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Hexanuclear and higher nuclearity clusters of the Groups 4–7 metals with stabilizing π-donor ligands

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Contents

Abstract

The chemistry of early transition element clusters with π-donor ligands is growing rapidly. We review the syntheses of these compounds, with an emphasis on progress in the last 6 years. The predominant synthetic routes to such clusters are spontaneous

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self-assembly, apparent fragment condensation, excision from solids, and global ligand substitution. Mechanistic conclusions about cluster-forming reactions are discussed where possible. We conclude with prospects for future research.

Keywords: Metalloclusters; Self-assembly; Fragment condensation; Excision; Global ligand replacement

1. Introduction

A leading attribute of the transition elements is their penchant to aggregate in cages and clusters. These contrast with the chains and rings of organic chemistry, although the science of elemental carbon clusters has proliferated for nearly two decades [1,2]. Mononuclear transition metal centers offer diverse labilities, oxidation states, magnetic susceptibilities, and optical characteristics; these properties in turn distinguish transition element cluster chemistry. Inviting opportunities await the cluster researcher, and the discipline is escalating accordingly [3,4].

Experimental studies of early transition metal clusters stabilized by halides, pseudohalides, and chalcogenides are extensive. We reserve the term *cluster* for assemblies of three or more metal atoms combined, at least partly, by metal–metal bonds [5,6]. Metals in Groups 4–7 are much inclined to unite through direct bonds; dimetallic units recurrently incorporate intermetal multiple bonds [7], with the tendency toward single bonds dominating as cluster nuclearity increases [8]. The rhenium(III) (d^4) halide and chalco-halide complexes are illustrative [9] (Fig. 1). The $[Re_2Cl_8]^{2-}$ anion **1** ($d_{Re-Re} = 2.24$ Å) [10] was the first recognized occurrence of quadruple bonding in chemistry [8,11]. A special class of triangulo-metal(III) halide clusters exemplified by $[Re_3(\mu_2\text{-}Cl)_3Cl_9]^{3-}$ (**2**), is unique to rhenium. In these trimers, cumulated rhenium-rhenium bonds ($d_{Re-Re} = 2.48$ Å) [12,13] fuse into a ring; peripheral μ_2-bridging ligands doubtless improve thermodynamic and kinetic stability. Upon increasing nuclearity from two to three, intermetal bond orders halve. In the hexanuclear cluster $[Re_6S_8Cl_6]^{4-}$, each Re^{III} center singly binds all four neighbors ($d_{Re-Re} = 2.60$ Å); the twelve metal–metal single bonds and eight bridging sulfides together enforce marked stability: the $[Re_6S_8Cl_6]^{4-}$ entity self-assembles from $ReCl_5$, S_8, and CsCl at 850 °C [14]. We note also the report of a hexanuclear rhenium bromide cluster $[Re_6Br_{12}]^0$, where single bonds conjoin $Re{\equiv}Re$ units [15].

Among the transition metals, cluster formation with metal–metal bonding is largely, but not exclusively, the provenance of the second and third row metals. Scheme 1 categorizes the major synthetic routes currently used to achieve molecular clusters in the laboratory [16]. The synthetic methods delineated are illustrative and should not be taken mechanistically.

Method A, spontaneous self-assembly, requires ligand decomplexation from mononuclear metal centers M to commence metal–metal bonding. A host of metal carbonyl clusters forms from pyrolysis of mononuclear carbonyl compounds in this fashion [17,18]. Spontaneous self-assembly admits minimal intervention by the chemist, and leads generally to unpredictable products.

Method B, apparent fragment condensation, requires preformed cluster constituents to merge, with ligand expulsion, into some larger entity. Shown in Scheme 1 are formal [2+2+2] additions of metal–metal dimers and [3+3] condensations of triangular clusters.

Method C, excision, disengages intact molecular clusters from extended cluster solids; exogenous ligands surrogate for intercluster bridging. The term ‘excision’ implies the emergent cluster has the same local composition and topology as its parent solid; for example, hexanuclear clusters are not ordinarily expected from excision reactions of solids based upon trinuclear entities.

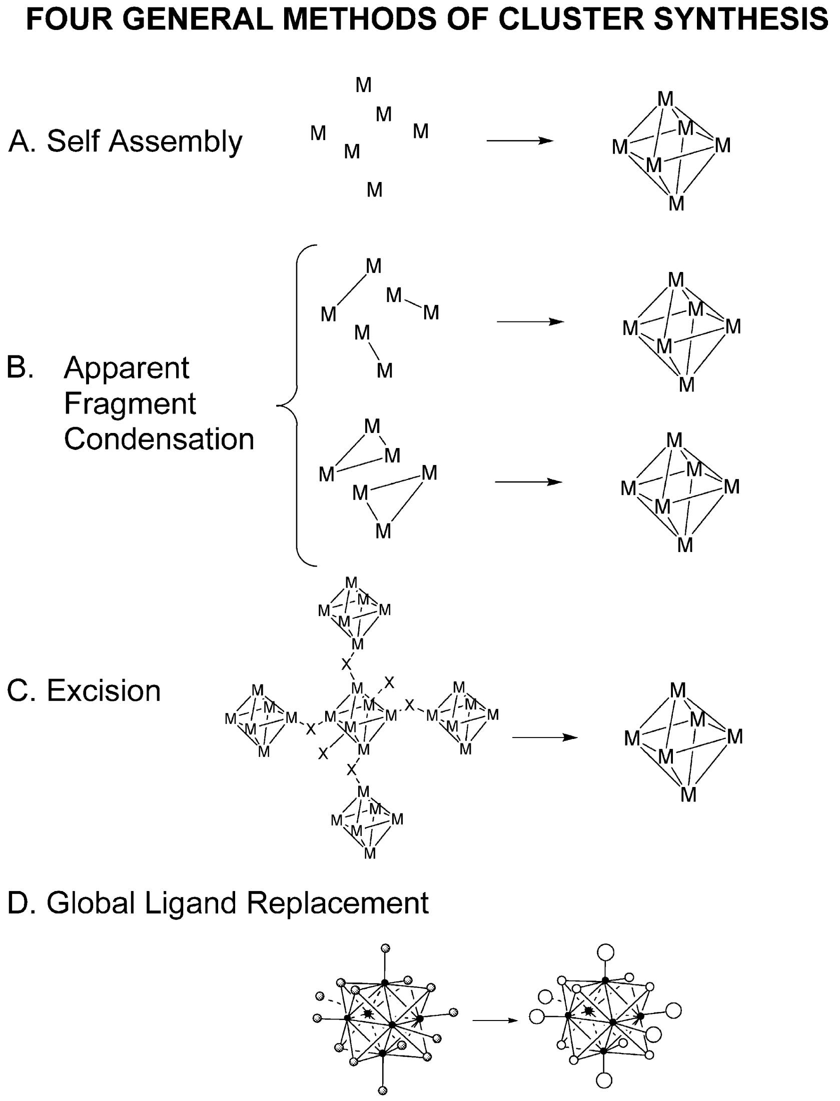
Method D, here named ‘global ligand replacement,’ applies to clusters whose entire ligand complement (including the core ligands, but not necessarily interstitial atoms) is substituted, possibly with a change in oxidation state; only the metal framework remains. Global ligand replacements presuppose that a metal cluster precursor of the correct nuclearity and geometry exists, but the effects upon electronic structure and properties are so extreme that we consider it a separate synthetic method. Indeed, certain tungsten sulfide clusters (vide infra) are, to date, exclusively attainable by global ligand replacement chemistry.

