Rhenium–Selenium–Chlorine Solid Phases: Cluster Excision and Core Substitution Reactions of Molecular Species

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Removal of intact clusters from the ternary phases $Re_6Se_{4+q}Cl_{10-2q}$ (q = 1–3) by the method of cluster excision has been investigated. The q = 1 phase $Re_6Se_5Cl_8$ ($Re_6Se^i_5Cl^i_3Cl^a_4Cl^{a-a}_{2/2}$) has a one-dimensional (chainlike) structure, the q = 2 phase $Re_6Se_6Cl_6$ ($Re_6Se^i_6Cl^i_2Cl^a_2Cl^{a-a}_{4/2}$) a two-dimensional (sheetlike) structure, and the q = 3 phase $Re_6Se_7Cl_4$ ($Re_6Se^i_7Cl^iCl^{a-a}_{6/2}$) a three-dimensional lattice. Treatment of $Re_6Se_5Cl_9$ and $Re_6Se_6Cl_6$ with excess R_4NCl in hot DMF or acetonitrile results in solubilization of the solid-state clusters, which were isolated in the molecular forms $(R_4N)[Re_6Se_5Cl_9]$ (R = Et, Pr (**1**), Bu (**7**)) and $(R_4N)_2[Re_6Se_6Cl_8]$ (R = Et (**4**), Pr (**5**)), respectively, in 78–85% yields. The structures of the clusters in these compounds were determined by X-ray analysis. Core Se/Cl atoms are disordered. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 8.894 (2) Å, b = 10.082 (2) Å, c = 18.540 (4) Å, α = 80.87 (1)°, β = 87.65 (2)°, γ = 87.36 (2)°, and Z = 2. The cluster $[Re_6Se_5Cl_9]^-$ contains an Re_6 octahedron which is face-capped to form a $[Re_6(\mu_3\text{-}Se)_5(\mu_3\text{-}Cl)_3]^{5+}$ core; each Re atom is bonded to a terminal chloride. Compound **5** crystallizes in the tetragonal space group $P4_2/mnm$ with a = 11.939 (3) Å, c = 16.806 (4) Å, and Z = 2. The cluster $[Re_6Se_6Cl_8]^{2-}$ has the $[Re_6Se_6Cl_2]^{4+}$ core and an analogous structure; the clusters in **4** and **5** are isostructural. These results demonstrate excision of the clusters known to be present in the solid phases by $Re–Cl^{a-a}$ bond rupture with chloride. Excision of clusters from $Re_6Se_7Cl_4$ has not been achieved. Reactions resulting in substitution of core chloride atoms have been performed. The molecular phase $Re_6Se_4Cl_{10}$ reacts with water in Pr_4NCl/DMF at 60 °C to give two isomeric clusters formulated as $(Pr_4N)_2[\alpha\text{-}Re_6Se_4O_2Cl_8]$ (**2**) and $(Pr_4N)_2[\beta\text{-}Re_6Se_4O_2Cl_8]$ (**3**) by X-ray structure determinations. Compound **2·2DMF** crystallizes in the monoclinic space group $P2_1/n$ with a = 12.146 (3) Å, b = 12.158 (2) Å, c = 19.316 (4) Å, β = 104.59 (2)°, and Z = 2. Compound **3** is obtained in monoclinic space group $C2/c$ with a = 22.610 (6) Å, b = 14.335 (4) Å, c = 17.399 (7) Å, β = 126.45 (3)°, and Z = 4. Both clusters contain the $[Re_6Se_4O_2Cl_2]^{4+}$ core but differ in position of the oxygen atoms; in the α-isomer they are at opposite ends of a body diagonal of the core whereas in the β-isomer they are trans on the same core face. Reaction of **1** or **7** with Li_2Se in THF affords a material identical to the excision product **5** or $(Bu_4N)_2[Re_6Se_6Cl_8]$ (**6**), respectively. The structure of **6** was confirmed by an X-ray structure determination. These results demonstrate Cl/Se core substitution. Substitution reactions of $[M_6L_8]^z$ cores are summarized; halide/chalcogenide replacements should be capable of extension and lead to new cluster types.

Introduction

Understanding the structural and reactivity relationships between molecules and extended solid arrays of comparable compositions presents an ongoing challenge. During the past three decades there have been extensive advances in the synthesis of molecular transition metal cages and clusters. A significant number of these cages[2,3] and clusters[4] have been shown to possess geometric and, in some cases, reactivity features similar to those exhibited by solids. This situation has provided an initial opportunity to examine the structural, electronic, and reactivity relationships between individual molecules and extended solids. In particular, recent experimentation has focused on systems which facilitate the conversion of molecules to solids at relatively low temperatures. Mainly, this has been accomplished by using the sol–gel process[5] or by the pyrolysis[6,7] of suitably soluble or volatile compounds to achieve the ultimate solid-state product. The molecule → solid conversion is illustrated schematically in Figure 1; in this example, clusters of various sizes are shown to aggregate with ligand loss to form solids. In this work, we consider the reverse process, also illustrated in Figure 1, viz., the conversion of insoluble solids to soluble molecules by reaction with appropriate ligands. We demonstrate the contribution of this process to the attainment of new discrete clusters and to an understanding of the paths connecting molecules and extended systems.

Our recent analysis of nonmolecular metal chalcogenide/halide solids has led to the recognition of three structural types.[4] One of these (type III) consists of extended arrays containing discrete, recognizable clusters, independent except for the bridging

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(8) In the i/a notation frequently used to describe solid-state structures,[4] ligand L^i (inner) bridges metal atoms in the core of a cluster and L^a (apical) is a terminal or bridging ligand external to the core. These ligands can function in the bridging interactions L^{a-a}, L^{a-i}, and L^{i-a}, only the first of which is represented in solids considered here.
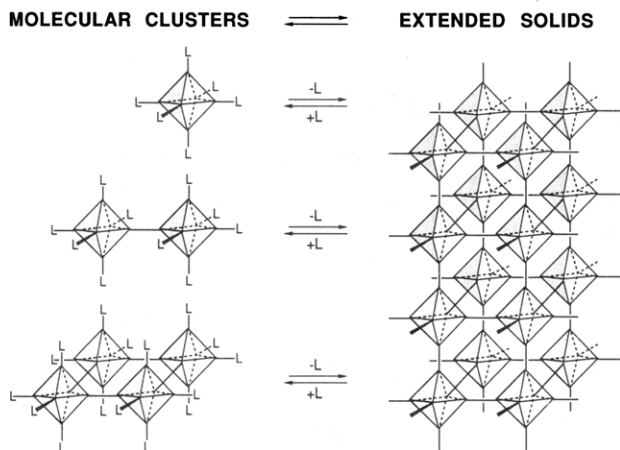
MOLECULAR CLUSTERS ⇌ **EXTENDED SOLIDS**

