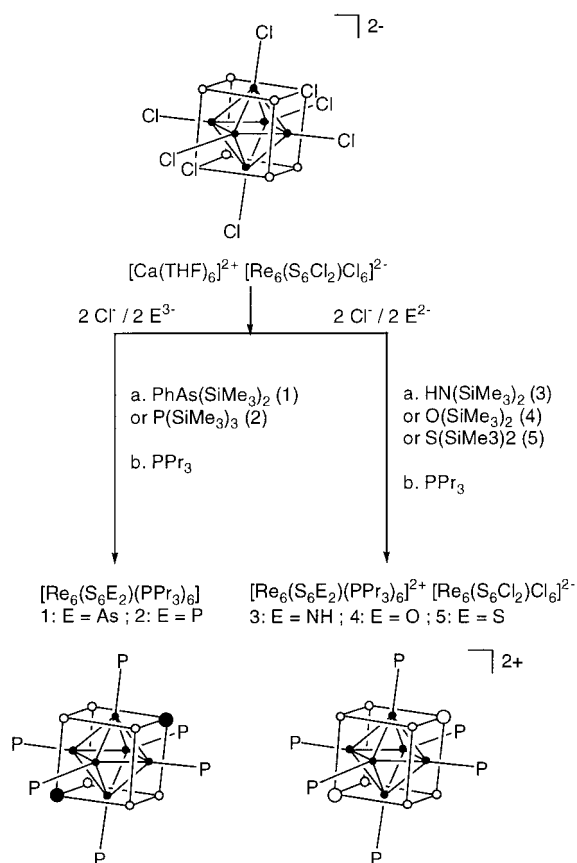


Figure 15. Synthetic scheme for the phosphine-substituted cluster labeled here as 1–5. The μ_3 -Cl and μ_3 -E ligands are ordered (2, 4, 5) or disordered (1, 3) over the μ_3 -face-capping cluster sites and are therefore only presented schematically in the pictures. Adapted from ref 93. Copyright 2000 Wiley-VCH.

during the reactions. The mechanism for the latter has not been addressed yet. Note, also, the salient counterexample of the partially substituted, reduced cluster *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]$ (Scheme 3), for which the remaining outer iodides can be exchanged by acetonitrile molecules in the absence of oxidant in the solution.

Another, elusive issue is the role of the nature, when relevant, of the cation in the starting material for inner or outer ligand exchange reactions in solution as $\text{Ca}(\text{THF})[\text{Re}_6\text{S}_6\text{Cl}_8]$ reacts further than $(\text{Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{Cl}_9]$ (see section B.1).

Finally, one way to enter in the ligand exchange chemistry of the mixed-ligand cluster cores is to start from the one- or two-dimensional polymers, $\text{Re}_6\text{Q}_5\text{Cl}_8$ and $\text{Re}_6\text{Q}_6\text{Cl}_6$, respectively, as discussed earlier (section III.A.2). In turn, the solvent molecule μ -coordinated to the excised molecular forms $\{[\text{Re}_6\text{Q}_5\text{Cl}_3]\text{Cl}_5(\mu\text{-solvent})\}$ and $\{[\text{Re}_6\text{Q}_6\text{Cl}_2]\text{Cl}_4(\mu\text{-solvent})_2\}$ or the inner chloride atoms even could be substituted by other ligands such as phosphines or N-heterocycles.

IV. Special Topics

A. Structural Correlations

1. Constraints Imposed by the Ligands and Mechanochemical Response of the Re_6 Core

As readily exemplified by the analysis of the data collected in Table 7, the Re–Re bond lengths change with both the elements and the chalcogen/halogen ratio. Thus, in the Re–S–Cl system the Re–Re distance is slightly shorter than that calculated for a Re–Re single bond (2.609 Å) using the Pauling bond order expression,⁹¹ with $d_n = d_1 - 0.6 \log n$, where n is Donnan and Allmann's bond-order value calculated as $n = |d_1/d_n|^5$ (d_n is the bond distance of order n ; d_1 is the bond distance of order 1).⁹² This core contraction, not observed for other systems such as Re–Se–Cl or Re–S–Br, is likely to reflect an internal pressure or constraint applied on the Re_6 octahedral core and which become significant for smaller ligands surroundings. This is further confirmed by the fact that, in the structures that contain one or two μ_3 -oxo face-capping ligands, the averaged Re–Re distance within these cluster faces is even shorter, 2.530 Å for $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_5\text{OCl}_7]_2\text{O}$,⁶⁴ 2.523 Å for $(\text{Bu}_4\text{N})_2\{[\text{Re}_6\text{S}_5\text{OCl}_2]\text{Cl}_6\}$,⁷⁴ and 2.557 Å for $\{[\text{Re}_6\text{S}_6\text{O}_2](\text{PPr}_3)_6\}\{[\text{Re}_6\text{S}_6\text{Cl}_2]\text{Cl}_6\} \cdot 2\text{CH}_3\text{CN}$.⁹³ Consistently, larger Re–Re distances are obtained when tellurium ligands are involved, with for example 2.643 Å in $\text{Re}_6\text{Te}_4\text{Br}_{10}$.²⁵

2. Re–L Distance as a Function of the X/Q Ratio

In the series $\{[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]\text{X}_6\}^{n-}$, where most structures are solved using a disordered mixed-ligand $\text{L} = [(4+n)/8\text{Y} + (4-n)/8\text{X}]$, the averaged $\langle \text{Re–L} \rangle$ distance can be estimated in first approximation by applying the same weighting scheme to the actual Re–Q and Re–X bond lengths:

$$\langle d(\text{Re}-\mu_3\text{-L}) \rangle = \frac{[(4+n)/8d(\text{Re}-\mu_3\text{-Q}) + (4-n)/8d(\text{Re}-\mu_3\text{-X})]}{(3)} \quad (3)$$

Table 7. Mean Interatomic Distances (Å) for the Series $[\text{Re}_6\text{Q}_{4+n}\text{X}_{10-n}]^{n-}$ ($n = 0-4$) in the Re–S–Cl, Re–S–Br, and Re–Se–Cl Systems

Re–S–Cl	$\text{Re}_6\text{S}_4\text{Cl}_{10}$ ²³	(a) $(\text{Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{Cl}_9]$ ²³ (b) $\text{RbRe}_6\text{S}_5\text{Cl}_9$ ²³	(a) $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_6\text{Cl}_8]$ ²³ (b) $\text{ZnRe}_6\text{S}_6\text{Cl}_8$ ³⁷	(a) $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7\text{Cl}_7]$ ²³ (b) $\text{Cs}_3\text{Re}_6\text{S}_7\text{Cl}_7$ ⁴³	(a) $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$ ⁴⁶ (b) $\text{Cs}_4\text{Re}_6\text{S}_8\text{Cl}_6 \cdot \text{CsCl}$ ⁴⁶
Re–Re	2.595(2)	(a) 2.589(7) (b) 2.594(4)	(a) 2.573(8) (b) 2.593(3)	(a) 2.570(10) (b) 2.591(3)	(a) 2.601(4) (b) 2.596(4)
Re–L	2.422(12)	(a) 2.418(45) (b) 2.416(14)	(a) 2.401(9) (b) 2.425(25)	(a) 2.395(19) (b) 2.408(11)	(a) 2.403(9) (b) 2.399(4)
Re–Cl ^a	2.319(11)	(a) 2.344(45) (b) 2.358(7)	(a) 2.362(12) (b) 2.379(5)	(a) 2.397(3) (b) 2.407(10)	(a) 2.451(4) (b) 2.421(10)
Re–S–Br		$\text{KRe}_6\text{S}_5\text{Br}_9$ ³⁴	$(\text{PPh}_4)_2[\text{Re}_6\text{S}_6\text{Br}_8]$ ³⁹	$(\text{PPh}_4)_3[\text{Re}_6\text{S}_7\text{Br}_7]$ ³⁹	$(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Br}_6] \cdot \text{H}_2\text{O}$ ⁴⁶
Re–Re		2.608(9)	2.601(10)	2.602(3)	2.594(7)
Re–L		2.502(43)	2.472(72)	2.444(19)	2.396(12)
Re–Br ^a		2.520(3)	2.534(13)	2.569(5)	2.595(10)
Re–Se–Cl	$\text{Re}_6\text{Se}_4\text{Cl}_{10}$ ¹⁵	(a) $\text{KRe}_6\text{Se}_5\text{Cl}_9$ ¹⁵ (b) $(\text{Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$ ⁴	(a) $\text{PbRe}_6\text{Se}_6\text{Cl}_8$ ¹⁵ (b) $(\text{NPr}^n)_4[\text{Re}_6\text{Se}_6\text{Cl}_8]$ ⁴⁹		$\text{Tl}_4\text{Re}_6\text{Se}_8\text{Cl}_6 \cdot \text{TlCl}$ ⁴⁶
Re–Re	2.615(5)	(a) 2.608(1) (b) 2.607(3)	(a) 2.611(1) (b) 2.613(3)		2.614(5)
Re–L	2.499(10)	(a) 2.501(13) (b) 2.499(8)	(a) 2.506(14) (b) 2.505(15)		2.523(3)
Re–Cl ^a	2.330(9)	(a) 2.373(6) (b) 2.353(5)	(a) 2.406(8) (b) 2.379(12)		2.431(8)

Thus, knowing that $d(\text{Re}-\mu_3\text{S}) < d(\text{Re}-\mu_3\text{Cl}) < d(\text{Re}-\mu_3\text{Se}) < d(\text{Re}-\mu_3\text{Br}) < d(\text{Re}-\mu_3\text{Te}) < d(\text{Re}-\mu_3\text{I})$, one expects that $d(\text{Re}-\mu_3\text{L})$ increases with n if $d(\text{Re}-\mu_3\text{Q}) > d(\text{Re}-\mu_3\text{X})$ and decreases with n if $d(\text{Re}-\mu_3\text{Q}) < d(\text{Re}-\mu_3\text{X})$. This turns out to be verified for the three systems for which sufficient data are available. Indeed, for two of them, Re–S–Cl and Re–S–Br, $d(\text{Re}-\mu_3\text{L})$ decreases when n increases, while, in the Re–Se–Cl system, the reverse is observed, in agreement with the above rule.