We focus here on hexanuclear and higher nuclearity clusters of Groups 4–7. Representative cluster structures are discussed in detail, but coverage is not exhaustive. Mixed-metal clusters are not considered [19,20], nor are cubane-type polyclusters [21]. Among hexanuclear clusters, two structures **I** and **II** (Fig. 2), each with idealized O_h symmetry, dominate. Prototype **I** is an octahedron of metal ions included within a cube of μ_3-face-bridging ligands; the cluster stoichiometry is $M_6(\mu_3\text{-}L)_8$. Prototype **II** has ligands edge-bridging the octahedron, with stoichiometry $M_6(\mu_2\text{-}L)_{12}$.

2. Spontaneous self-assembly

2.1. Hexanuclear zirconium halide clusters

Many metal clusters are prepared from high temperature self-assembly reactions of solid precursors. The



Scheme 1.

interstitially-stabilized zirconium halide clusters are exemplary [22,23]. First isolated from solid-state thermal reactions, these type **II** clusters consist of Zr_6 atoms edge-bridged by halides with halide termini. Such clusters were first prepared over 25 years ago in extended solid phases, and were then alleged to be stoichiometric analogues of reduced Group 5 halides [24]. The apparent binary phase 'Zr_6Cl_{15}' was observed infrequently, as black cubes. Other phases, formulated as Zr_6Cl_{12} and $K_2ZrCl_6{\cdot}Zr_6Cl_{12}$ were observed when ZrCl was disproportionated [25] in the presence of H_2. This circumstance was later deemed suggestive of hydride incorporation into the cluster [22,23]. Early

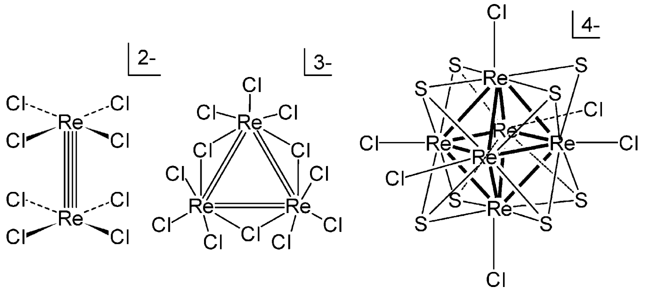


Fig. 1. Cluster complexes of rhenium(III).

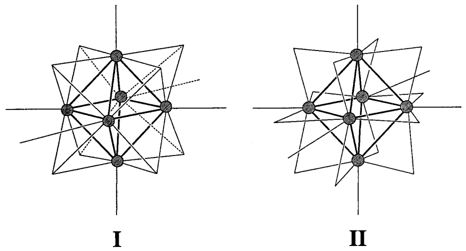


Fig. 2. Prototypical hexanuclear clusters. Prototype **I** consists of an octahedron of metal centers inscribed within a cube of eight face-bridging μ_3-ligands. In prototype **II**, a metal octahedron is circumscribed by a cubeoctahedron of 12 μ_3-edge-bridging ligands.

diffraction data sets contained unrefined electron density at the core center. In some cases, systematic errors from uncorrected X-ray absorption eliminated any apparent interstitial density.

The directed inclusion of interstitial elements greatly augments yields, and has allowed preparation of over 60 zirconium halide cluster phases. Usual starting materials are elemental Zr, $ZrCl_4$, alkali metal halide (if at all) and elemental interstitial. Welded tantalum tubes are the reaction vessels of choice, inasmuch as Zr reacts with B, C, O, Al, Si and Pt, which constitute more usual containers. Re-examination of all available data compelled the conclusion that all known, non-hydridic zirconium halide clusters contain a single interstitial atom at the core center [26]. Inelastic neutron scattering results on $Li_6[Zr_6Cl_{18}H]$ were interpreted as evidence for a μ_3-H resting atop one Zr_3 face with a Zr–H distance of approximately 2.0 Å [27]. Subsequent neutron diffraction studies [28] discerned μ_3-hydride bridging above the triangular faces of the Zr_6 octahedron in $(PPh_4)_3[Zr_6Cl_{18}H_5]$; variable temperature NMR measurements in acetone-d_6 indicated rapid hydride motion at room temperature and at -60 °C.

Hexanuclear zirconium hydride clusters have more recently yielded to solution-phase preparation, but no low-temperature means yet exists for encapsulating interstitials. Cotton et al. [29], have pioneered the self-assembly of penta- and hexanuclear zirconium halide clusters from reduction of ZrX_4 ($X = Cl$, Br) with 2 equiv. Bu_3SnH in the presence of excess phosphine. The reaction is compatible with methylene chloride or arene solvents. Careful NMR integration [30,31] against counterion resonances measures the number of associated hydrides in diamagnetic clusters. The cluster $[Zr_6Cl_{18}H_5]^{3-}$ has been characterized by X-ray and time-of-flight neutron diffraction analysis [32].

Lesser quantities of tributylstannane (1.6 equiv.) permit isolation of pentanuclear clusters $[Zr_5Cl_{12}(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2(PMe_3)_5]$, $[Zr_5Cl_{12}H_4(PEt_3)_5]$, and $[Zr_5Cl_{12}H_4(PMe_2Ph)_5]$ in 15–20% yields [33]. Hydrogen atoms were refined from X-ray crystallographic data for the compound $[Zr_5Cl_{12}(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2(PMe_3)_5]$; these were modeled with two hydrides bridging *trans*-disposed edges of the Zr_5 square pyramid; two other hydrides, also *trans* to each other, cap the triangular Zr_3 faces not involved in edge-bridging.

Oxidation of $[Zr_6Cl_{18}H_5]^{3-}$ by 1 equiv. $TiCl_4$ yields paramagnetic $[Zr_6Cl_{18}H_5]^{2-}$, which can be re-reduced to $[Zr_6Cl_{18}H_5]^{3-}$ by 1 equiv. Na/Hg amalgam [34].

2.2. A vanadium selenide cluster: $[V_6Se_8(O)(PMe_3)_6]$

The interstitially stabilized type **I** vanadium selenide cluster $[V_6Se_8(O)(PMe_3)_6]$ was prepared [35] serendipitously from the reaction of $(\eta^5\text{-}C_5H_5)VCl_2(PMe_3)_2$ with $(Me_3Si)_2Se$ in 40% yield. V–V distances range from 2.794(3) to 2.839(3) Å. Side products of the reaction are uncharacterized. Inasmuch as the six vanadiums(III) (d^2) furnish only twelve metal–metal bonding electrons (one per edge of the V_6 octahedron), the interstitial atom is likely essential to thermodynamic stability.