Figure 1. Schematic illustration of the aggregation of molecular clusters with ligand loss to form extended solids and of the formation of molecular clusters from solids by the process of cluster excision. Clusters are depicted with an arbitrary shape; potential intercluster bridging atoms in the solid are omitted.

interactions between them. The halide-bridged nonmolecular solids Re_3Cl_9 ($[Re_3Cl^i_3]Cl^a_3Cl^{a-a}_{6/2}$) and Mo_6Cl_{12} ($[Mo_6Cl^i_8]$-$Cl^a_2Cl^{a-a}_{4/2})^{4,8}$ are two of the many substances belonging to type III. These compounds are soluble in common donor solvents such as acetone, DMF, Me_2SO, and nitriles to afford the solvated clusters $Re_3Cl_9(solv)_3^{9-12}$ and $Mo_6Cl_{12}(solv)_2.^{13-15}$ These species retain the triangular $Re_3Cl^i_3$ and face-capped octahedral Mo_6-Cl^i_8 cores of the solid-state clusters, as do the familiar species $[Re_3Cl_{12}]^{3-16}$ and $[Mo_6Cl_{14}]^{2-},^{17}$ which are solubilized when the solids are treated with excess chloride.[4]

Many clusters in type III solids have not been prepared in molecular form. Removal of the intact cluster cores $[M_mX^i_x]$, $[M_mQ^i_q]$, or $[M_mX^i_xQ^i_q]$ (X = halide, Q = chalcogenide) from solids in soluble molecular form, a process we have termed *cluster excision*,[4] provides a route to clusters not yet obtained or not obtainable by solution methods at ordinary temperatures. Excision reactions have frequently not been explicitly described or recognized as such. However, with the abundance of structurally determined solids and, in many cases, the structural stability associated with a metal–metal-bonded framework and M–X/Q bridging interactions, the concept of *intact core removal* appears viable.

We wish to elaborate excision reactions to the point of synthetic utility using as initial objects compounds insoluble in neat solvents and containing clusters not (yet) synthesized by solution methods. The ternary phases $Re_6Se_{4+q}X_{10-2q}$ (X = Cl^-, Br^-; q = 0–3)[18-23] meet these requirements; many of their leading features have been summarized.[21,22] They contain the cluster cores Re_6-

$Se^i_{4+q}X^i_{4-q}$ consisting of a Re^{III}_6 metal–metal-bonded octahedron whose faces are capped with Se/X atoms. Two phases (Re_6-Se_4X_{10}) are molecular, while others contain clusters linked in chainlike ($Re_6Se_5Cl_8$), sheetlike ($Re_6Se_6Cl_6$), and three-dimensional ($Re_6Se_7Br_4$) arrangements. The latter phases present three types of bridging networks that must be surmounted if cluster excision is to be successful. One cluster contained in these phases has been obtained in molecular form by a nonexcision method,[24] but its properties are uninvestigated. These clusters have been prepared only by high-temperature reactions; methods of solution synthesis yielding a *specific* cluster core are not obvious. As will be shown, the clusters present in two of these phases have been excised. Furthermore, they are subject to reactions of core substitution in solution to yield additional clusters that are in fact derivatives of the clusters present in the solid state.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere. All solvents were dried and degassed prior to use. Quaternary ammonium chlorides were recrystallized and dried at 90 °C in vacuo. Lithium selenide was prepared as described.[25] Elemental rhenium and selenium were used as powders; $ReCl_5$ was a commercial sample (Cerac).

Crystalline materials of the $Re_6Se_{4+q}Cl_{10-2q}$ phases (q = 0–3) were obtained using slightly modified versions of reported methods.[18,20,23] In a typical preparation, stoichiometric quantities of the starting materials Re, Se, and $ReCl_5$ (10% excess) were mixed and loaded into a fused quartz tube of dimensions 100 mm (length), 10 mm (o.d.), and 6 mm (i.d.). The tube was sealed under ca. 0.005 mmHg and placed in a tube furnace, in which the temperature was raised (1 deg/min) to the desired final temperature (780 °C for q = 0, 800 °C for q = 1, 850 °C for q = 2, 950 °C for q = 3). These temperatures were maintained for at least 4 d, followed by cooling to room temperatures at 5 deg/min. The solid-state materials thus prepared were washed with acetonitrile and ether. Their identities were established by microprobe analyses and X-ray powder diffraction. The former were made by a Cameca MBX electron microprobe using a Tracor Northern TN-1310 wavelength-dispersive spectrometer with a TN-5502 EDS system and a stage automation system. Analytical results for single crystals and pressed pellets of bulk materials were found to be consistent. The following results were obtained for the indicated phases: $Re_{5.76}Se_4Cl_{9.36}$ for $Re_6Se_4Cl_{10}$, $Re_{5.75}Se_5Cl_{7.80}$ for Re_6-Se_5Cl_8, $Re_{5.80}Se_6Cl_{5.82}$ for $Re_6Se_6Cl_6$, and $Re_{5.80}Se_7Cl_{3.81}$ for $Re_6Se_7Cl_4$.

For the $Re_6Se_{q+n}Cl_{10-2q}$ phases for which X-ray diffraction data are available (q = 0,[20] 2[23]), line positions and relative intensities were found to be in agreement with calculated powder patterns. For other phases (q = 1, 3), the d spacings (Å) and relative intensities (in parentheses) of the more prominent lines are as follows. q = 1: 7.394 (43), 6.976 (100), 6.784 (22), 2.315 (16), 2.191 (6), 2.107 (11), 2.040 (7), 1.926 (14), 1.737 (18). q = 3: 7.709 (38), 6.697 (85), 6.593 (100), 6.886 (25), 2.704 (16), 2.504 (20), 2.217 (19), 2.191 (20), 2.180 (17), 2.146 (17), 2.139 (19), 2.103 (17), 2.080 (40), 2.042 (26), 2.023 (28), 1.985 (43), 1.970 (33).