3. Re– μ -X Bond Length as a Function of the $[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]^{(6-n)+}$ Core Charge

A consistent observation for all Re–Q–X systems for which sufficient data are available (Table 7) has been that the Re– μ -X bond distance increases with n in the series $\{[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]\text{X}_6\}^{n-}$.^{23,36} This can be explained in terms of Coulombic interactions between the net positive core charge of $[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]^{(6-n)+}$ and that of the negatively charged X^- apical ligand shell. As n increases, the net cluster core charge decreases from 6+ for $n = 0$ to 2+ for $n = 4$; thus, the attractive Coulombic interactions between the cluster core and its apical ligands decrease and the mean Re– μ -X distance increases. The same interpretation was given for a similar effect in the series $[\text{Mo}_6(\text{Se}_n\text{Cl}_{8-n})\text{Cl}_6]^{(2+n)-}$ ($n = 0-2$),⁹³ by Ebihara and co-workers.⁹⁴

4. Distribution of the Cluster Core Inner μ_3 -Ligands

Most X-ray structure determinations of hexanuclear rhenium chalcogenide clusters salts of the type $\{[\text{Re}_6(\mu_3\text{Q})_{4+n}(\mu_3\text{X})_{4-n}](\mu\text{X})_6\}^{n-}$, where $0 \leq n \leq 3$, conclude to the occurrence of disordered chalcogen and halogen μ_3 -ligands on the eight positions of the pseudocube. The origin of this disorder can be either geometric or orientational.⁹⁵ Indeed, there are 6, 3, and 3 geometric isomers for $n = 0, 1$, and 2, respectively (Figure 16), whose random distribution in the crystal generates geometrical disorder. When no geometric isomer exist ($n = 3$), the random orientation of a single isomer creates an orientational disorder in the crystal.

A few exceptions have, however, been reported. *Partial* ordering occurs for some of the ligands, as

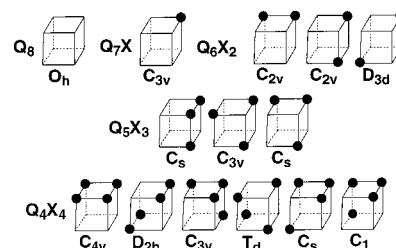


Figure 16. All possible geometric isomers for a $[\text{Re}_6(\mu_3\text{Q})_{4+n}(\mu_3\text{X})_{4-n}]^{(6-n)+}$ cluster core ($n = 0-4$) together with their Schönflies point group symmetry symbol.

for the oxo–chalcogenide derivatives (sections III.A.1 and III.B.1)^{49,64,74} and the μ_3 -imido-functionalized clusters (section III.B.1),⁷⁵ where solely the heteroatom loci proved to be neatly ordered in the solid-state structure refinements. Complete ordering of the inner ligands has been reported in the case of $[\text{Re}_6\text{Te}_6\text{Cl}_2]\text{Cl}_4(\text{TeCl}_2)_2$, an $n < 4$ cluster (section II.D.1).²⁶

Finally, one should note that those instances where ordering has been observed correspond to situations of uttermost relative steric demands of the ligand set, i.e., oxygen versus sulfur and chlorine or tellurium versus chlorine.

B. Reactions in Molten Salts

Following the seminal observation by Fedorov, Mironov, and co-workers that the octahedral cluster is retained^{2,96} upon reacting $\text{Re}_6\text{Te}_{15}$ with bromine to afford $\text{Re}_6\text{Te}_4\text{Br}_{10}$, the reaction of octahedral chalcogenide rhenium cluster derivatives has been further explored in molten salts such as KSCN or KCN, thus, the reaction of $\text{Re}_6\text{Te}_{15}$ in molten KSCN and subsequent treatment with an aqueous solution of CsCl which led to the first soluble cyanide-substituted octahedral rhenium cluster salt, $\text{Cs}_3\text{K}\{[\text{Re}_6\text{S}_6(\text{Te}_{0.66}\text{S}_{0.34})_2](\text{CN})_6\}$.^{97,98} Similarly, the reaction of $\text{Re}_6\text{S}_4\text{Br}_{10}$, $\{[\text{Re}_6\text{S}_4\text{Br}_4]\text{Br}_6\}$, with KSCN followed by cation exchange affords small amounts of $(\text{PPh}_4)_3[\text{Re}_6\text{S}_7\text{Br}_7]$ (see section II.D.4).³⁹

Likewise, upon reaction in molten KCN at 600 °C, the 3D polymer $\text{Re}_6\text{Se}_8\text{Br}_2$ (see section II.E.3) breaks

into the water-soluble molecular salt $K_4\{[Re_6Se_8](CN)_6\}^{99}$ or, similarly, $NaCs_3[Re_6S_8(CN)_6]$ and $NaCs_3[Re_6Se_8(CN)_6]$ can be obtained by a high-temperature exchange reactions in molten NaCN of $Cs_4[Re_6S_8Br_6]$, $CsBr$ and $Cs_4[Re_6Se_8I_6]$,⁴⁶ respectively.¹⁰⁰ In light of this success, it would be of interest to probe the reactivity of the halogen-bridged 3D polymers $\{[Re_6-Q_7X]X_3\}$ in molten salts since all previous attempts to dismantle these sets of compounds have failed so far.

More recently, the reaction of KCN with either ReS_2 or $ReSe_2$ at 800 and 650 °C for 2 days gave the polymeric 1D and 2D phases $K_4[Re_6S_{10}(CN)_2]$ and $K_4[Re_6Se_{10}(CN)_4]$, respectively.¹⁰¹

Again, it is striking that in these molten salt reactions, and similarly to what was observed in organic solution reactions (see section III.B.3), apical halide substitution for μ -cyanide ligands are observed only on octahedral rhenium cluster compounds that have their inner ligand shells purely made of chalcogen atoms. Consistently, one observes that in the reaction of a cluster core containing μ_3 -halogen ligands, such as in the $Re_6S_4Br_{10}$ vs KSCN case, it is the inner μ_3 -bromide ligands which get substituted.³⁹

Finally, a coordination chemistry^{37,68} of these water-soluble cyanide-substituted octahedral rhenium cluster ligands^{97,98} is developing rapidly. Novel coordination polymers constructed out of the alkaline-earth or metallic cations coordination spheres include $Cs_2Mn_3[Re_6Se_8(CN)_6]_2 \cdot 15H_2O$ and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$ ¹⁰² and $(Pr_4N)_2M(H_2O)_5[Re_6X_8(CN)_6] \cdot H_2O$ ($X = S, Se$; $M = Mn, Ni$)¹⁰³ and a new class of porous materials with $[Zn(H_2O)_2][Re_6S_8(CN)_6] \cdot 7H_2O$, $Cs_2[trans-Fe(H_2O)_2]_3[Re_6S_8(CN)_6]_2 \cdot 12H_2O$,¹⁰⁰ and $[Cd_2(H_2O)_4][Re_6S_8(CN)_6] \cdot 14H_2O$,¹⁰⁴ as well as 3D cluster-expanded Prussian blue analogues, $M_4[Re_6Q_8(CN)_6]_3 \cdot xH_2O$ ($M = Ga, Q = Se$; $M = Fe, Q = Te$).¹⁰⁵ Two-dimensional compounds have also been prepared with $Cs_2[trans-Fe(H_2O)_2][Re_6S_8(CN)_6]$.¹⁰⁰ Recent results include the synthesis of $Na_2Zn_3[Re_6Se_8(CN)_6]_2 \cdot 24H_2O$, a compound exhibiting a porous three-dimensional framework isotypic with that of $Na_2Zn_3[Fe(CN)_6]_2 \cdot 9H_2O$, by reaction between $[Zn(H_2O)_6]^{2+}$ and $Na_4[Re_6Se_8(CN)_6]$. Upon using a slight excess of the zinc reactant, $[Zn(H_2O)_6]^{2+}$ incorporates instead of Na^+ to yield the ion-exchanged compound $[Zn(H_2O)_6]_2Zn_3[Re_6Se_8(CN)_6]_2 \cdot 18H_2O$.¹⁰⁶ Also, the face-capped octahedral clusters $[Re_6Q_8(CN)_6]^{4-}$ ($Q = S, Se$) are used to space apart partially hydrated Co^{2+} ions, thus forming extended porous framework, that display strong and reversible color changes, from orange to intense blue-violet, upon exposure to certain organic solvents. Three phases have been reported: $[Co_2(H_2O)_4][Re_6S_8(CN)_6] \cdot 10H_2O$; $Cs_2[Co(H_2O)_2][Re_6S_8(CN)_6] \cdot 2H_2O$; $[Co(H_2O)_3]_4[Co_2(H_2O)_4][Re_6S_8(CN)_6]_3 \cdot 44H_2O$.¹⁰⁷

These developments now allow to envision the construction of ligand-bridged extended arrays in the solid state, thereby reassembling multicluster networks of diverse dimensionalities from divergent molecular precursors, taking advantage of the stereochemistry of the cluster core as well as of the diversity of shape, size, redox activity, and binding preferences of bridging, functional molecular spacers.