2.3. Hexanuclear niobium and tantalum halide clusters

Niobium and tantalum each possess an extensive cluster chemistry in their lower oxidation states [36]. Octahedral halide clusters with edge-bridging halides $[M_6(\mu_2\text{-}Cl)_{12}Cl_6]^z$ (M = Nb, Ta) (prototype **II**) were structurally characterized by Pauling and coworkers [37]; the cluster cores are empty, unlike the zirconium analogues. Reduction of $NbCl_5$ with the elemental metal and an auxiliary chloride source assembles clusters:

$$14NbCl_5 + 16Nb + 20NaCl \rightarrow 5Na_4Nb_6Cl_{18} \quad (1)$$

Use of a 10:7 mole ratio of NaX to MX_5 inhibits formation of noncluster complexes, and of di- and tetranuclear clusters byproducts [38], as does excess niobium in the form of the elemental foil [39]. Aqueous acidic workup in the presence of tin(II) chloride (to suppress oxidation) provides the discrete cluster $M_6X_{14}(H_2O)_4 \cdot 4H_2O$.

$[Nb_6X_{12}]^{z-}$ and $[Ta_6X_{12}]^{z-}$ clusters are redox-promiscuous, possessing five (Nb; $z = 1+$ to $5+$) and four (Ta; $z = 1+$ to $4+$) accessible oxidation states. Disproportionation reactions therefore complicate ligand substitution chemistry. Reliable means of substituting the six terminal halides still await, because of the competing side reactions that frequently occur.

Metathesis reactions with thiocyanate and azide salts yield crystalline cluster compounds $A_4Nb_6X_{12}X_6$ ′ (A = alkali metal; $X = Cl^-$, Br^-; $X' = NCS^-$, N_3^-), however, reaction periods of weeks are needed [40–42]. Neutral and anionic ligands replace bound water in the aquo complexes $[M_6X_{12}X_2(H_2O)_4] \cdot 4H_2O$ (M = Nb, Ta; X = Cl, Br). Titration of methanol solutions of $[Ta_6X_{12}X_2(H_2O)_4] \cdot 4H_2O$ with alkali metal hydroxides affords the solvates $[Ta_6X_{12}(OCH_3)_2(CH_3OH)_4]$. Apical methoxide substitution of oxidized $[Ta_6Cl_{12}]^{4+}$ occurs by evaporation of alkaline methanol solutions [43]. Alternatively, dissolution of the Nb and Ta hydrates $[M_6X_{12}X_2(H_2O)_4 \cdot 4H_2O]$ (X = Cl, Br) in aliphatic alcohols, followed by evaporation, gives insoluble crystalline $[M_6X_{12}(ROH)_6]X_2$ (M = Nb, Ta; X = Br, Cl; R = CH_3, C_2H_5, *i*-C_3H_7, and *i*-C_4H_9). ^{1}H-NMR and conductivity measurements of the bromide clusters reveal that axial halides are exchanged before the bound water ligands [44].

Cis- and *trans*-isomers of the phosphine complexes $[Ta_6Cl_{12}Cl_2(PR_3)_4]$ (R = C_2H_5, *n*-C_3H_7, and *n*-C_4H_9) are separable by fluorisil- or silica gel chromatography; only the *trans* isomers are obtained for the niobium analogues. Preparation involves stirring the chloro species

$[Ta_6Cl_{12}Cl_2(H_2O)_4]\cdot 4H_2O$ for three to seven days at room temperature or reflux. Oxidation by $NOBF_4$ gives mono- and dicationic complexes without *cis-trans* isomerization [45].

Recently, trifluoromethanesulfonate (triflate)-terminated niobium and tantalum halide clusters were reported. These are accessible through reaction of triflic acid with the chloride-terminated species as their tetrabutylammonium salts, shown for tantalum [46]:

$$(Bu_4N)_2[Ta_6Cl_{12}Cl_6] + 6HOSO_2CF_3 \rightarrow (Bu_4N)_2[Ta_6Cl_{12}(OSO_2CF_3)_6] + 6HCl \quad (2)$$

Cyclic voltammetry of the tantalum cluster reveals two reversible one-electron reductions at 0.93 and 0.33 V versus SCE. The oxidizing capability of $(Bu_4N)_2[Ta_6Cl_{12}(OSO_2CF_3)_6]$ precludes metatheses with halides and pseudohalides; triflate substitution invariably accompanies cluster reduction, necessitating excess ligand. The one-electron reduced cluster $[Ta_6Cl_{12}(OSO_2CF_3)_6]^{3-}$ is found as an intermediate, and exogenous ligand reactivity decreases in the order $CN^- > I^- > NCS^- > Br^- > Cl^-$. The trend correlates with neither nucleophilicity nor polarizability, and is not understood. Refluxing a methylene chloride solution of $(Bu_4N)_2[Ta_6Cl_{12}(OSO_2CF_3)_6]$ and Bu_4NCl affords the reduced cluster $(Bu_4N)_3[Ta_6Cl_{18}]$, contrary to electrochemical expectations: the $2Cl^-/Cl_2$ couple falls at 1.25 V versus SCE. Chloride oxidation is believed to be assisted by loss of Cl_2 in the stream of nitrogen passed over the reaction mixture. In the presence of such reductants as NCS^-, Br^- and I^-, the twice-reduced core $[Ta_6Cl_{12}]^{2+}$ is observed. Simple nonredox substitutions of the triflate ligand have not yet been reported for anionic or neutral ligands.

Recently, the cluster $[Nb_6Cl_{12}(OSO_2CF_3)_6]^{3+}$ was prepared [47] from the reaction of $(Bu_4N)_3[Nb_6Cl_{18}]$ with neat methyl triflate, in the absence of air, moisture, and light. This method is attractive because the side product and excess methyl triflate are easily removed under vacuum, and neither oxidizes the product cluster. Substitutions of triflate were achieved in high yields by reactions with tetrabutylammonium halides and thiocyanate. The mixed chloro-bromide cluster $[Nb_6(\mu_2\text{-}Cl)_{12}Br_6]^{3-}$ was characterized by electron paramagnetic resonance (EPR), showing 41 of 55 expected lines (^{93}Nb $I = 9/2$, 100%) centered at $g = 1.95$.

The salt $Rb_3[Nb_6SBr_{17}]$ has been prepared [48], wherein a trigonal prismatic array of niobium atoms encloses an interstitial sulfide. The anion is a straight-chain polymer of ligand-bridged $[Nb_6(S)(\mu_2\text{-}Br)_{12}Br_6]^{4-}$ units. Two apical bromides engage in μ_2-*trans*-intercluster bridging to form an extended chain. The mean Nb–Nb distance along triangular faces is 2.97 Å; that along the rectangular faces of the Nb_6 prism is 3.28 Å, with the mean Nb–S distance being 3.28 Å. Extended Hückel molecular orbital calculations indicate weak intertriangular Nb–Nb bonds along the rectangular faces of the Nb_6 trigonal prism.