Cluster Excision Reactions. (a) $Re_6Se_5Cl_8 \rightarrow (Pr_4N)[Re_6Se_5Cl_9]$. Crystalline $Re_6Se_5Cl_8$ (300 mg, 0.17 mmol) was suspended in 30 mL of a DMF solution containing 350 mg (1.60 mmol) of Pr_4NCl. This mixture was maintained at 60 °C for 18 h and filtered while hot to remove a small amount (ca. 20 mg) of black powder. To the dark red filtrate was added 200 mL of ether, causing precipitation of an orange powder. Diffusion of ether into a 5-mL DMF solution of this material resulted in the separation of rodlike crystals. After 3 d, the solid was collected and washed quickly with 5 mL of acetonitrile and with 2 × 15 mL of ether to give 275 mg (80%) of product as dark red crystals. An analytical sample was recrystallized from hot acetonitrile. Anal. Calcd for $C_{12}H_{28}Cl_9NRe_6Se_5$: C, 7.14; H, 1.40; Cl, 15.81; N, 0.69; Re, 55.38; Se, 19.57. Found: C, 7.37; H, 1.47; Cl, 15.97; N, 0.88; Re, 54.86; Se, 19.40. The Et_4N^+ and Bu_4N^+ salts were prepared in 80–85% yields by analogous procedures and were obtained as dark red crystalline solids.

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Table I. Crystallographic Data^a for $(Pr_4N)[Re_6Se_5Cl_9]$ (1), $(Pr_4N)_2[\alpha\text{-}Re_6Se_4O_2Cl_8]\cdot2DMF$ (2), $(Pr_4N)_2[\beta\text{-}Re_6Se_4O_2Cl_8]$ (3), $(Et_4N)_2[Re_6Se_6Cl_8]$ (4), $(Pr_4N)_2[Re_6Se_6Cl_8]$ (5), and $(Bu_4N)_2[Re_6Se_6Cl_8]$ (6)

	1	2	3	4	5	6
formula	$C_{12}H_{28}Cl_9NRe_6Se_5$	$C_{30}H_{70}Cl_8N_4O_4Re_6Se_4$	$C_{24}H_{56}Cl_8N_2O_2Re_6Se_4$	$C_{16}H_{40}Cl_8N_2Re_6Se_6$	$C_{24}H_{56}Cl_8N_2Re_6Se_6$	$C_{32}H_{72}Cl_8N_2Re_6Se_6$
fw	2017.4	2267.5	2121.3	2135.1	2247.3	2359.5
cryst system	triclinic	monoclinic	monoclinic	tetragonal	tetragonal	tetragonal
a, Å	8.894 (2)	12.146 (3)	22.610 (6)	11.427 (2)	11.939 (3)	14.294 (2)
b, Å	10.082 (2)	12.158 (2)	14.335 (4)			
c, Å	18.540 (4)	19.316 (4)	17.399 (7)	17.705 (3)	16.806 (4)	13.944 (2)
α, deg	80.87 (1)					
β, deg	87.65 (2)	104.59 (2)	126.45 (3)			
γ, deg	87.36 (2)					
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P4_2/mcm$	$P4_2/mnm$	$I4/mmm$
Z	2	2	4	2	2	2
V, Å^3	1638.6 (6)	2760 (1)	4536 (3)	2311.9 (7)	2396 (1)	2849.2 (8)
T, K	173	173	223	198	198	198
ρ_{calc}, g/cm^3	4.089	2.728	3.106	3.067	3.115	2.750
μ, mm^{-1}	28.37	16.16	19.65	20.84	20.12	16.93
$R,^b$ %	8.17	7.89	6.64	6.48	4.41	9.10
$R_w,^c$ %	8.67	8.10	7.19	7.55	4.68	7.07

^{a} All data collected with Mo Kα radiation (λ = 0.710 69 Å). ^{b} $R = \sum\|F_o\| - |F_c\|/\sum|F_o|$. ^{c} $R_w = \{\sum[w(|F_o| - |F_c|^2)]/\sum[w|F_o|^2]\}^{1/2}$.

(b) $Re_6Se_6Cl_6 \rightarrow (Pr_4N)_2[Re_6Se_6Cl_8]$. Crystalline $Re_6Se_6Cl_6$ (430 mg, 0.24 mmol) was suspended in 30 mL of an acetonitrile containing 380 mg (1.7 mmol) of Pr_4NCl, and the mixture was refluxed for 24 h. All solid dissolved to form a dark red solution. Addition of 50 mL of ether caused separation of an orange microcrystalline solid. This material was collected and recrystallized by ether diffusion into a solution in 7 mL of DMF. After 5 d, the solid was collected, washed with ether (3 × 25 mL), and dried to afford the product as 380 mg (78%) of dark red, rhombohedral crystals. Anal. Calcd for $C_{24}H_{56}Cl_8N_2Re_6Se_6$: C, 12.79; H, 2.51; Cl, 12.59; N, 1.24; Re, 49.58; Se, 21.29. Found: C, 13.01; H, 2.61; Cl, 12.30; N, 1.40; Re, 49.26; Se, 21.20.

(c) $Re_6Se_6Cl_6 \rightarrow (Et_4N)_2[Re_6Se_6Cl_8]$. Crystalline $Re_6Se_6Cl_6$ (330 mg, 0.18 mmol) was suspended in 60 mL of an acetonitrile solution containing 400 mg (2.4 mmol) of Et_4NCl, and the mixture was heated at reflux for 24 h. The solid completely dissolved to form a dark red solution. Upon the addition of 50 mL of ether, an orange microcrystalline solid separated. This material was collected and recrystallized by diffusing ether into a solution of 5 mL of DMF. After 3 d, the solid was collected, washed with ether (3 × 25 mL), and dried to afford the product as 260 mg (80%) of dark red, rod-shaped crystals. The identity of this compound was established by a single-crystal X-ray structure determination.

Core Conversion Reactions. (a) $(Pr_4N)_2[\alpha\text{-}Re_6Se_4O_2Cl_8]$. Crystalline $Re_6Se_4Cl_{10}$ (290 mg, 0.16 mmol) was suspended in a solution of 280 mg (1.3 mmol) of Pr_4NCl in 15 mL of wet DMF. The mixture was heated at 60 °C for 48 h to give a dark red solution, which was filtered, and the filtrate was reduced in volume to 10 mL in vacuo. Ether (ca. 30 mL) was added to incipient cloudiness, and the solution was stored at 7 °C for 3 d. The microcrystalline solid collected by filtration (ca. 200 mg) was suspended in 10 mL of acetonitrile to form a dark red solution and an orange solid. The solid was collected and dissolved in 0.5 mL of DMF into which ether was slowly diffused. The product was obtained as 50 mg (14%) of large cubelike orange crystals. This compound was identified by a single-crystal X-ray structure determination.