C. Diversity of the Redox Chemistry in the $\{[Re_6Q_{4+n}X_{4-n}]X_6\}^{n-}$ Series

The presently available electrochemical data on halides and chalcogenides of Mo_6 , W_6 , and Re_6 octahedral cluster anions have been collected in Table 8. The first report²³ described the cyclic voltammetry in acetonitrile of $(Bu_4N^+)_n[Re_6S_{4+n}Cl_{10-n}]^{n-}$ with $n = 1-3$. A striking difference of behavior was revealed when going from $[Re_6S_5Cl_9]^-$, which undergoes a quasi-reversible reduction at -0.075 V/ECS, to $[Re_6S_6Cl_8]^{2-}$ and $[Re_6S_7Cl_7]^{3-}$, which both proved to give up one electron upon a quasi-reversible process at ca. 1.0 V/ECS, while being inert to any kind of reduction process in the cathodic regime (Figure 17). This contrasted behavior which correlates with both the net cluster charge and the chalcogen/halogen ratio, suggests that significant modifications of the cluster core electronic structure underlie this redox chemistry. Another striking observation is the reversible one-electron oxidation process for $(Bu_4N)_4[Re_6S_8X_6]$ ($X = Cl, Br$), at potentials as low as ca. 0.3 V/ECS, hence providing an exquisite entry into the charge-transfer chemistry of open-shell cluster forms (Figure 17).^{46,70,112} This was recently exemplified by the electrocrystallization¹⁰⁸ and structural characterization of paramagnetic $(Bu_4N^+)_3[Re_6S_8Cl_6]^{3-}$ ($g = 2.44$) and the discovery of the luminescence properties of such open-shell, 23-electron species (see section IV.D.3).¹¹²

Sasaki and co-workers have significantly extended the electrochemistry of these systems to $(Bu_4N)_{4-n}[Re_6S_8Cl_{6-n}L_n]$ ($L = py$ or cpy ; $n = 2-3$, $py = pyridine$; $n = 2$, $cpy = 4$ -cyanopyridine)⁸⁸ or $(Bu_4N)_4[Re_6Q_8(CN)_6]$,¹⁰⁹ whose cluster cores all exhibit a reversible oxidation wave at various potentials in CH_3CN , ranging from $E_{1/2} = 0.06$ to 0.92 V vs SCE for $(Bu_4N)_4[Re_6Te_8(CN)_6]$ and $(Bu_4N)[mer-Re_6S_8Cl_3(py)_3]$, respectively (see Table 8).¹¹⁰ Then, the study of the cpy derivative having revealed that the ligand-reduction waves of the two chemically equivalent cpy ligands coordinated in a *cis* or *trans* orientation to the $[Re_6(\mu_3-S)_8]^{2+}$ core are split in the cyclic voltammogram, these electrochemical studies have been extended to a series of *trans*- or *cis*- $[Re_6(\mu_3-S)_8Cl_4(L)_2]^{2-}$ complexes with N-heterocyclic ligands (see Table 6 and section III.B).¹¹¹ Thus, the $E_{1/2}$ values for the $Re^{III}_6/Re^{III}_5Re^{IV}$ couple become more positive in the order $L = dmap < mpy < py < bpy < cpy < pz$ suggesting that the coordination of electron-withdrawing groups make the $[Re_6(\mu_3-S)_8]^{2+}$ core more difficult to oxidize. A good linear correlation between the $E_{1/2}$ and pK_a values of the N-heterocyclic ligands ($E_{1/2} = 0.8737 - 0.0197(pK_a)$) demonstrates that the σ electrons of the latter affect the closely spaced HOMO levels of the rhenium clusters. It is further concluded that an electronic interaction through the $[Re_6(\mu_3-S)_8]^{2+}$ core is responsible for the observed 90–140 mV splitting of the ligand-reduction waves. In addition, the second ligand-reduction wave of the bpy complexes is quenched by traces of water as well as by addition of the proton donor imidazole (Scheme 4).

Table 8. Electrochemical Properties of Hexanuclear Cluster Molecules ($E_{1/2}$ vs SCE in V)^a

redox system		$E_{1/2}$	solvent	ref
[Mo ₆ Cl ₁₄] ⁻²⁻		23/24 e ⁻	1.36	CH ₃ CN 120
	[Re ₆ S ₈ Cl ₆] ^{2-/3-}	22/23 e ⁻	1.09	CH ₃ CN 70
	[Re ₆ S ₇ Cl ₇] ^{2-/3-}	23/24 e ⁻	1.02	CH ₃ CN 23
	[Re ₆ Se ₈ (μ-dpph) ₂ I ₄] ^{3+/2+}	23/24 e ⁻	1.01	CH ₂ Cl ₂ 85
[(Mo ₆ Br ₇ S)Cl ₆] ⁻²⁻		22/23 e ⁻	1.01	CH ₂ Cl ₂ 94
	[W ₆ Cl ₈ Br ₆] ⁻²⁻	23/24 e ⁻	0.99	CH ₂ Cl ₂ 129
		23/24 e ⁻	0.99	CH ₃ CN 23
	[W ₆ Cl ₁₄] ⁻²⁻	23/24 e ⁻	0.93	CH ₂ Cl ₂ 129
		23/24 e ⁻	0.92	CH ₃ CN 88
	<i>mer</i> -[Re ₆ S ₈ Cl ₃ (py) ₃] ^{0/-}	23/24 e ⁻	0.81	CH ₃ CN 111
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (pz) ₂] ⁻²⁻	23/24 e ⁻	0.80	CH ₂ Cl ₂ 129
	[W ₆ Br ₁₄] ⁻²⁻	23/24 e ⁻	0.80	CH ₂ Cl ₂ 130
[(Mo ₆ Br ₇ S)Cl ₅ (CH ₃ CN)] ^{1-/2-}		23/24 e ⁻	0.78	CH ₃ CN 88
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (cpy) ₂] ⁻²⁻	23/24 e ⁻	0.74	CH ₃ CN 111
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (bpy) ₂] ⁻²⁻	23/24 e ⁻	0.74	CH ₂ Cl ₂ 85
	<i>cis</i> -[Re ₆ Se ₈ (μ-dpph) ₂ I ₄] ^{+/-}	23/24 e ⁻	0.74	CH ₃ CN 88
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (py) ₂] ⁻²⁻	23/24 e ⁻	0.71	CH ₂ Cl ₂ 85
	<i>trans</i> -[Re ₆ Se ₈ (μ-dpph) ₂ I ₄] ^{+/-}	23/24 e ⁻	0.70	CH ₃ CN 111
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (mpy) ₂] ⁻²⁻	23/24 e ⁻	0.63	CH ₃ CN 111
	<i>cis</i> - and <i>trans</i> -[Re ₆ S ₈ Cl ₄ (dmap) ₂] ⁻²⁻	23/24 e ⁻	0.63	CH ₂ Cl ₂ 94
		23/24 e ⁻	0.62	CH ₂ Cl ₂ 94
	[Re ₆ S ₈ (CN) ₆] ^{3-/4-}	23/24 e ⁻	0.55	CH ₃ CN 109
		23/24 e ⁻	0.59	CH ₂ Cl ₂ 94
		23/24 e ⁻	0.57	CH ₂ Cl ₂ 129
[(Mo ₆ Cl ₇ S)Br ₆] ^{2-/3-} [(Mo ₆ Cl ₇ Se)Br ₆] ^{2-/3-} [(Mo ₆ Cl ₇ S)Cl ₆] ^{2-/3-}	[W ₆ I ₁₄] ⁻²⁻	23/24 e ⁻	0.56	CH ₂ Cl ₂ 129
	[W ₆ I ₈ Br ₆] ⁻²⁻	23/24 e ⁻	0.56	CH ₂ Cl ₂ 94
		23/24 e ⁻	0.53	CH ₂ Cl ₂ 93b
	[(Mo ₆ Cl ₆ Se ₂)Cl ₆] ^{2-/3-} isomer B	22/23 e ⁻	0.53	CH ₂ Cl ₂ 93b
	[Mo ₆ Se ₈ (PET ₃) ₆] ^{1+/0}	19/20 e ⁻	0.49	THF 131
	[Mo ₆ S ₈ (PET ₃) ₆] ^{1+/0}	19/20 e ⁻	0.47	THF 131
	[(Mo ₆ Cl ₆ Se ₂)Cl ₆] ^{2-/3-} isomer A	22/23 e ⁻	0.43	CH ₂ Cl ₂ 93b
		23/24 e ⁻	0.33	CH ₃ CN 109
	[Re ₆ Se ₈ (CN) ₆] ^{3-/4-}	23/24 e ⁻	0.34	CH ₂ Cl ₂ 94
		23/24 e ⁻	0.30	CH ₂ Cl ₂ 85
[(Mo ₆ Br ₇ S)Cl ₆] ^{2-/3-}	[Re ₆ Se ₈ (μ-dpph)I ₄] ⁻²⁻	23/24 e ⁻	0.29	CH ₃ CN 46, 84
	[Re ₆ S ₈ Br ₆] ^{3-/4-}	23/24 e ⁻	0.30	CH ₃ CN 46, 112
	[Re ₆ S ₈ Cl ₆] ^{3-/4-}	23/24 e ⁻	0.22	CH ₂ Cl ₂ 131
		19/20 e ⁻	0.22	CH ₂ Cl ₂ 131
		23/24 e ⁻	0.065	CH ₃ CN 109
	[Re ₆ Te ₈ (CN) ₆] ^{3-/4-}	24/25 e ⁻	-0.07	CH ₃ CN 23
	[Re ₆ S ₅ Cl ₉] ^{1-/2-}	24/25 e ⁻	-0.22	CH ₃ CN 70
	[Re ₆ Se ₅ Cl ₉] ^{1-/2-}	23/24 e ⁻	-0.22	CH ₂ Cl ₂ 93b
		23/24 e ⁻	-0.29	CH ₂ Cl ₂ 93b
	[Mo ₆ Se ₈ (PET ₃) ₆] ^{0/1-}	20/21 e ⁻	-0.93	THF 131
[(Mo ₆ Cl ₆ Se ₂)Cl ₆] ^{3-/4-} isomer B [(Mo ₆ Cl ₆ Se ₂)Cl ₆] ^{3-/4-} isomer A	[Mo ₆ S ₈ (PET ₃) ₆] ^{0/1-}	20/21 e ⁻	-0.96	THF 131
	[Mo ₆ S ₈ (PET ₃) ₆] ^{0/1-}	20/21 e ⁻	-1.05	CH ₂ Cl ₂ 131
	[Mo ₆ Se ₈ (PET ₃) ₆] ^{0/1-}	20/21 e ⁻	-1.05	CH ₂ Cl ₂ 131
	[Mo ₆ Cl ₁₄] ^{2-/3-}	24/25 e ⁻	-1.70	CH ₂ Cl ₂ 129
	[Mo ₆ Se ₈ (PET ₃) ₆] ^{1-/2-}	21/22 e ⁻	-1.91	THF 131
	[Mo ₆ S ₈ (PET ₃) ₆] ^{1-/2-}	21/22 e ⁻	-1.97	THF 131