2.4. Hexanuclear niobium iodide clusters and derivatives

Hexanuclear niobium iodide clusters deviate from their congeners in that the interior iodides bridge Nb_3 faces rather than Nb_2 edges. The Nb_6 core resides within an I_8 cube, completing a type **I** structure analogous to those of $[Re_6Q_8]^{2+}$ (Fig. 1) and group 6 $[M_6X_8]^{4+}$ clusters. The nineteen-electron $[Nb_6I_8]^{3+}$ cluster embedded within Nb_6I_{11} [49,50] conforms to cluster prototype **I**. In the network cluster solid Nb_6I_{11}, bridging apical iodides link cubic $[Nb_6I_8]^{3+}$ cores. Nb_6I_{11} is prepared from the thermal decomposition of Nb_3I_8 at 950 °C:

$$13Nb_3I_8 \rightarrow 4Nb_6I_{11} + 15NbI_4 \quad (3)$$

An excess of elemental niobium enhances yields by scavenging NbI_4:

$$11NbI_4 + 13Nb \rightarrow 4Nb_6I_{11} \quad (4)$$

Addition of cesium iodide to the reaction feedstock allows isolation of the reduced phase $CsNb_6I_{11}$ [51]. Addition of elemental sulfur to Nb_6I_{11} or Nb_3I_8 generates the quasi-linear cluster polymer Nb_6I_9S [52]. All known hexanuclear niobium iodides are several electrons more reduced than are their kindred, Group 5 halide clusters $[M_6(\mu_2\text{-}X)_{12}X_6]^z$. The most oxidized representatives are Nb_6I_{11} itself and Nb_6I_9S, where the bonding electron count [53] is nineteen; the related phase $CsNb_6I_{11}$ has an electron count of 20.

Nb_6I_{11} experiences a higher-order phase transition [54] ($Pccn \rightarrow P2_1cn$) at 274 °C. Structurally, a twist deformation of the Nb_6 unit relative to one of its quasi-trigonal axes occurs, with concomitant loss of an inversion center. Anisotropic vibration of the intercluster bridging iodides, inferred from the crystal structure, is believed to assist the phase transition. A close approach of the HOMO and LUMOs of the lower-temperature phase with increasing temperature induces a spin crossover from a doublet to a quartet ground state [55,56]. However, the energy change associated with the spin crossover does not itself drive the phase transition. The entropy of the phase transition ΔS_{trs} is too large to attribute to the change in spin state, and may involve vibrational changes deriving from the intercluster μ_2-bridging iodides [54].

Idiosyncratically, solid phases containing hexanuclear niobium iodide clusters consume hydrogen gas in the high-temperature phase. This proton-coupled reduction of a network cluster solid is unique in chemistry. At 300 °C, Nb_6I_{11} reacts with H_2 at 760 torr to form the hydrido cluster phase $Nb_6(H)I_{11}$ where the hydride resides inside the niobium core [57]. Single crystal neutron diffraction analysis [58,59] of the deuteride $Nb_6(D)I_{11}$ establishes conclusively the interstitial nature of the hydride, which occupies the geometric center of the Nb_6I_8 cluster. The hydrido cluster is diamagnetic at low temperature, and the phase transition, now accompanied by a spin singlet-to-triplet transition, moves to 324 °C. The one-electron reduced phase $CsNb_6I_{11}$ likewise absorbs H_2 with interstitial incorporation, at 400 °C, with small metric changes in cell and cluster dimensions [60]. The chain compound Nb_6SI_9 forms a hydride at 650 torr of H_2 upon prolonged heating at 300 °C [52].

2.5. Niobium and molybdenum oxide clusters derived from vertex- and edge-bridged $M_6(\mu_2\text{-}O)_{12}$ cores

A growing chemistry of niobium- [61,62] and molybdenum [63] oxide clusters continues to emerge. These reduced oxide species are distinct from the familiar polyoxometallates [64], where d^0 metal centers form oxide-bridged cages without metal–metal bonding. [We use the term ‘cage’ to mean multinuclear aggregates of metal ions, joined through bridging ligands, and not through direct metal–metal bonds. This use of the term is not universal [8].] All reduced Nb and Mo clusters consist of edge-bridged $M_6(\mu_2\text{-}O)_{12}$ clusters **II**. Unlike type **II** niobium and tantalum halide clusters, the oxide species aggregate through shared vertices (Nb) or edges (Mo).

2.5.1. Niobium oxide clusters

A great number of metal–metal bonded octahedral oxoniobate clusters have been prepared from spontaneous self-assembly reactions at elevated temperatures. Syntheses employ various solid starting materials, often including oxide salts of electropositive counterions, mixed with Nb or NbO as reductants. Niobium containers are optimal reaction vessels, which avoid introducing undesired components into the reaction mixture.

Intracluster Nb–Nb distances span a 0.4 Å-range about 2.84 Å; the Nb–O^i distances fall between 2.02 and 2.13 Å [65]. Observed Nb–O^i bond lengths approximate the quantity $1/2 \times \sqrt{2} \times d_{\mathrm{Nb-Nb}} = 0.707 \times 2.84$ Å $= 2.01$ Å. Each Nb resides within 0.05 Å of the plane of the surrounding O^i ions. Condensed solids, built of vertex-sharing Nb_6 clusters, therefore assemble strainlessly, and many such cluster-networks are known. Formal cluster condensation may occur along three mutually perpendicular axes. The descriptor $[p \times q \times r]$ specifies vertex-sharing condensates, where p, q, and r are integer numbers of Nb_6 octahedra condensed along three dimensions. The isolated, hexanuclear Nb_6O_{18} cluster is denoted $[1 \times 1 \times 1]$; the $Nb_{11}O_{21}$ dicluster in $K_4Al_2Nb_{11}O_{21}$ [66] is labeled $[1 \times 1 \times 2]$, and the one dimensional polymer becomes $[1 \times 1 \times \infty]$ (Fig. 3). Many different condensation modes have been identified crystallographically; intersection through shared Nb vertices is common to all. The binary oxide NbO represents the limit of vertex-sharing in three dimensions: $[\infty \times \infty \times \infty]$.

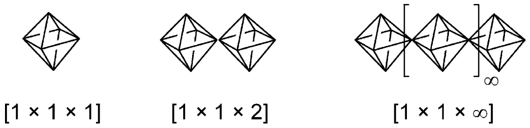


Fig. 3. Cartoon depicting the formal condensation of vertex sharing $Nb_6(\mu_2\text{-}O)_6$ clusters and appertaining $[p \times q \times r]$ designations.

All reduced oxoniobium phases, including those containing discrete Nb_6O_{12} clusters, are close-packed and the large negative charges necessitated by the oxide count (as in $Mg_3Nb_6O_{11}$ [67]) indicate that solubilization in common media will be difficult.

Chemical bonding in vertex-sharing oxoniobate clusters [68] and in NbO [69] has been discussed within the extended Hückel approximation.