(b) $(Pr_4N)_2[\beta\text{-}Re_6Se_4O_2Cl_8]$. Crystalline $Re_6Se_4Cl_{10}$ (130 mg, 0.073 mmol) was suspended in a solution of 15 mL of DMF containing 0.60 mL (33 mmol) of water and 280 mg (0.79 mmol) of Pr_4NCl. The mixture was heated at 60 °C for 18 h to yield a dark red solution, which was filtered to remove a small amount of solid (ca. 5 mg). Addition of 100 mL of ether to the filtrate produced a dark red oil, which was converted to a powder by washing with 5 mL of acetonitrile followed by 6 × 25 mL of ether. This material was dissolved in 1 mL of DMF, into which ether was slowly diffused. After 7 d, dark red, block-shaped crystals were isolated and washed with ether to give 100 mg (66%) of product. This compound was identified by a single-crystal X-ray structure determination.

(c) $(Pr_4N)_2[Re_6Se_6Cl_8]$. An orange solution of 120 mg (0.060 mmol) of $(Pr_4N)[Re_6Se_5Cl_9]$ in 40 mL of THF and 2 mL of Me_2SO was treated with 35 mg (0.38 mmol) of Li_2Se and 50 mg (0.23 mmol) of Pr_4NCl. The mixture was stirred for 30 min, and the brown precipitate was collected and dissolved in 2 mL of DMF. Slow diffusion of ether into this solution caused the formation of dark red, rhombohedral crystals. After 3 d, the crystalline material was collected to give 69 mg (57%) of product. The compound was demonstrated by an X-ray structure determination to be identical to the excision product of $Re_6Se_6Cl_6$ and Pr_4NCl.

(d) $(Bu_4N)_2[Re_6Se_6Cl_8]$. A dark orange solution of 30 mg (0.015 mmol) of $(Bu_4N)[Re_6Se_5Cl_9]$ in 30 mL of THF was treated with 5.0 mg (0.054 mmol) of Li_2Se. The mixture was stirred for 3 h, and the dark brown precipitate was collected and dissolved in 5 mL of acetonitrile. Ether was slowly diffused into this solution, resulting in the formation of dark red, rod-shaped crystals. After 4 d, these were collected and washed with ether to afford 21 mg (59%) of product. This compound was identified by a single-crystal X-ray structure determination.

X-ray Data Collection and Reduction. Experimental details for compounds 1–6 are given in Table I. Dark red crystals of these compounds were grown by vapor diffusion of ether into saturated solutions in DMF. Crystals were coated with grease, transferred to a Nicolet P3F diffractometer, and cooled with a nitrogen stream. Lattice parameters were obtained from least-squares analyses of 25 machine-centered reflections with $20° \leq 2\theta \leq 40°$. The compounds showed no significant decay upon monitoring three check reflections periodically throughout the course of the data collections. The raw intensity data were converted to structure factor amplitudes and their esd's by corrections for scan speed, background, and Lorentz and polarization effects using the program XDISK of the SHELXTL PLUS program package. Crystal faces were not well-defined; therefore, empirical absorption corrections based on the observed variation in intensity of azimuthal (Ψ) scans were applied to all data sets using the program XEMP. Compound 1 crystallized in the triclinic system; statistics identified the space group as $P\bar{1}$. Compounds 2 and 3 crystallized in the monoclinic system. Systematic absences identified the space group of 2 as $P2_1/n$ and of 3 as either Cc or $C2/c$; the latter was selected on the basis of statistics. Compounds 4–6 crystallized in the tetragonal system; examination of the intensities of symmetry-equivalent reflections indicated that the three structures were centrosymmetric with $4/mmm$ symmetry. Systematic absences of 4–6 identified the space groups as $P4_2/mcm$, $P4_2/mnm$, and $I4/mmm$, respectively.

Structure Solution and Refinement. The structures were solved by direct methods and were refined using standard least-squares and Fourier techniques. All Re and terminal Cl atoms were refined anisotropically. All other atoms were described isotropically unless otherwise noted. Hydrogen atoms were assigned idealized locations with the uniform value B_{iso} = 0.8 Å^2 and were introduced in the later stages of the refinements unless stated otherwise. Each cluster core consists of an Re_6 octahedron whose faces are capped by combinations of Se, Cl, and O atoms in a cubelike arrangement.

The asymmetric unit of compound 1 consists of two crystallographically distinct half-cluster anions and one cation. No unique site for the Se atoms could be located in either cluster, whose $Re_6Se_5Cl_3$ cores were refined with site occupancies of 0.625 Se and 0.375 Cl. The asymmetric unit of 2 consists of one-half cluster anion, one cation, and one DMF solvate molecule. Two unique oxygen sites in the $Re_6Se_4Cl_2O_2$ cores were located, but the other positions were disordered and were refined with the occupancies 0.666 Se and 0.333 Cl. All atoms were refined anisotropically except for core capping atoms. The asymmetric unit of 3 contains one-half cluster anion and one disordered cation. Two unique O and two unique Se sites in the $Re_6Se_4Cl_2O_2$ core were found, but the other four capping sites were disordered and were refined with the occupancies 0.5 Se and 0.5 Cl. One of the terminal Cl atoms was
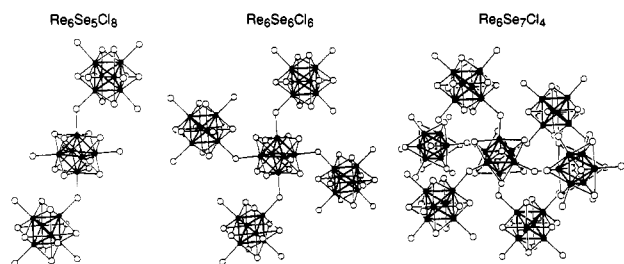
Figure 2. Depictions of the structures of the phases $Re_6Se_{4+q}Cl_{10-2q}$ (q = 1–3),[23] which contain $Re_6Se_{4+q}Cl_{4-q}$ cores (q = 1–3): dark spheres, Re; open spheres, Se/Cl. Clusters are bridged by chloride atoms in a chain ($Re_6Se_5Cl_8$), sheet ($Re_6Se_6Cl_6$), or three-dimensional network ($Re_6Se_7Cl_4$). The structure of $Re_6Se_6Cl_6$ was drawn from published coordinates.[23] Coordinates of the other two structures have not been published. Depictions were produced from coordinates of isostructural compounds: Mo_6Cl_{12}[27] for $Re_6Se_5Cl_8$ and Nb_6I_{11}[28] for $Re_6Se_7Cl_4$.