^a $E^\circ(\text{Fc}/\text{Fc}^+) = 0.446$ (in CH₂Cl₂) and 0.543 V (in THF) vs KSCE (SCE).

Since no general trend can be easily driven out upon the influence of the number of μ₃-halide and the nature of μ-ligands on redox processes potentials, a thorough analysis of the electronic structures of the closed- and open-shell cluster cores is now needed to discuss further their rich redox and photochemistry.

D. IR and UV–Visible Spectroscopies

1. Infrared and Raman Spectroscopies

There is only one report of infrared and Raman data conducted on Re₆Se₄Cl₁₀ in the solid state.²¹ The authors note that the simple spectra (Figure 18) indicate *T_d* symmetry for the molecule.⁹⁵ This implies μ₃-Cl and μ₃-Se ligands alternate at the vertexes of the (μ₃-X)₈ ligand set pseudocube which can be symbolized by two interpenetrating tetrahedra. Thus, the disordered motif refined in their crystallographic

study would be the consequence of a random orientation disorder of the molecular units in the crystal.

2. UV–Visible Spectroscopy

The UV–vis absorbance spectra between 300 and 700 nm of DMF solutions of (Bu₄N⁺)_{*n*}[Re₆Q_{4+*n*}Cl_{10-*n*}]^{*n*-} (Q = S, *n* = 1–3; Q = Se, *n* = 1, 2) and Re₆S₅Cl₈ have been reported (Figure 19 and Table 9).^{22,70} Absorption spectra of DMF solutions of Re₆S₅Cl₈ and (Bu₄N)-[Re₆S₅Cl₉] are very similar with a single and small shoulder near 360–380 nm. This shoulder is much more pronounced in the case of the DMF solutions of (Bu₄N)₂[Re₆S₆Cl₈] and (Bu₄N)₃[Re₆S₇Cl₇] with, in addition, two other smaller ones at 330 and 460 nm. The absorbance spectra of the selenides are closely related to their sulfido analogues, albeit slightly shifted toward longer wavelengths. Thus, the spectra of (Bu₄N)[Re₆Se₅Cl₉] have a small shoulder near

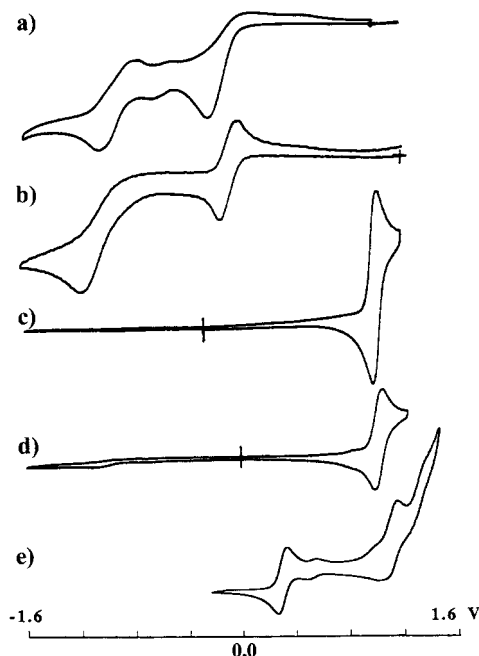


Figure 17. Cyclic voltammograms at a platinum electrode vs SCE in acetonitrile containing 0.1 M $(\text{Bu}_4\text{N})\text{PF}_6$ (scan rate 0.1 V s^{-1}) of (a) $[\text{Re}_6\text{S}_5\text{Cl}_9(\text{DMF})]^-$, (b) $(\text{Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{Cl}_9]$, (c) $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_6\text{Cl}_8]$, (d) $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7\text{Cl}_7]$, and (e) $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$. Modified—(e) has been added—from ref 23. Copyright 1993 American Chemical Society.

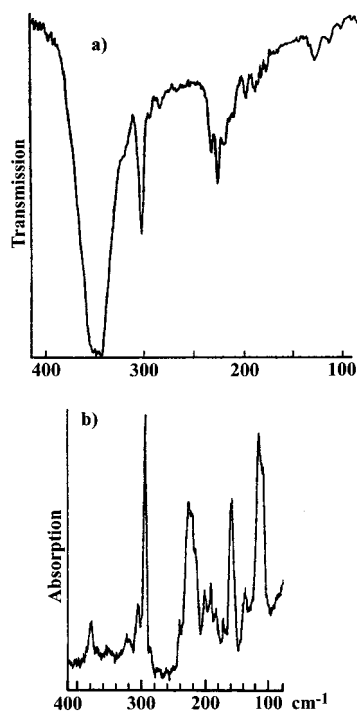


Figure 18. IR (a) and Raman (b) spectra for $\text{Re}_6\text{Se}_4\text{Cl}_{10}$. Reprinted from ref 21. Copyright 1985 Plenum Publishing Corp.

380–400 nm plus a weak additional one around 500 nm, and $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$ presents a main shoulder at 400 nm as well as two similar additional smaller ones.