Recently $Ti_2Nb_6O_{12}$, a reduced niobium oxide phase, has been described, where discrete Nb_6O_{12} clusters interconnect through rhombic $Nb_2(\mu_2\text{-}O)_2$ junctures that link neighboring cores, Fig. 4 [70]. Similar M_2Q_2 (Q = S, Se) rhombs appear in Mo_6Q_8 and Re_6Q_8 phases. Also known are mixed niobium oxohalide phases containing the cluster cores $[Nb_6Cl_{11}O]^+$ [71], $[Nb_6Cl_{12-x}O_x]^{(4-x)+}$ ($x = 2$–4) [72], and $[Nb_6Cl_6O_6]^{1-}$ [73,74]. Solids containing the tantalum cluster core $[Ta_6X_9O_3]^+$ (X = Cl,Br) have also been identified [75].

2.5.2. Molybdenum oxide clusters

Molybdenum forms oligomeric oxde clusters with finite chain segments of *trans*-oriented, edge-sharing octahedra. The solid phases that contain these clusters have been reviewed [63,76]. Fig. 5 depicts the cluster dimer $[Mo_{10}O_{14}]^{3-}$ [77]. The limit of edge-sharing condensation is realized in the infinite chain compounds $M_nMo_4O_6^-$ [78].

Single-cluster hexanuclear molybdenum oxide species are few. The mixed-cation salt $Ca_{16+x}Mo_{2-x}Mo_{12}O_{46}$

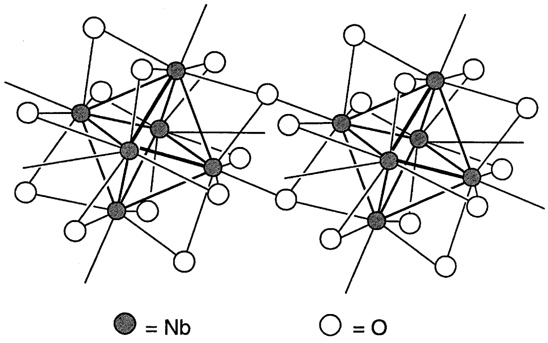


Fig. 4. Rhomb-linked type **II** oxoniobate clusters, as occur in $Ti_2Nb_6O_{12}$.

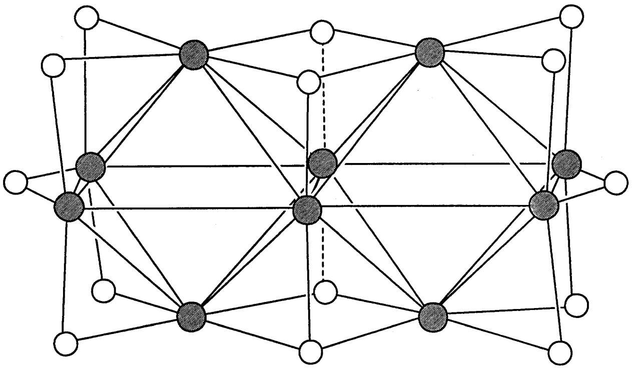


Fig. 5. Structure of $[Mo_{10}O_{26}]^{4-}$. Exopolyhedral ligands (oxides) are omitted for clarity.

possesses isolated $[Mo_6(\mu_2\text{-}O)_{12}O_6]$ clusters. Exopolyhedral oxides bridge with noncluster Mo ions; inner μ_2-O ions coordinate to Ca^{2+} counterions. The network solid $BaMo_6O_{10}$ accommodates intact Mo_6O_{12} clusters linked through intercluster Mo–Mo bonds to form sawtooth-shaped chains. Recently, the molybdate $LaMo_2O_5$ has been shown [79], by powder-neutron scattering, to contain isolated Mo_6O_{18} clusters and alternating sheets of fused, triangular Mo_3 clusters.

The single example of a hexanuclear tungsten oxide cluster occurs in $Sn_6W_{16}O_{44}$ [80] of the type **II**, originally misformulated as $Sn_6W_{16}O_{46}$ [81]. It is prepared by heating W, WO_3, and SnO_2 in the molar ratio 4:4:5 at 800 °C in a quartz ampule for seven days. The structure contains discrete W_6O_{12} octahedra, with Sn^{2+} counterions. The scarcity of similar tungsten oxide clusters and the complete absence of condensed, edge-sharing tungsten multiclusters have been speculatively attributed to relativistic destabilization [82] of the lower oxidation states of tungsten relative to tungsten(VI) and tungsten metal [63].

A recent report [83] describes the synthesis and crystal structure of $Pr_4Mo_9O_{18}$. In this complicated and labyrinthine structure, Mo_3, Mo_7, and Mo_9 aggregates interconnect through extensive intercluster oxide bridging. No solution-phase reactions of these entities have been described.

2.6. *Hexanuclear chromium chalcogenide clusters and their hydrides*

There is a small series of 20-electron, neutral chromium-chalcogenide type **I** clusters $[Cr_6Q_8(PR_3)_6]$ (Q = S, Se, Te), all members of which self-assemble from mononuclear precursors or Cr_2S_3. The first is the telluride cluster of Steigerwald et al. [84], prepared by the reaction of the zerovalent olefin complex (2,4-dimethylpentadienyl)$_2$Cr with triethylphosphine and elemental chalcogen in toluene in 38% yield. The same cluster was also prepared by reaction of $(\eta^3\text{-}C_3H_5)_2Cr(PEt_3)_2$ with chalcogen and additional PEt_3, but in undisclosed yield. $[Cr_6Te_8(PEt_3)_6]$ is a Curie paramagnet from 100 to 300 K; $\mu_{eff} = 2.8$ BM, indicating two unpaired electrons.

Chromium sulfide and selenide clusters have been synthesized from chromium(II) chloride and sodium polychalcogenides in low yield in methanol [85]:

$$CrCl_2 + Na_2Se_x + PEt_3 \rightarrow Cr_6Se_8(PEt_3)_6 + Cr_6Se_8(H)(PEt_3)_6 \quad (5)$$

Hydrido and non-hydrido clusters form in the approximate ratio 5:4, respectively [86]. Sulfide analogues are prepared similarly. The hydride originates from solvent, as proved by repeating the synthesis in CH_3OD, which gives the deuteride cluster. Selective oxidation of the hydride cluster in acetone with ferrocenium hexafluorophosphate allows separation from the non-hydride, which is insoluble in acetone.

The hydride is believed to be interstitial because of its inertness toward both acids and bases. Reaction of $Cr_6S_8(PEt_3)_6$ with elemental sulfur in refluxing toluene yields the dimer $Cr_{12}S_{16}(PEt_3)_{10}$ [87], where the chromium of one cluster binds the core sulfur of another. This, too, incorporates H atoms from protic solvents [88].

Recently, Crawford, Hee, and Long [89] have prepared $[Cr_6S_8(PEt_3)_6]$ by evaporation of Cr_2S_3, under high vacuum, in the presence of triethylphosphine. The cluster was identified by FAB mass spectrometry and NMR; no isolated yield was reported. The authors state that this synthesis method typically leads to mixtures of products.