disordered across a 2-fold axis, and one carbon atom of the cation was disordered over two positions; both were refined with 0.5 site occupancies. The unique Se positions were refined anisotropically; hydrogen atoms were not included. Compound **4** crystallized with the cluster on an *mmm* site with two unique Re positions and two unique capping atom positions in the $Re_6Se_6Cl_2$ core. No unique site could be located for the Se positions, and each capping position was isotropically refined as 0.75 Se and 0.25 Cl. The cation occurs on the 222 position, and its unique N and α-C atoms were refined anisotropically. Hydrogen atoms were not included in the refinement. In compound **5**, the cluster also occurs on an *mmm* site with two unique Re atoms and two unique capping positions. Initially, the structure was refined with core Se and Cl atoms randomly disordered over these two capping sites, but during later stages of the refinement, thermal parameters indicated that an Se atom was located at one of the capping positions. The other capping position was disordered and was refined as 0.5 Se and 0.5 Cl. The cation crystallized on the $\bar{4}$ position. All atoms except that at the disordered capping site were refined anisotropically; during the final stages of refinement, hydrogen atoms were included. Compound **6** contained the cluster on a 4/*mmm* site with two unique Re positions and one unique capping position. The latter was refined as 0.75 Se and 0.25 Cl. The cation was disordered on the $\bar{4}m2$ position. One C atom was disordered over two positions and was refined with 0.5 occupancy factors. Hydrogen atoms were not included in the refinement. In the last cycles of refinement for the structures, all parameters shifted by <1% of the esd of the parameter and final difference Fourier maps showed no significant residual electron density. Final R factors are presented in Table I. Other crystallographic data are available elsewhere.[26]

Results and Discussion

Re–Se–Cl Solid Phases. The recent finding that Re(III) can be substituted for Mo(II) in the Chevrel phases has led to the synthesis of a large family of solid-state materials.[21,22] Among these are the series of phases $Re_6Se_{4+q}X_{10-2q}$ (q = 1–3) belonging to type III solids[4] and containing face-capped halide-bridged $Re_6Se_{4+q}X_{4-q}$ cluster cores as the principal structural motif.[18–23] All phases contain Re(III). The synthesis of these compounds has been achieved by the reaction of $ReCl_5$, rhenium metal, and elemental selenium in an evacuated silica tube at 780–950 °C.[20,23] Pertinent structural features of these phases, on which cluster excision experiments have been performed, are briefly outlined. Structures are presented in Figure 2.

The crystal structure of $Re_6Se_4Cl_{10}$ (not shown) consists of the discrete molecules $Re_6Se^i_4Cl^i_4Cl^a_6$. Stepwise substitution of core chloride with selenide leads to polymerization of the core units by means of terminal chloride bridging interactions and affords three additional phases. In the first phase, $Re_6Se_5Cl_8$ = $Re_6Se^i_5Cl^i_3Cl^a_4Cl^{a-a}_{2/2}$, each cluster is bridged to two others via trans $Re–Cl^{a-a}$ interactions, leading to a one-dimensional chainlike structure in which the chains run parallel to one another. The clusters within the chain are tilted, causing a bridge angle of
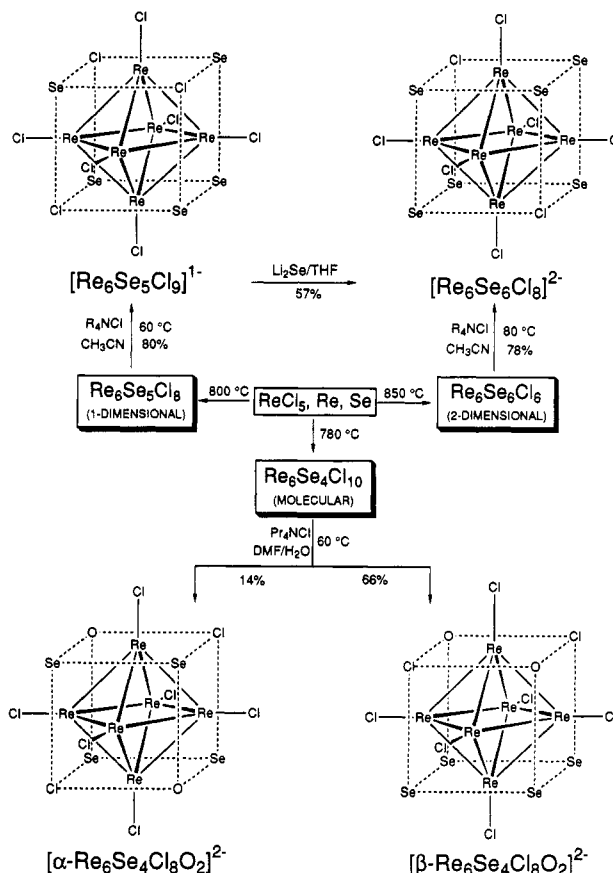

Figure 3. Reaction scheme illustrating the excision of clusters from the phases $Re_6Se_5Cl_8$ and $Re_6Se_6Cl_6$ and core conversion reactions in which chloride is substituted by selenide or oxide. For the sake of definiteness, core atom positions are specified, but some atoms are actually disordered.