The UV–visible spectra for acetonitrile solutions of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{Q} = \text{S}$) have been reported by Holm et al.⁴⁶ and confirmed, in the case of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$, by further stud-

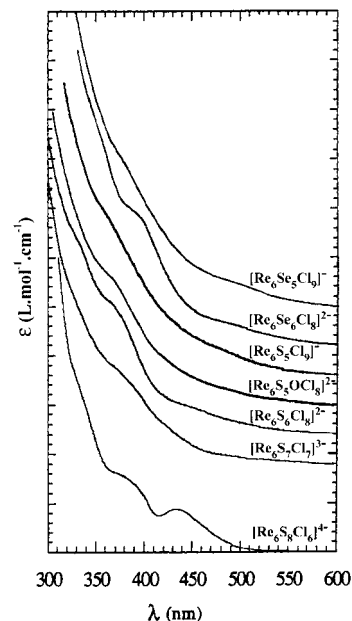


Figure 19. UV–vis absorbance spectra for $(\text{Bu}_4\text{N}^+)_n- [\text{Re}_6\text{Q}_{4+n}\text{Cl}_{10-n}]^{n-}$ (in DMF for $\text{Q} = \text{S}$, $n = 1$; in CH_3CN for $n = 2-4$; $\text{Q} = \text{Se}$, $n = 1, 2$), as well as $(\text{Bu}_4\text{N}^+)_2[\text{Re}_6\text{S}_5\text{OCl}_8]^{2-}$. For each spectrum, the concentration was $3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, and the extrema of absorbance are few tenths and $6000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

ies,^{70,87,112,113} except for the absence of a weak peak at 537 nm, whose occurrence likely indicates the presence of small amounts of $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ (Figure 20).¹¹² Within the series $[\text{Re}_6\text{S}_{4+n}\text{Cl}_{10-n}]^{n-}$ ($n = 1-4$), the intense absorption at 436 nm is observed for the tetraanion ($n = 4$) only.^{22,70} In addition, this peak experiences a red shift upon going from μ -chlorine, to μ -bromide, and, finally, to μ -iodide ligands (see Table 9), perhaps an indication of halide ligand-to-metal charge transfer.⁴⁶ The spectrum for acetonitrile solutions of $(\text{Bu}_4\text{N}^+)_3[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ (Figure 20) is strikingly different from any of the former. The occurrence of two large peaks at 490 and 540 nm and a large near-IR absorption (Figure 20) again demonstrate that a significant change of electronic structure of the cluster anion occurs upon the one-electron oxidation. The wide near-IR absorption band between 700 and 1800 nm ($\lambda_{\text{max}} \sim 1254 \text{ nm}$, $\epsilon \sim 500 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)⁷⁰ may correspond to electronic transitions from a fully to a partially occupied metal orbital or to a charge-transfer band between localized Re^{III} and Re^{IV} states. A similar absorption band has been observed for the paramagnetic hexanuclear molybdenum clusters anions (Mo_6^{13+}) $[\text{Mo}_6(\text{X}_7\text{Q})\text{X}'_6]^{2-}$ ($\text{X} = \text{X}' = \text{Cl}, \text{Br}; \text{Q} = \text{S}, \text{Se}$) and $[\text{Mo}_6(\text{Cl}_6\text{Se}_2)\text{Cl}_6]^{3-}$.^{93a,b}

Finally, the UV–vis absorption spectrum of the solvated cluster core $[\text{Re}_6\text{S}_8(\text{H}_2\text{O})_6]^{2+}$ in 1 M HClO_4 has been reported and shows four peaks ranging from 216 to 409 nm (see Table 9).⁴⁷

3. NMR Spectroscopy

The majority of NMR studies of hexanuclear rhenium chalcohalide clusters have used the nuclei ^1H and ^{31}P to characterize the stereochemistry of clusters where organic ligands have partially substituted the terminal halogen ligands. ^{31}P NMR resonances

Table 9. λ_{max} (nm) of UV–Vis Absorbance Spectra for Various Hexanuclear Rhenium Chalcogenide Clusters

cluster (in CH ₃ CN)	λ_{max} abs (ϵ_{M} L·mol ^{−1} ·cm ^{−1})	ref
[Re ₆ S ₈ Cl ₆] ^{4−}	377 (sh, 1860), 434 (1050), 537 (140)	46
[Re ₆ S ₈ Br ₆] ^{4−}	401 (sh, 1540), 443 (945), 545 (90)	46
[Re ₆ S ₈ I ₆] ^{4−}	393 (sh, 3290), 420 (2200), 507 (755)	46
[Re ₆ S ₈ Cl ₆] ^{3−}	378 (sh, 1820), 489 (785), 544 (1190)	46, 79
[Re ₆ S ₈ Br ₆] ^{3−}	395 (sh, 2380), 492 (781), 541 (1270)	46, 79
[Re ₆ S ₈ I ₆] ^{3−}	534 (590), 586 (sh, 353)	46, 79
[Re ₆ Se ₈ I ₆] ^{3−}	477 (sh, 2060), 525 (1180), 609 (1190)	46, 79
[Re ₆ S ₈ Cl ₆] ^{3−•}	sh 381, 489 (850), 544 (1230), 1250 (400)	112
[Re ₆ S ₈ (H ₂ O) ₆] ^{2+•a}	216 (44 000), 260 (13 200), 360 (1540), 409 (875)	47
<i>trans</i> -[Re ₆ S ₈ Cl ₄ (py) ₂] ^{2−}	424 (sh, 1070), 373 (sh, 2400), 306 (sh, 10 400), 270 (sh, 25 100), 240 (sh, 38 300), 226 (52300)	88
<i>cis</i> -[Re ₆ S ₈ Cl ₄ (py) ₂] ^{2−}	422 (sh, 1260), 373 (sh, 2390), 303 (sh, 8350), 268 (sh, 16900), 239 (sh, 39 200), 227 (51 300)	88
<i>trans</i> -[Re ₆ S ₈ Cl ₄ (cpy) ₂] ^{2−}	521 (sh, 310), 320 (11 800), 269 (sh, 27 500), 239 (sh, 41 300), 222 (65 500)	88
<i>cis</i> -[Re ₆ S ₈ Cl ₄ (cpy) ₂] ^{2−}	529 (sh, 320), 316 (11 800), 240 (sh, 36 000), 223 (64 000)	88
<i>mer</i> -[Re ₆ S ₈ Cl ₃ (cpy) ₃] [−]	421 (1050), 374 (sh, 2320), 269 (sh, 28 400), 240 (sh, 36 600), 226 (49 000).	88
<i>trans</i> -[Re ₆ S ₈ Cl ₄ (py) ₂] ^{1−}	1408 (370), 545 (1190), 494 (890), 269 (sh, 32 000), 252 (38 000), 227 (53 300)	88
<i>trans</i> -[Re ₆ S ₈ Cl ₄ (cpy) ₂] ^{1−b}	1417 (350), 545 (1180), 493 (890), 310 (sh, 14 700), 275 (sh, 30 000), 223 (66 000).	88
<i>mer</i> -[Re ₆ S ₈ Cl ₃ (cpy) ₃] ^{•b}	1380 (360), 547 (1210), 495 (850)	88

^a In 1 M HClO₄. ^b In CH₂Cl₂.

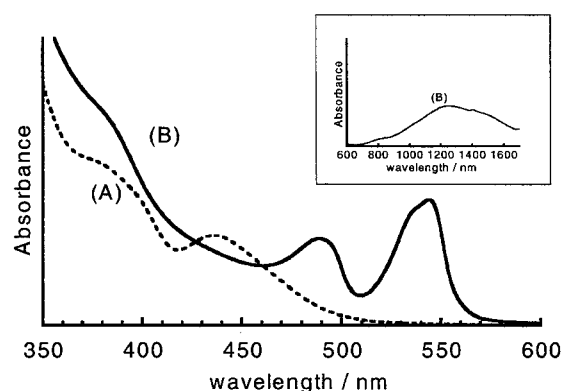


Figure 20. Electronic absorption spectra for acetonitrile solutions ($C = 2.8 \times 10^{-4}$ M) of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$ ((A) two poorly resolved shoulders at 335 and 380 nm and a peak of larger intensity at 436 nm ($\epsilon_{\text{M}} = 8.6 \times 10^2$ L·mol^{−1}·cm^{−1})) and $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_8\text{Cl}_6]$ ((B) one poorly resolved shoulder (381 nm), two large peaks (489 nm, $\epsilon_{\text{M}} = 8.5 \times 10^2$ L·mol^{−1}·cm^{−1}; 544 nm, $\epsilon_{\text{M}} = 1.23 \times 10^3$ L·mol^{−1}·cm^{−1}), and a very wide band centered around 1250 nm (700–1750 nm, $\epsilon_{\text{M}} = 4 \times 10^2$ L·mol^{−1}·cm^{−1})). Reprinted from ref 112. Copyright 1999 Royal Society of Chemistry Journals U.K.

have been observed within the ranges of -35.7 to -17.6 ppm and -23.1 to -16.2 ppm (with respect to an 85% solution of H₃PO₄ at 0 ppm) for the system Re–Se–I^{82,83} and Re–S–Br,⁸⁰ respectively. By comparison of the shifts from isostructural molecules obtained in both systems, it was concluded that the peaks are shifted to higher frequency in the latter system. The highest frequency signals, -15.1 and -10.6 ppm, have been observed for the condensed clusters $[\text{Re}_{12}\text{Se}_{16}(\text{PET}_3)_{10}](\text{BF}_4)_4 \cdot 4\text{CH}_2\text{Cl}_2$ ⁸² and *trans*- $[\text{Re}_{12}\text{Se}_{16}(\text{PET}_3)_8(\text{MeCN})_2](\text{SbF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$,⁸³ respectively.