2.7. *Molybdenum and tungsten halide clusters*

The halide clusters of molybdenum- and tungsten(II) are type **I** hexanuclear species, where eight μ_3-halides cap the faces of a metal octahedron. The binary halides, nominally MoX_2 or WX_2, are lamellar polymers of the kind $M_6(\mu_3\text{-}X)_8X_2^aX_{4/2}^a$ [90,91]. Treatment with hydrohalic acids liberates the clusters as hydronium salts.

High temperature disproportionations were the earliest conduit to $M_6^{II}X_{12}$ networks, Mo_6Cl_{12} being typical [92]:

$$9MoCl_3 \xrightarrow{\text{'red heat'}} Mo_6Cl_{12} + 3MoCl_5 \quad (6)$$

Yields are modest, but improve if aluminum is used as the reductant in melts:

$$6MoCl_5 + 6Al \rightarrow Mo_6Cl_{12} + 6AlCl_3 \quad (7)$$

This protocol gives quantitative yields for molybdenum(II) chlorides and bromides; yields of the tungsten analogues are nearer 50% [93]. High-temperature reduction of WCl_4 with Fe powder, Hg [94] Sb, or Bi [95] provides alternative tungsten cluster syntheses in comparable or greater yield. The tungsten halide phases are easily oxidized, even by water [96].

Crawford and Long [97] have prepared two D_{3d}-symmetic isomeric clusters $[W_6O_6Cl_{12}]^{2-}$ and also $[W_6O_7Cl_{11}]^{3-}$. These are type **II** clusters where both chlorides and oxides are edge-bridging ligands. In all cases, all six terminal ligands are chlorides. These species are prepared in a self-assembly reaction, by reduction of $WOCl_4$ with elemental bismuth. An amorphous black solid is obtained, which liberates all three clusters upon treatment with concentrated hydrochloric acid. The clusters are isolated as tetrabutylammonium salts after metathesis with Bu_4NBr; separation requires successive recrystallizations, and overall yields are low. Quasi-relativistic, hybrid density-functional calculations indicate that the isomers of $[W_6O_6Cl_{12}]^{2-}$ are equienergetic within the accuracy of the calculation.

The most advanced understanding of any high-temperature spontaneous cluster assembly derives from the decarbonylative syntheses of W_6I_{12} and related phases of Franolic et al. [98]. Thermolysis of $W(CO)_6$ in the presence of 7 equiv. I_2 yields at least four isolable clusters, as temperature varies. Self-assembly culminates in cyclomatrix polymers of the octahedral $[W_6I_8]^{4+}$ nucleus; the following sequence was proposed: $[W_3I_9]^- \rightarrow [W_4I_{11}]^- \rightarrow [W_5I_{13}]^- \rightarrow [W_6I_{14}]^{2-}$, with trinuclear clusters being first arrested at 145 °C. Similarly, the pentanuclear entity $[Mo_5Cl_{13}]^{2-}$ has been found in $AlCl_3/BiCl_3/KCl/Bi$ melts used to assemble Mo_6Cl_{12} [99,100].

2.8. Chevrel phases

The Chevrel phases, named for their discoverer [101] are solid networks of low-valent, hexanuclear and higher nuclearity molybdenum sulfide, selenide, and telluride clusters [102]. They have begotten a vast physicochemical effort and a review literature [103] so extensive that only recent highlights are summarized here. Chevrel solids are mainly remarkable for their superconducting abilities which persist at temperatures as high as 15 K ($PbMo_6S_8$) and despite magnetic fields (up to 60 T, $PbMo_6S_8$) [104,105].

The preponderance of Chevrel-type compounds contain hexanuclear clusters of formula $M_xMo_6Q_8$ ($Q = S$, Se, Te; M = nothing, main group, transition metal, or lanthanide ions). The 20-electron binary solid Mo_6S_8 contains cluster units **I**, so distorted that the Mo_6 unit may be considered a trigonal antiprism stretched along an S_6 axis. Augmenting the Mo_6Q_8 electron count regularizes the core structure. Average intercluster Mo–Mo distances fall from 2.780 Å in Mo_6S_8 to 2.706 Å in $PbMo_6S_8$ [106]. This effect is consistent with electronic occupancy of M–M bonding orbitals, and concurs with an extended Hückel treatment [107].

Corbett [108] disputes the electronic rationale of distorted Mo_6Q_8 Chevrel clusters, arguing that intercluster steric clashes among capping chalcogenides stretch the molybdenum core along a threefold axis. This distortion avoids weakening the *inter*cluster Mo_2Q_2 linkages (Mo_6S_8: d_{Mo-Mo} 3.084 Å; $d_{intercluster\ Mo-S}$ 2.425 Å). The advent of undistorted, discrete, molecular $Mo_6Q_8(PR_3)_6$ clusters (vide infra) ostensibly vindicates Corbett's hypothesis.

$$Pb + 6\,Mo + S_8 \longrightarrow PbMo_6S_8$$

1. Raise temperature to 1000 °C over 7 d.
2. Heat at 1000 °C, 24 h.
3. Air quench; shake vigorously.
4. Reheat to 1200 °C, 24 h.
5. Air quench.
6. Grind under He atmosphere.
7. Anneal at 1150 °C, 36 h.
8. Then anneal at 1200 °C, 8 h.
9. Air quench

Scheme 2.

Syntheses of Chevrel phases rely on ceramic methods, ultrapure elemental feedstocks, long reaction periods, and temperatures frequently exceeding 1000 °C [109]. The preparation of Delk and Sienko [110], Scheme 2, is representative.

Such ceramic treatments rarely yield to mechanistic examination. In the last decade, Johnson and coworkers [111] have prepared microquantities of $A_xMo_6S_8$ phases from 'nanoscale' superlattices, with monitoring by low-angle X-ray powder diffraction and differential thermal analysis (DTA). Such superlattices consist of elemental layers of known, Ångstrom-scale thickness, which are heated as solids. The layer thickness accelerates reactant diffusion and renders nucleation rate-limiting; kinetic products can potentially be trapped even at temperatures over 1000 °C. If elemental layers exceed a critical depth, a binary compound crystallizes at the reactant interfaces. Below critical thickness, the superlattice transforms into an amorphous phase, from which the final, crystalline product nucleates.

Exploratory investigations find that the binary molybdenum–selenium system requires Mo layers less than 9 Å thick to circumvent crystallizing molybdenum(IV) selenide [112]. Introduction of copper to the reaction system permits synthesis of Chevrel-type solids of the formula $Cu_xMo_6Se_8$. Fig. 6 depicts the process graphically.