132°, and are twisted by 26° with respect to each other. The second phase, $Re_6Se_6Cl_6$ = $Re_6Se^i_6Cl^i_2Cl^a_2Cl^{a-a}_{4/2}$, is isostructural with Mo_6Cl_{12}[27] and possesses a layered or sheetlike two-dimensional arrangement. Each cluster is linked to four other clusters by $Re–Cl^{a-a}$ bridges with an angle of 133°. The third phase, $Re_6Se_7Cl_4$, has not been fully characterized by X-ray analysis but is expected to have the $Re_6Se^i_7Cl^iCl^{a-a}_{6/2}$ structure on the basis of results for $Re_6Se_7Br_4$.[23] This compound has a three-dimensional lattice in which each cluster is linked to six others by bromide bridges and is closely related to the structure of Nb_6I_{11}.[28]

At the outset of this study, the chemistry of molecular cluster compounds with the cores $Re_6Se_{4+q}X_{4-q}$ was limited to two examples, which were realized by nonexcision methods. Salts of $[Re_6Se_5Cl_9]^-$ with organic cations[21,22,24] have been prepared from cubic $KRe_6Se_5Cl_9$,[18,29] which contains discrete clusters. Recrystallization of this compound from wet ethanol is reported to yield $K[Re_6Se_5Cl(OH)_2]Cl_6·H_2O$, in which two hydroxide groups have replaced chlorides in the core of the parent cluster.[21,22] We report here cluster excision reactions of two solid phases and certain core substitution reactions, one of which interrelates molecular and bridged cluster phases. Reactions are summarized in Figure 3.

Cluster Excision. Treatment of the one-dimensional bridged phase $Re_6Se_5Cl_8$ with excess R_4NCl (R = Et, Pr, Bu) in warm acetonitrile or DMF results in the slow formation of dark red solutions from which the salts $(R_4N)[Re_6Se_5Cl_9]$ can be isolated

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(26) See the paragraph at the end of this article concerning supplementary material available.

(27) Schäfer, H.; von Schnering, H.-G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281.
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(29) Perrin, A.; Leduc, L.; Potel, M.; Sergent, M. *Mater. Res. Bull.* **1990**, *25*, 1227.
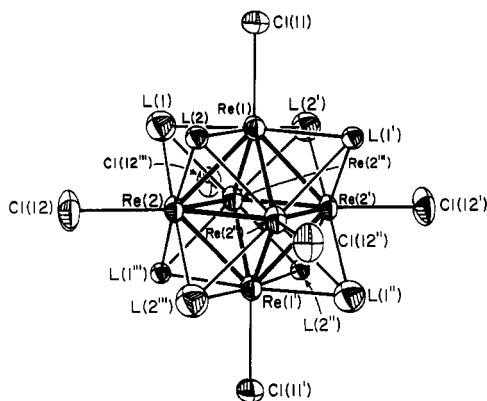
Figure 4. Composite presentation of the structures of [Re₆Se₅Cl₉]⁻ and [Re₆Se₆Cl₈]²⁻ as found in compounds **1**, **4**, **5**, and **6**, showing 50% probability ellipsoids and the generalized atom-labeling scheme. Atoms L are disordered Se/Cl. In **1**, there are two independent clusters, each with inversion symmetry. The clusters in **4** and **5** have *mmm* symmetry with two independent positions for both Re and L atoms. The cluster in **6** has 4/*mmm* symmetry with two independent positions for Re atoms and one unique position for L atoms.

Table II. Ranges and Mean Values of Interatomic Distances (Å) in Excised Clusters

dist		(Pr₄N)[Re₆Se₅Cl₉]	(Pr₄N)₂[Re₆Se₆Cl₈]
Re–Re	mean	2.612 (6)	2.613 (3)
	range	2.601 (2)–2.625 (2)	2.611 (2)–2.618 (3)
Re–Lᵃ	mean	2.490 (12)	2.505 (15)
	range	2.467 (6)–2.508 (5)	2.482 (5)–2.520 (5)
Re–Clₜᵇ	mean	2.346 (9)	2.379 (12)
	range	2.337 (8)–2.361 (9)	2.370 (13)–2.387 (7)

ᵃ L = core Se/Cl. ᵇ Terminal distance.

in good yields. For example, the Pr₄N⁺ salt reported here was obtained in 80% yield. Under similar conditions, the two-dimensional solid Re₆Se₆Cl₆ affords the dark red cluster salts (R₄N)₂[Re₆Se₆Cl₈] (R = Et, Pr) in 78–80% yields. These crystalline compounds are freely soluble in solvents such as acetone, acetonitrile, DMF, Me₂SO, and THF. The Pr₄N⁺ salts of the two clusters have been formulated on the basis of total elemental analysis and crystal structure determinations. In addition, (Et₄N)₂[Re₆Se₆Cl₈] was identified by an X-ray structure determination.

Both clusters possess structures analogous to those present in their parent solid phases.[21–23] As seen in the composite Figure 4, which represents both clusters, the excised species retain the Re₆ octahedra; all terminal ligands are chloride atoms. Because of disorder of the capping atoms,[30] core compositions were inferred from crystallographic determination of the number of cations, and are fully consistent with the results of elemental analysis. The ranges and mean values of core bond distances in Table II are essentially coincident with those of the clusters in extended lattices. For example, the corresponding mean values in Re₆-Se₅Cl₈[23] are 2.603 (1) (Re–Re), 2.497 (4) (Re–L), and 2.333 (7) Å (Re–Clₜ). It is certain that the Se:Cl capping atom ratios in the solid state and excised clusters are the same. Substitution of core chloride by other ligands has been observed (vide infra), but to our knowledge substitution of core chalcogenide by halide has not been demonstrated. In the excision reactions, chloride fulfills the functions of bridge cleavage and ligation of "vacant" rhenium sites of emergent clusters.

We have as yet been unable to excise clusters from the three-dimensional lattice of Re₆Se₇Cl₄. The solid phase has proven unreactive to the systems R₄NCl/DMF, Et₃P/THF, RNH₂, or pyridine/MeCN under reflux conditions with the potential

(30) In addition to statistical disorder of a given core structure, the Re₆Se₅Cl₃ and Re₆Se₆Cl₂ cores have four and three isomers, respectively. Disorder of Se/Cl capping atoms is in such cores is well precedented.[18–24]

Figure 5. Structure of [α-Re₆Se₄Cl₈O₂]²⁻, showing 50% probability ellipsoids and the atom-labeling scheme. Primed and unprimed atoms are related by an inversion center; L = disordered Se/Cl.

excision reagent present in large excess and to NaCl/AlCl₃ (350–450 °C) and LiCl (600–800 °C) melts.