A detailed ⁷⁷Se and ¹²⁵Te NMR investigation has also enabled the stereochemistry of the inner ligands in $\{[\text{Re}_6\text{Te}_{8-n}\text{Se}_n](\text{CN})_6\}^{4-}$ ($n = 0-8$) to be studied.³⁰

E. Luminescence Properties

As the difference with the mono-, di-, and trianions within the chalcogenide series $[\text{Re}_6\text{S}_{4+n}\text{Cl}_{10-n}]^{n-}$ ($n = 1, 2, 3$), the tetraanions $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ ($\text{Q} = \text{S}, \text{X} = \text{Cl}$,

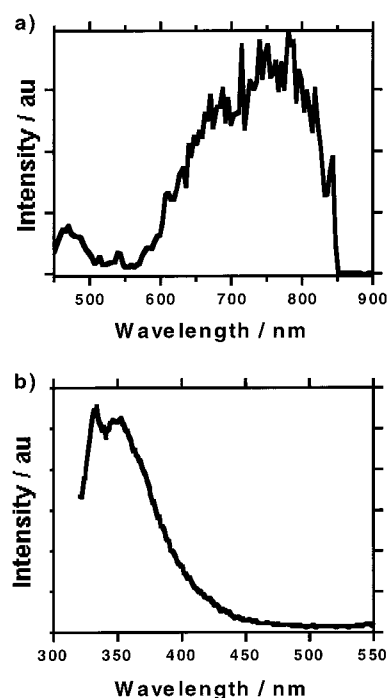


Figure 21. (a) Luminescence spectra for acetonitrile solutions of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$ (5.0×10^{-5} M) for excitations at 390 nm (maximum at 720 nm). (b) Luminescence spectra for acetonitrile solutions of $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_8\text{Cl}_6]$ (2.0×10^{-5} M) for excitations at 270 nm (maxima at 320 and 355 nm).

Br, I; $\text{Q} = \text{Se}, \text{X} = \text{Cl}, \text{Br}, \text{I}$)^{88,112} as well as the paramagnetic 23-electron cluster trianion $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ ¹¹² are luminescent, and the emission spectra of acetonitrile solutions of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$ and $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_8\text{Cl}_6]$ are reported in Figure 21a,b,¹¹⁴ respectively. The values of the maxima for the emission peaks are reported in Table 10. It should be noted that the luminescence of the tetraanions $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ occurs for excitation wavenumbers in the range of those of its singular large absorption band centered at 430 nm. Altogether, the luminescence for the tetraanions shifts slightly to a longer wavelength and their emission lifetimes (τ_{em}) as well as quantum yields (ϕ_{em}) decrease as the terminal halide changes from Cl to Br and I. Also, emission spectra are similar¹¹² to that for the hexanuclear molybdenum-

Table 10. Photophysical Data for Hexanuclear Chalcogenide and Halide Molecular Metal Clusters

salt	$\lambda_{\text{excitation}}$ (nm)	λ_{max} (nm)	τ_{em} (μs)	ϕ_{em}	ref
(Bu ₄ N) ₄ [Re ₆ S ₈ Cl ₆] ^a	390	720	5.1	0.037	112, 114
	436	750		0.031	113
(Bu ₄ N) ₄ [Re ₆ S ₈ Cl ₆] ^a	355	770	6.3	0.039	87
(Bu ₄ N) ₄ [Re ₆ S ₈ Br ₆] ^a	355	780	5.4	0.018	87
	436		3.9	0.012	113
(Bu ₄ N) ₄ [Re ₆ S ₈ I ₆] ^a	355	800	4.4	0.015	87
	436		2.6	0.011	113
(Bu ₄ N) ₃ [Re ₆ S ₈ Cl ₆] ^a	270	320, 350			112, 114
(Bu ₄ N) ₂ [Re ₆ Se ₈ (μ -dpph)I ₄]	436	787	2.4	0.007	85
(Bu ₄ N){ <i>mer</i> -[Re ₆ S ₈ (PET ₃) ₃ Br ₃]}	436	760	4.2	0.019	113
<i>trans</i> -[Re ₆ S ₈ (PET ₃) ₄ Br ₂]	436	740	5.7	0.008	113
<i>cis</i> -[Re ₆ S ₈ (PET ₃) ₄ Br ₂]	436	750	4.2	0.019	113
<i>trans</i> -[Re ₆ Se ₈ (PET ₃) ₄ I ₂]	436	750	5.4	0.037	113
<i>cis</i> -[Re ₆ Se ₈ (μ -dpph) ₂ I ₂]	436	790	3.2	0.012	85
<i>trans</i> -[Re ₆ Se ₈ (μ -dpph) ₂ I ₄]	436	770	2.1	0.008	85
<i>cis</i> -[Re ₆ Se ₈ (PET ₃) ₄ I ₂]	436	750	6.0	0.029	113
[Re ₆ S ₈ (PET ₃) ₅ Br]Br	436	740	7.0	0.043	113
[Re ₆ Se ₈ (PET ₃) ₅ I]I	436	740	6.5	0.085	113
[Re ₆ S ₈ (PET ₃) ₆]Br ₂	436	720	10.0	0.044	113
[Re ₆ Se ₈ (PET ₃) ₆]I ₂	436	730	10.8	0.068	113
[Re ₆ Se ₈ (μ -dpph) ₃](SbF ₆)	436	779	6.5	0.031	85
[Re ₆ S ₈ (MeCN) ₆](SbF ₆) ₂	436	690	14.8	0.100	113
[Re ₆ S ₈ (py) ₆](SbF ₆) ₂	436	690	14.0	0.163	113
[Re ₆ S ₈ (DMF) ₆](SbF ₆) ₂	436	680	18.9	0.203	113
[Re ₆ S ₈ (Me ₂ SO) ₆](SbF ₆) ₂	436	660	22.4	0.238	113
(Bu ₄ N) ₂ [Mo ₆ Cl ₈ Cl ₆] ^a	436	805	180	0.19	132, 133
(Bu ₄ N) ₂ [Mo ₆ Br ₈ Br ₆] ^a	436	825	130	0.23	132, 133
(Bu ₄ N) ₂ [Mo ₆ Cl ₈ Br ₆]	355		140		134
(Bu ₄ N) ₂ [Mo ₆ Cl ₈ I ₆]	355		86		134
(Bu ₄ N) ₂ [W ₆ Cl ₈ Cl ₆] ^a	355	833	1.5	0.02	135
(Bu ₄ N) ₂ [W ₆ Cl ₈ Br ₆] ^a	355	814	2.3	0.04	135
(Bu ₄ N) ₂ [W ₆ Cl ₈ I ₆] ^a	355	802	3.0	0.07	135
(Bu ₄ N) ₂ [W ₆ Br ₈ Cl ₆] ^a	355	766	9.7	0.10	135
(Bu ₄ N) ₂ [W ₆ Br ₈ Br ₆] ^a	355	758	15	0.15	135
(Bu ₄ N) ₂ [W ₆ Br ₈ I ₆] ^a	355	752	15	0.25	135
(Bu ₄ N) ₂ [W ₆ I ₈ Cl ₆] ^a	355	701	10	0.11	135
(Bu ₄ N) ₂ [W ₆ I ₈ Br ₆] ^a	355	698	22	0.25	135
(Bu ₄ N) ₂ [W ₆ I ₈ I ₆] ^a	355	698	30	0.39	135
[P(C ₆ H ₅) ₄][Re ₆ S ₈ (CN) ₆] ^a	355	720	11.2	0.056	110
[P(C ₆ H ₅) ₄][Re ₆ Se ₈ (CN) ₆] ^a	355	720	17.1	0.140	110
[P(C ₆ H ₅) ₄][Re ₆ Te ₈ (CN) ₆] ^a	355	750	0.57	0.004	110
Cs ₃ K[Re ₆ S ₈ (CN) ₆] ^b	355	720	1.2	0.009	110
K ₄ [Re ₆ Se ₈ (CN) ₆] ^b	355	720	1.9	0.015	110
K ₄ [Re ₆ Te ₈ (CN) ₆] ^b	355	750	0.42	0.004	110

^a In CH₃CN. ^b In water.

(II) and tungsten(II) clusters,^{132,133} although, in the case of the molybdenum one, both τ_{em} and ϕ_{em} are significantly larger (see Table 10). Further comparison of these systems show that the halide terminal dependences of τ_{em} and ϕ_{em} go in opposite trends for rhenium and molybdenum clusters on the one hand and the tungsten one on the other. In the molybdenum and tungsten cases, this was explained in terms of π -back-donation.¹³⁵

Finally, the cyano-substituted chalcogenide hexanuclear rhenium(III) clusters [Re₆Q₈(CN)₆]⁴⁻ (Q = S, Se, Te) also exhibit luminescence at room temperature with emission quantum yields and lifetimes decreasing in the order Se > S >> Te (see Table 10).¹⁰⁹

The luminescence of the sulfidorhenium clusters was anticipated by Arratia-Pérez and Hernández-Acevedo,¹¹⁵ who also predicted it recently for [Re₆Se₈X₆]⁴⁻ (X = Cl, I),¹¹⁶ on the basis of the similitude in their calculations of their electronic structures to that calculated for [W₆Cl₁₄]²⁻ which also is luminescent. Now, just why are these M₆Q₈-based clusters

luminescent is an open question which can only be tackled by further in-depth investigations of their electronic structures.