The critical Mo thickness for $MoSe_2$ nucleation in the copper-molybdenum-selenium is 12 Å. Thicker Mo layers precrystallize $MoSe_2$, and require prolonged annealing to produce $Cu_xMo_6Se_8$ while consuming $MoSe_2$. Thinner layers directly generate the Chevrel phase, with neither diffraction peaks nor exotherms corresponding to $MoSe_2$ being evident. Notably, below the critical dimension, impurities attributed to condensed Mo_9Se_{11} or $Mo_{12}Se_{14}$ (vide infra) clusters are observed. Heating of indium–molybdenum–selenium superlattices to 550 °C produces amorphous solids; extended annealing from 600 to 700 °C nucleates the

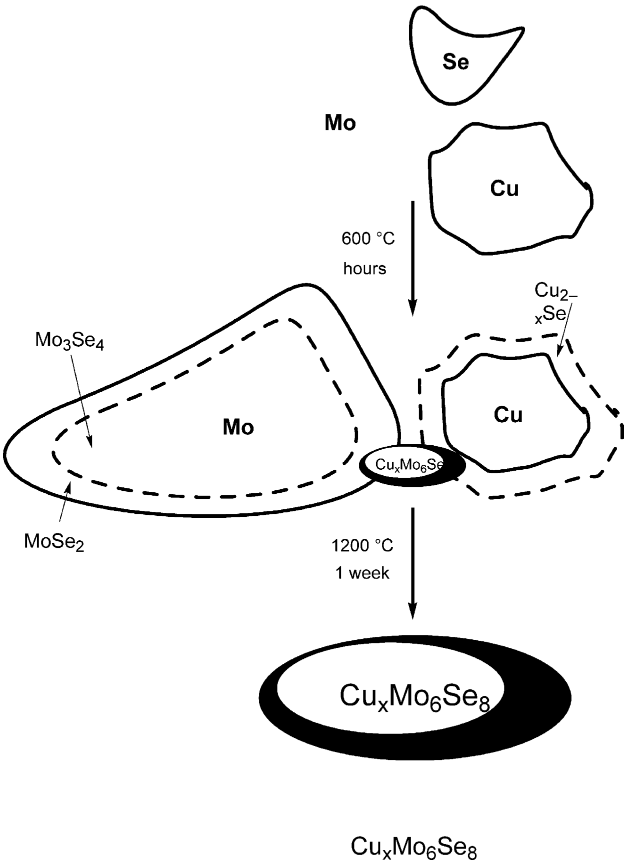


Fig. 6. Interfacial nucleation of $Cu_xMo_6Se_8$ from Ångstrom scale superlattices.

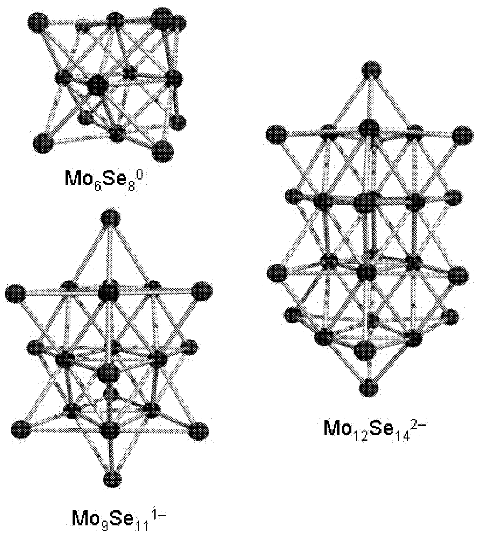


Fig. 7. Selected polynuclear clusters occurring in molybdenum Chevrel phases.

known [113] condensed Chevrel phase $In_{3.3}Mo_{15}Se_{19}$; still further heating at higher temperatures produces $MoSe_2$ [114].

A homologous series of condensed clusters [115] is describable as uniaxially condensed octahedra. Two representatives and the Mo_6Q_8 cluster cores are depicted in Fig. 7. All known clusters of nuclearity nine or greater are synthesized in high temperature, solid-state reactions. Table 1 categorizes the members of the series according to overall oxidation state and metal–metal bonding electron count. Little is known of these condensed clusters' chemical or spectroscopic properties. The best-studied is the nonanuclear cluster in $M_2Mo_9S_{11}$ (M = K, Rb) [116]. The potassium compound self-assembles quantitatively from MoS_2, K_2MoS_4, and Mo at 1500 °C; the resulting solid is a network of $[Mo_9S_{11}]^{2-}$ clusters with K^+ ions filling intercluster channels. The metastable phase $Cu_2K_{1.8}Mo_9S_{11}$ is synthesized from $K_2Mo_9S_{11}$ by topotatic intercalation of copper at 750 °C (300 hr); above 800 °C, $Cu_2K_{1.8}Mo_9S_{11}$ degrades to $Cu_xMo_6S_8$ and the infinite-chain compound KMo_3S_3. Deintercalation of copper with 12 M hydrochloric acid at 80 °C affords metastable $K_{1.8}Mo_9S_{11}$, which superconducts at temperatures below 4.5 K.

Table 1
Condensed molybdenum Chevrel phases

Cluster	VEC [a]	Metal oxidation states
$[Mo_9S_{11}]^0$	**32**	**5Mo(II), 4Mo(III)**
$[Mo_{12}S_{14}]^{2-}$	**46**	**10Mo(II), 2Mo(III)**
$[Mo_{15}S_{17}]^{3-}$	**59**	**14Mo(II), 1Mo(III)**
$[Mo_{18}S_{20}]^{4-}$	**72**	**18Mo(II)**
$[Mo_{21}S_{23}]^{5-}$	**85**	**1Mo(I), 20Mo(II)**
$[Mo_{24}S_{26}]^{6-}$	**98**	**2Mo(I), 22Mo(II)**
$[Mo_{27}S_{29}]^{7-}$	111	3Mo(I), 24Mo(II)
$[Mo_{30}S_{32}]^{8-}$	124	4Mo(I), 26Mo(II)
$[Mo_{33}S_{35}]^{9-}$	137	5Mo(I), 28Mo(II)
$[Mo_{36}S_{38}]^{10-}$	**150**	**6Mo(I), 30Mo(II)**
$[Mo_{6/2}S^{2-}_{6/2}]_\infty$		**1Mo(I), 2Mo(II)**

Entries for known species in boldface.
[a] VEC: valence electron count = Σ(metal d-electrons).

The infinite chain polymer $^1(Mo_3Se_3)^-_\infty$ has been realized for some years; the Mo_3 intertriangle distance in this compound is 2.25 Å. In a unique excision reaction, the lithium salt $Li[Mo_3Se_3]$ forms colloidal suspensions in polar solvents, such as dimethyl sulfoxide, while retaining the infinite chain structure. Topochemical counterion extraction has been demonstrated for $In[Mo_3Se_3]$ by treatment with HCl at 420 °C; Li^+ can be reversibly intercalated into the resulting solid in up to 4.5 equiv. [117]. $Li[Mo_3Se_3]$ is also soluble, upon sonication, in propylene carbonate; the Li^+ cations are subject to capture by 12-crown-4 [118]. Surfactant-induced self-assembly of $Li[Mo_3Se_3]$ polymers into different mesophases has also been reported [119]. $[Mo_3Se_3]^-$ chains have been incorporated into organic polymers, where the counterion is a poly(ammonium) chain [120]. Yang and collaborators [121] have used $LiMo_3Se_3$ as a sacrificial template for preparing gold nanowires. Osterloh and coworkers [122] have prepared composites of $[Mo_3Se_3]^-$ chains and CdSe- or Au nanoparticles by combining solutions of each at room temperature, and then acidifying (for gold-containing nanocomposites). The resulting materials were characterized by transmission electron microscopy, scanning tunneling microscopy, temperature-dependent conductivity, and absorption and emission measurements. Their method of synthesis is evocatively named 'stringing up the pearls.'