Core Conversion Reactions. These reactions, in which core halide or selenide atoms are substituted, are summarized in Figure 3. The possibility of such reactions with retention of the Re₆ octahedron was first realized here in experiments with the molecular solid Re₆Se₄Cl₁₀. Upon heating of this compound in wet DMF at 60 °C for 48 h in the presence of equimolar Pr₄NCl, [α-Re₆Se₄O₂Cl₈]²⁻ was isolated in low yield as its orange crystalline Pr₄N⁺ salt. With this result in hand, a second reaction was conducted in which a DMF reaction mixture containing Re₆-Se₄Cl₁₀, equimolar Pr₄NCl, and a large excess (ca. 230-fold) of water was heated at 60 °C for 18 h. After workup, [β-Re₆-Se₄O₂Cl₈]²⁻ was obtained as its dark red Pr₄N⁺ salt in 66% yield. X-ray structural determinations of both compounds revealed the presence of two cations per cluster anion, the latter maintaining the structural motif of the starting compound. No water molecules were found in either structure. With the retention of Reᴵᴵᴵ₆ formulation and four core selenide atoms, the cation:anion ratio requires substitution of chloride in the initial Re₆Se₄Cl₄ core by oxide rather than by hydroxide in both clusters.[31,32] It should be noted that all solid-state and molecular clusters examined here are electron-precise (24e), completely metal–metal-bonded species.

The structures of the two clusters, set out in Figures 5 and 6, reveal that they are diastereomers. In both, core oxygen atoms were located. The centrosymmetric α-isomer contains oxygen atoms located at the opposite ends of a body diagonal of the Se₄O₂Cl₂ cubelike portion of the core. In the β-isomer, the oxygen atoms occupy trans positions of a cube face and are related by an imposed C₂ axis which contains the atoms Re(1,4). These are two of the possible 16 diastereomers of an A₄B₂C₂ cube. Selected interatomic distances for the two clusters are collected in Table III. The nonbonded distances convey cluster shapes, which are highly distorted from the near-cubic arrangement found for [Re₆Se₅Cl₉]⁻ and [Re₆Se₆Cl₈]²⁻. This is primarily because the Re–O distances are ca. 0.4 Å shorter than the Re–L distances. Thus the α-isomer is compressed along the O(1)···O(1') diagonal (5.11 (2) Å) by 1 Å when that distance is compared to the mean of the other three diagonals (6.11 Å). In the β-isomer, the short O(1)···O(1') separation (4.09 (1) Å) distorts the O(1,1')L(1,1')

(31) To our knowledge, the μ₃-OH bridge has not been established in any Re(III) compound. It is known in compounds of Re(I): (a) Ciani, G.; Sironi, A.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* **1977**, 1667. (b) Nuber, B.; Oberdorfer, F.; Ziegler, M. L. *Acta Crystallogr.* **1981**, *B37*, 2062.

(32) Somewhat related to the formation of [Re₆Se₄O₂Cl₈]²⁻ clusters is the finding that reaction of Nb₂Cl₆(tht)₃ (tht = tetrahydrothiophene) with concentrated aqueous H₂SO₄ affords [Nb₃(μ₃-O)₂(SO₄)₆(OH₂)₃]⁵⁻: Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1276. However, in this case some metal oxidation has occurred.
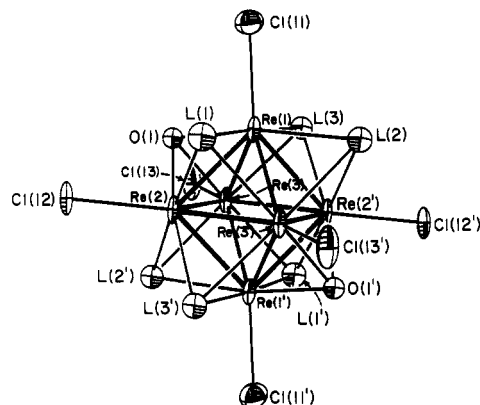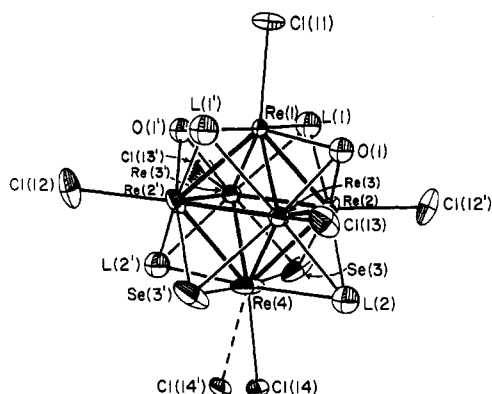
Figure 6. Structure of $[\beta\text{-Re}_6\text{Se}_4\text{Cl}_8\text{O}_2]^{2-}$, showing 50% probability ellipsoids and the atom-labeling scheme. Primed and unprimed atoms are related by a C_2 axis; Cl(14) is disordered across this axis; L = disordered Se/Cl.

Table III. Selected Interatomic Distances (Å) for $[\alpha\text{-Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]^{2-}$ and $[\beta\text{-Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]^{2-}$

$[\alpha\text{-Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]^{2-}$		$[\beta\text{-Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]^{2-}$	
Re(1)–O(1)	2.086 (14)	Re(1)–O(1)	2.059 (21)
Re(2)–O(1)	2.096 (14)	Re(2)–O(1)	2.088 (26)
Re(3)–O(1)	2.068 (14)	Re(3)–O(1)	2.094 (20)
Re(1)–L(1)^a	2.488 (3)	Re(1)–L(1)	2.475 (7)
Re(1)–L(2)	2.524 (2)	Re(2)–L(1)	2.509 (7)
Re(1)–L(3)	2.497 (3)	Re(2)–L(2)	2.509 (7)
Re(2)–L(1)	2.511 (3)	Re(2)–Se(3)	2.523 (5)
Re(2)–L(2')	2.501 (3)	Re(3)–L(1')	2.501 (5)
Re(2)–L(3')	2.520 (3)	Re(3)–L(2)	2.486 (6)
Re(3)–L(1')	2.527 (3)	Re(3)–Se(3')	2.517 (4)
Re(3)–L(2')	2.494 (3)	Re(4)–L(2)	2.486 (6)
Re(3)–L(3)	2.500 (3)	Re(4)–Se(3)	2.527 (6)
Re(1)–Re(2)	2.532 (1)	Re(1)–Re(2)	2.522 (2)
Re(1)–Re(3)	2.598 (1)	Re(1)–Re(3)	2.516 (2)
Re(2)–Re(3)	2.601 (1)	Re(2)–Re(3)	2.535 (3)
		Re(2)–Re(4)	2.608 (2)
		Re(3)–Re(4)	2.614 (2)
Re(1)–Cl(11)^b	2.350 (5)	Re(1)–Cl(11)^b	2.349 (11)
Re(2)–Cl(12)	2.361 (5)	Re(2)–Cl(12')	2.357 (7)
Re(3)–Cl(13)	2.354 (6)	Re(3)–Cl(13)	2.372 (13)
		Re(4)–Cl(14)	2.419 (14)
O(1)···O(1')	5.11 (2)	O(1)···O(1')	4.09 (1)
L(1)···L(1')	6.115 (5)	L(1)···L(1')	4.95 (1)
L(2)···L(2')	6.116 (4)	L(2)···L(2')	4.97 (1)
L(3)···L(3')	6.107 (6)	Se(3)···Se(3')	5.05 (1)
O(1)···L(2')	3.27 (1)	O(1)···L(2)	3.30 (2)
L(1)···L(3')	4.983 (4)	L(1)···Se(3)	3.53 (1)
L(1)···L(3)	3.538 (4)		