F. Subtle Ligand Shell Variations Neatly Characterized by Mass Spectrometry

It is only recently that high-resolution mass spectrometry has been applied to characterize all-inorganic species such as molybdenum halide cluster anions.¹¹⁷ Liquid secondary ion mass spectrometry (LSIMS) proved to be efficient for identifying the present heterosubstituted rhenium clusters.^{37,74,75} Since LSIMS, together with electrospray mass spectrometry (ESMS) or fast atom bombardment mass spectrometry (FABMS), is of high resolution, each low-resolution peak is the envelope of all the high resolution peaks that are due to the different isotopic composition and that can be simulated very accurately, hence providing a fingerprint for each cluster formulation. It is therefore a very efficient

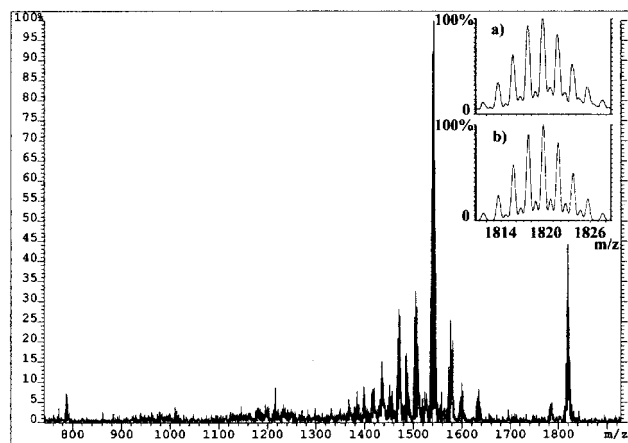


Figure 22. Negative LSIMS for $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_5\text{OCl}_8]$, together with the (a) observed and (b) calculated isotopic ion distribution for the parent ion $\{(\text{Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{OCl}_8]\}^-$, at $m/z = 1819.6$. Reprinted from ref 74. Copyright 1995 American Chemical Society.

method to reveal the precise composition of such clusters, especially when an ambiguity remains on the nature of one of the elements (Figure 22).

G. Electronic Structure

An extensive analysis of the electronic structure of Mo_6Q_8 clusters, the fundamental unit of the Chevrel–Sergent phases, to which the electronic structure of $\text{Re}_6\text{L}_8\text{L}'_6$ is related, is to be found in a seminal paper by Hughbanks and Hoffmann.¹¹⁸ Calculations of the electronic structure for a few $\text{Re}_6\text{L}_8\text{L}'_6$ cluster phases have been performed by Certain and Lissillour using tight-binding band-structure calculations and the “solidlike” extended Huckel method.¹¹⁹ The authors used a three-band model which come from the observation that, in all calculations of the convoluted density of state (DOS), the electronic structures are very similar; thus, the Fermi level area is described by means of a general pattern of three bands, labeled from bottom to top B1, B2, and B3 (Figure 23). The B1 band is essentially based on L ligand p orbitals, and B2 together with B3 is mainly composed of 12 and 18 d rhenium levels, respectively. Since B1 and B2 are filled, the Fermi level of these compounds lies between B2 and B3 which explains, depending upon the extend of the gap, their insulator to semiconductor behavior. The authors anticipate

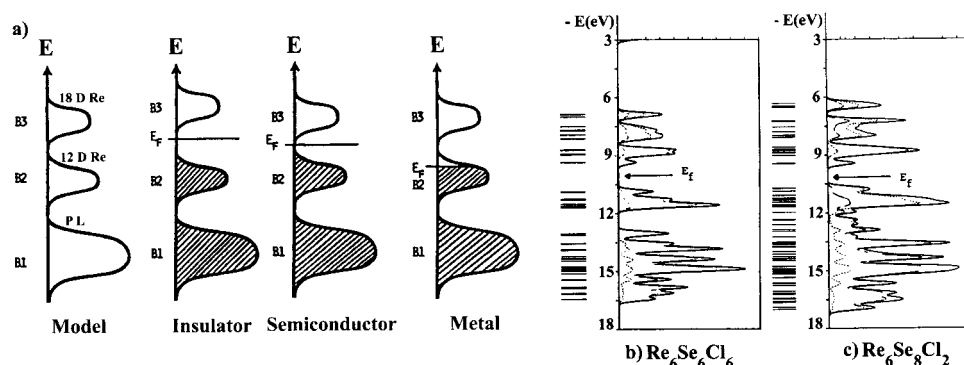


Figure 23. (a) Three band model for convoluted density of states (partial p L DOS in dotted line, partial d M DOS in dashed line, total DOS in continuous line) for (b) $\text{Re}_6\text{Se}_6\text{Cl}_6$ and (c) $\text{Re}_6\text{Se}_8\text{Cl}_2$. Reprinted from ref 119. Copyright 1986 from Wiley-VCH.

Table 11. Organic Radical Cations and Hexanuclear Rhenium Chalcogenide Cluster Anion Hybrid Salts

phase formulation	physical properties	ref
$(\text{TMTTF})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$	insulator, diamagnetic	4
$(\text{TMTTF})_2[\text{Re}_6\text{Se}_5\text{Cl}_9]$	semiconductor, spin Peierls	136
$(\text{TMTSF})_2[\text{Re}_6\text{S}_5\text{Cl}_9]$	semiconductor	136
$(\text{TTF})_3[\text{Re}_6\text{Q}_6\text{Cl}_8]\text{Cl}$ (Q = S, Se)	insulator, antiferromagnetic	4, 121
$(\text{TSeF})_3[\text{Re}_6\text{Se}_6\text{Cl}_8]\text{Cl}$	insulator, antiferromagnetic	4
$(\text{BEDT-TTF})_4^+[\text{Re}_6\text{Se}_5\text{Cl}_9]^- \cdot \text{guest}$	metal	122
$(\text{BEDT-TTF})^+[\text{Re}_6\text{Se}_5\text{Cl}_9]^- \cdot \text{solvent}$	insulator with uniform, noninteracting antiferromagnetic chain of spins	125
$(\text{cis-[10]TTFphane})^+[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$	insulator, diamagnetic	137
$(\text{cis-[12 TTFphane})_2^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator, paramagnetic	137
$(\text{BET-TTF})_2^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	semiconductor, paramagnetic	138
$(\text{BES-TTF})_2^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	semiconductor, paramagnetic	138
$(\text{MeS})_4\text{-TTF}]_2^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator, paramagnetic	120
$(\text{MeSe})_4\text{-TTF}]^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator, paramagnetic	120
$(\text{MeSe})_4\text{-TTF}]_2^+[\text{Re}_6\text{S}_6\text{Cl}_8]^- \cdot 2\text{DMF}$	insulator, diamagnetic	120
$(\text{MeTe})_4\text{-TTF}]^+[\text{Re}_6\text{S}_5\text{Cl}_9]^- \cdot 1.5\text{DMF}$	insulator, diamagnetic	120
$(\text{EtTe})_4\text{-TTF}]^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator, paramagnetic	120
$(\text{EtTe})_4\text{-TTF}]_2^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator, paramagnetic	120
$[\text{bis}(\text{DMTTF})\text{ethane}]_3[\text{Re}_6\text{Se}_6\text{Cl}_8]$	spin Peierls transition	139
$[\text{bis}(\text{DMTTF})\text{ethane}]_3[\text{Re}_6\text{S}_6\text{Cl}_8]$	spin ladder	139
$[\text{bis}(\text{DMTTF})\text{ethane}]_2[\text{Re}_6\text{S}_5\text{Cl}_9]$ (Y = S, Se)	insulator, paramagnetic	139
$[\text{bis}(\text{DMTTF})\text{ethane}]_5[\text{Re}_6\text{Se}_5\text{Cl}_9][\text{Re}_6\text{Se}_6\text{Cl}_8]$	insulator, paramagnetic	139
$[\text{cryptophane}]^+[\text{Re}_6\text{S}_5\text{Cl}_9]^-$	insulator	140
$\beta\text{-[BDT-TTP]}_6[\text{Re}_6\text{S}_6\text{Cl}_8] \cdot 2\text{CH}_2\text{ClCHCl}_2$	metal	127

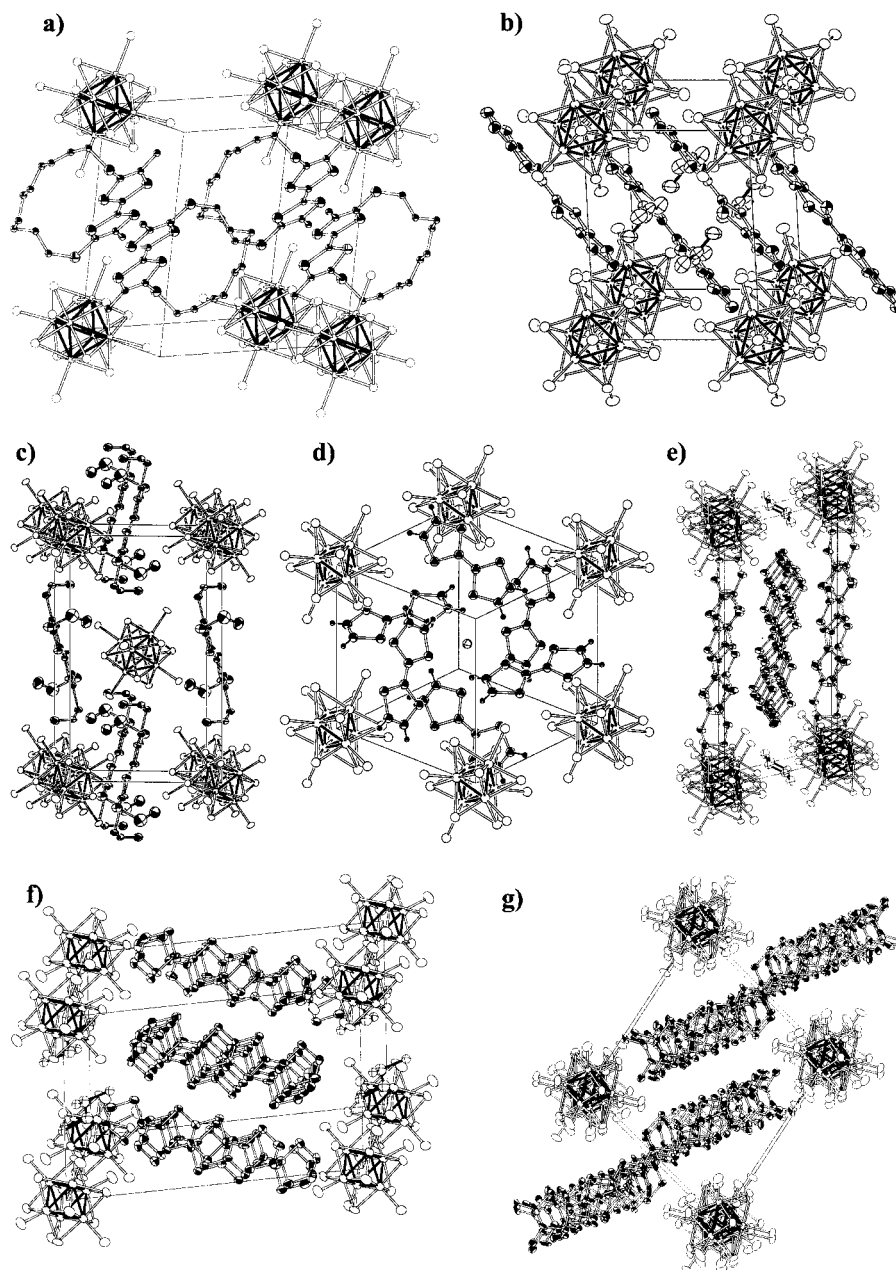


Figure 24. Organic radical cation arrays templated by rhenium chalcogenide cluster anions, as exemplified here by the projections of the unit cell content of a set of binary and ternary associations assembled by electrocrystallization: (a) (*cis*-[10]TTFphane)₂[Re₆S₆Cl₈]; (b) (BET-TTF)₂[Re₆S₅Cl₉]; (c) [EtTe]₄-TTF[Re₆S₅Cl₉]; (d) (TSeF)₃[Re₆Se₆Cl₈]Cl; (e) (BEDT-TTF)₄[Re₆S₆Cl₈]·guest; (f) β-(BDT-TTP)₆[Re₆S₆Cl₈]·(CH₂ClCHCl₂)₂; (g) [bis(DMTF)ethane]₅[Re₆S₅Cl₉][Re₆S₆Cl₈].

that removal of the intercalated metal cation (for example Pb in Pb[Re₆Se₆Cl₈]) would give a metal.

DFT calculations have been performed recently by Arratia-Pérez and Hernández-Acevedo on the octahedral [Re₆Q₈X₆]⁴⁻ (Q = S, X = Cl, Br, I;¹¹⁵ Q = Se, X = Cl, I)¹¹⁶ cluster ions. Manifolds of closely spaced unoccupied energy levels are found to be mainly localized on the octahedral rhenium core with some contributions from the μ₃-Q ligands, while the cluster highest occupied molecular orbital (HOMO) for all calculated structures would appear to be largely centered on the terminal halide ligands. Note that, as far as the cluster reactivity is concerned, one should be aware of the difficulty at reasoning on one individual orbital since the orbital character may

vary entirely from one to the other because the energy levels are so close to each other. In addition, calculations typically handle poorly the negative charge of molecular species. This is particularly relevant in the case of the tetranionic form, [Re₆(μ₃-Q)₈(μ-X)₆]⁴⁻, where electrostatic contributions to the core-μ-ligand interactions are likely to be significant. Therefore, the sizable percentage of the terminal halide contribution to the cluster HOMO may well be an artifact altogether. Finally, the authors conclude that the hexarhenium cluster ions have the same singlet ground state as W₆Cl₁₄²⁻ (spanning the Γ₆⁺ symmetry) and should therefore be diamagnetic. Note that the calculated charge distributions are as follows: [Re₆^{-0.21}S₈^{-0.16}Cl₆^{-0.24}], [Re₆^{-0.23}S₈^{-0.17}Br₆^{-0.21}],

$[\text{Re}_6^{-0.26}\text{S}_8^{-0.21}\text{I}_6^{-0.12}]$, $[\text{Re}_6^{-0.34}\text{Se}_8^{+0.04}\text{Cl}_6^{-0.38}]$, and $[\text{Re}_6^{-0.43}\text{Se}_8^{-0.03}\text{Cl}_6^{-0.20}]$, with negatively charged rhenium atoms a rather unexpected outcome.

Several major questions remain unanswered and will require further theoretical work. For example, why are the potentials of the redox couples $[\text{Re}_6\text{Q}_8]^{2+}/[\text{Re}_6\text{Q}_8]^{3+}$ so much lower than those of their chalcogenide counterparts? Furthermore, a sound investigation and discussion of the electronic structures of the open-shell forms $[\text{Re}_6\text{Q}_8]^{3+}$ is in dire need. A prominent unsettled question concerns the reactivity of the oxidized, 23-electron cluster forms: why are the radical anions $[\text{Re}_6\text{Q}_8\text{X}_6]^{3-}$ more reactive toward the substitution of μ -halides by cyanides and phosphine ligands, or N-heterocycles, than their reduced forms or, rather, is it essentially the higher positive charge of the cluster core which favors outer ligand exchange (section III.B.4)? Then, what is the nature of the electronic transition responsible for the intense absorption at 430 nm in $[\text{Re}_6\text{Q}_8]^{2+}$? All of these interrogations relate to key issues for further developments of the many, yet unexplored facets of the chemistry and physics of these luminescent and magnetic, organic–inorganic hybrid molecules.

H. Opportunities in Chemistry of Molecular Materials by Manipulating a Rare Set of Isosteric Anions

Right from the initial discovery of their solution phase chemistry these chalcogenide hexanuclear rhenium cluster anions have been engaged (sections II.D.2 and III.A.1)⁴ in the construction of ordered molecular assemblies upon their electrochemical association with tetrathiafulvalene-based cation radical molecules.¹⁰⁸ Thus, if one probes the interplay between the molecular properties (size, shape, functionality, charge, redox properties,...) of organic and inorganic electroactive precursors and the structural organization and functions of associated integrated O–I hybrid salts,¹²⁰ a large variety of binary or ternary salts have been obtained and shown to adopt remarkable molecular architectures (Table 11 and Figure 24), as exemplified by the series of molecular antiperovskite series $(\text{TTF})_3[\text{Re}_6\text{Q}_6\text{Cl}_8]\text{X}$ ($\text{Q} = \text{S}, \text{Se}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$)^{36,121} or the series of metallic pseudopolymorphs $\beta''\text{-(BEDT-TTF)}_4(\text{guest})\cdot[\text{Re}_6\text{Q}_6\text{Cl}_8]$,^{70,122,123,124} where a host of electronic and magnetic properties such as antiferromagnetism^{36,121,125} or metallic behavior¹²⁷ are currently being explored.

A particularly interesting aspect of this solid-state chemistry of molecular ions lies in the opportunity now offered to unravel unprecedented situations where one concentrates on the template charge effect, for a given size and shape of the (all-inorganic) molecular anion. This contrasts with the classical approach in inorganic solid-state chemistry where the (organic) template size, volume, and shape is preferably tuned with less variability of its charge itself.¹²⁸ One particularly relevant example addresses the important issue of the manipulation of band filling in low-dimensional molecular metals. Thus, our capacity to change the cluster anion charge and hence to modify the band filling, Fermi surface, and therefore the metallic character of the robust organic slabs

within the two-dimensional metal¹²⁷ $\beta\text{-(BDT-TTP)}_6\text{-}[\text{Re}_6\text{S}_6\text{Cl}_8]\cdot 2\text{CH}_2\text{ClCHCl}_2$ is nicely exemplified by the synthesis of $\beta\text{-(BDT-TTP)}_8[\text{Re}_6\text{S}_7\text{Cl}_7]\cdot 4\text{CH}_2\text{Cl}_2$. Regardless of their stoichiometries, the two compounds have essentially identical slab geometries and band structures. Therefore, different electron counts result in different Fermi levels and Fermi surfaces topologies, as expected.¹²⁸

V. Acknowledgments

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