^{a} L = core Se/Cl. ^{b} Terminal Re–Cl distances.

face to a rectangular shape, the L(1)···L(1') distance being 4.95 (1) Å. The opposite face, L(2,2')Se(3,3'), for example, has nearly equal diagonals of mean value 5.01 Å.

A second type of core conversion reaction is presented in Figure 3. Reaction of $[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$ with a (4–6)-fold excess of Li_2Se in THF at room temperature affords $[\text{Re}_6\text{Se}_6\text{Cl}_8]^{2-}$, isolated in 57% ($\text{Pr}_4\text{N}^+$) and 59% ($\text{Bu}_4\text{N}^+$) yields as the indicated salts. The first of these was crystallographically identical to the compound resulting from cluster excision with Pr_4NCl. The second compound was identified by an X-ray structure determination; cluster metric parameters are essentially indistinguishable from those in Table II. Plausible alternative products in this reaction are species in which clusters are bridged by selenide, most likely as μ_2-Se, and the core structure is retained. While we do not know the course of the substitution reaction, its outcome places selenide in the most electrophilic position (as core μ_3-Se) in $[\text{Re}_6\text{Se}_6\text{Cl}_8]^{2-}$ and, consequently, suggests that this cluster is the thermodynamic product.

Table IV. $[\text{M}_6\text{L}_8]^z$ Core Substitution Reactions

Substitution reactions of $[\text{M}_6\text{X}_8]^z$ cores have precedents of somewhat restricted scope.[21,22,33–39] Because they have not been summarized, we include the listing of core transformations in Table IV. Reactions 1–6 involve the $[\text{Mo}_6\text{X}_8]^{4+}$ core with, usually, X = Cl. Of these, reactions 2 and 3 entail substitution of X^i by X^a atoms, while the others utilize exogenous reactants in excess. The most striking of these transformations is that accomplished by McCarley et al.,[39] whereby in reaction 6 all core chlorides are replaced by sulfide (under apparently vigorous conditions and with partial reduction of the M_6 fragment). Reactions 7–9 have been established for $\text{Re}_6\text{Q}_{4+q}\text{X}_{4-q}$ cores ($q = 3, 4$). Reaction 9 implies access to the unknown clusters $[\text{Re}_6\text{Se}_7\text{Cl}_7]^{3-}$ and $[\text{Re}_6\text{Se}_8\text{Cl}_6]^{4-}$ by further core substitution. We have not yet been able to prepare these species under relatively mild conditions and may have to resort to more forcing conditions.

Summary. The following are the principal results and conclusions from this investigation.

(1) The clusters present in the one-dimensional (chainlike) phase $\text{Re}_6\text{Se}_5\text{Cl}_8$ and the two-dimensional (sheetlike) phase $\text{Re}_6\text{Se}_6\text{Cl}_6$ can be excised by reaction with chloride under mild conditions to afford $[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$ and $[\text{Re}_6\text{Se}_6\text{Cl}_8]^{2-}$, respectively, which were identified by elemental and X-ray structural analysis. Such reactions must have an associative component, involving coordination of attacking chloride prior to bridge cleavage. These results emphasize the use of the excision method to obtain clusters that have not been or cannot be prepared by more conventional methods.

(2) Under a variety of conditions, the three-dimensional phase $\text{Re}_6\text{Se}_7\text{Cl}_4$ has not yet been excised. This may result from obstruction to significant lattice penetration by the excision reagent. For the excision method to achieve optimal utility, methods must be developed for type III solids of this sort (i.e., those in which *each* cluster metal atom is involved in at least one

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(36) (a) Nannelli, P.; Block, B. P. *Inorg. Chem.* **1968**, *7*, 2423. (b) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *Polyhedron* **1984**, *3*, 475.
(37) Michel, J. B.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 1864.
(38) Ebihara, M.; Toriumi, K.; Saito, K. *Inorg. Chem.* **1988**, *27*, 13.
(39) McCarley, R. E.; Zhang, X.; Spink, D. A.; Hur, N. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; American Chemical Society: Washington, DC, 1990; INOR-140.

M–L^{a-a} interaction). Several such solids contain clusters unknown in molecular form.[4] With the exceptions of $K_3Zr_6Cl_{15}Be$[40] and Nb_6I_{11},[41] all solids that have yielded to excision possess one- or two-dimensional structures.

(3) The molecular solid $Re_6Se_4Cl_{10}$ undergoes core chloride substitution reactions with water to give two clusters $[Re_6Se_4O_2Cl_8]^{2-}$, which are diastereomers with different relative positions of the oxygen atoms. The cluster $[Re_6Se_5Cl_9]^-$ can be converted to $[Re_6Se_6Cl_8]^{2-}$ with Li_2Se under mild conditions. Pr_4N^+ salts of this cluster obtained by excision of $Re_6Se_6Cl_6$, which is known to contain the $[Re_6Se_6Cl_2]^{4+}$ core,[21-23] are identical. These findings provide a clear connection between a solid-phase cluster and a molecular cluster and support the identification of the excised clusters in **1**. These reactions are part of the limited base of $[M_6L_8]^z$ core substitution reactions (Table IV), which should be capable of extension.

Experiments on cluster excision from other types of solid-state materials, and on the viability of halide/chalcogenide substitution as a process leading to new clusters, are in progress.

Supplementary Material Available: Crystallographic data for the compounds in Table I, including tables of intensity collections, positional and thermal parameters, and interatomic distances and angles (15 pages). Ordering information is given on any current masthead page.

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