Tungsten analogues of the Chevrel phases are unknown.

2.9. Chalcogenide and chalco-halide clusters of technetium and rhenium

Rhenium forms a sizable class of hexanuclear, octahedral type **I** clusters [123,124]; the more recent technetium analogues are still in early phases of study [125]. These species are isoelectronic with the molybdenum(II) and tungsten(II) halide clusters, and together they form the most extensive series of isoelectronic clusters known [126,127].

The overwhelming majority of $[Re_6Q_8]^{2+}$ clusters are prepared in high temperature, spontaneous self-assembly reactions, typically in melts. The products can be extended solid networks of clusters in one, two, or three dimensions; or isolated, 'zero-dimensional' molecular clusters [128]. Intercluster bridging entities can be halides, chalcogenides, polychalcogenides, or nothing; absent other ligands, Re_6S_8 and Re_6Se_8 clusters bind one another through rhombic $Re_2(\mu_4\text{-}Q_2)_2$ linkages, Fig. 8 [129,130].

The system of ternary (halide-free) Re_6 and Tc_6 chalcogenide solids is now so well developed that structural trends have emerged [131]. Smaller countercations favor more intimate networks with smaller intercluster bridging. For example, the Re_6 octahedra in $Li_4Re_6S_{11}$ are joined by $\mu_2\text{-}S^{2-}$ ligands [132] whereas two $\mu_2\text{-}S^{2-}$, three $\mu_2\text{-}S_2^{2-}$, and one $\mu_2\text{-}S_3^{2-}$ are necessary to accommodate cesium in $Cs_4Re_6Se_{13.5}$ [133]. More highly charged cations can relax the steric requirements for intercluster void space: the compounds $M_2^{II}Re_6S_{11}$ (M = Eu, Sr, Ba) [134] are isotypic with $Li_4Re_6S_{11}$. A variant, involving cyanide-ligated clusters with bridging disulfides, has recently appeared; the resulting clusters are linked in a two-dimensional polymer [135].

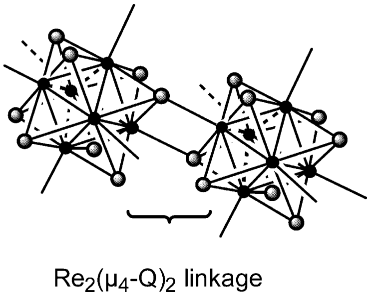


Fig. 8. Rhombic $Re_2(\mu_4\text{-}Q_2)_2$ intercluster unit prevalent in rhenium(III) chalco-halide solids.

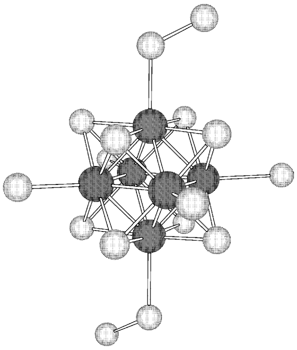


Fig. 9. Structural unit of $Tl_4Re_6Q_{12}$ (Q = S, Se).

The compounds $Tl_4Re_6Q_{12}$ (Q = S, Se) are two of the better-studied ternary rhenium(III) chalcogenides [136]. These phases were prepared in sealed quartz vessels by reactions (8) and (9) at the indicated temperatures:

$$4TlSe + 6Re + 8Se \rightarrow Tl_4Re_6Se_{12} \quad (1150\ ^\circ C) \tag{8}$$

$$4TlS + 6Re + S_8 \rightarrow Tl_4Re_6S_{12} \quad (1050\ ^\circ C) \tag{9}$$

The cluster is of type **I** with two *trans*-disposed disulfide bridges to neighboring clusters; the other four bridging ligands are sulfides; see Fig. 9. Bond order calculations [137] indicate Re–Re single bonds, consistent with 24 metal–metal binding electrons (24-electrons/12 Re–Re bonds). Electrical resistivity measurements confirm semiconductivity. Magnetometry experiments reveal temperature-independent diamagnetism in the range 25–300 K. Partial oxidation is achieved through topotactic deintercalation of thallium(I) to give a material of limiting stoichiometry $Tl_{1.8}Re_6S_{12}$; further oxidation causes decomposition. The oxidized compound is a paramagnet from 32 to 292 K with $\mu_{eff} = 0.95$, giving a measured, average spin $S = 1.46$. This value exceeds the expected $S = 1.1$ for 2.2 holes per formula unit, for unknown reasons.

Studies of halide-terminated $[Re_6Q_8]$ clusters and their progeny have yielded much progress. The roster of such compounds is lengthy, and includes molecular clusters and extended solids alike. Past attention has focused on connectivity relationships among quaternary metal–rhenium–chalcogenide halides. The concept of 'dimensional reduction' relates compounds such as $Re_6Se_8Cl_2$ (two-dimensional), $CsRe_6Se_8Cl_3$ (also two-dimensional), $Cs_2Re_6Se_8Cl_4$ (one-dimensional), and $Cs_5Re_6Se_8Cl_7 \equiv Cs_4Re_6Se_8Cl_6 \cdot CsCl$. These phases differ in their incorporation of chloride, which coordinates apically to Re^{III}, satisfying the ligation requirements of the clusters and annulling their tendency to bind one another through rhombic Re_2Q_2 linkages. Using dimensional reduction, one extrapolates from known networks to unknown polymers of lesser connectivity, or even to monoclusters, thereby identifying auspicious synthesis prospects. The same investigations identified several such Re_6Q_8 (Q = S, Se) phases, including the then-unknown molecular clusters. All such phases are prepared by spontaneous self-assembly in cesium- or thallium(I) halide melts. Dimensional reduction is likewise applicable to noncluster solids [138,139].

The preparations of two clusters, in molten media at 850 °C, are illustrative:

$$6Re + S_8 + 5CsBr + Br_2 \rightarrow Cs_4Re_6S_8Br_6 \cdot CsBr \quad (10)$$

$$6Re + 8Se + 4CsI + I_2 \rightarrow Cs_4Re_6Se_8I_6 \quad (11)$$

Yields are nearly quantitative, as judged by X-ray powder diffraction. These phases, which are salts of molecular Re_6Q_8 clusters, are water soluble at low pH; ion exchange with corresponding tetraalkylammonium halides solubilizes the cluster in polar organic solvents. The resulting clusters are redox-active, with one-electron oxidation occurring upon exposure to acids, or on standing in air [140–142]. Jahn–Teller distortions in the 23-electron clusters $[Re_6S_8Cl_6]^{3-}$, $[Re_6S_8(CN)_6]^{3-}$, and $[Re_6Se_8(CN)_6]^{3-}$ were quantified with temperature-dependent X-ray crystallography; it was found that D_{4h} and D_{2h}-distorted clusters can coexist in the crystalline solids [143]. Relativistic density-functional calculations using a Slater-orbital basis set and the BP86 functional indicate the D_{4h} structure to be marginally more stable [144].

Explorations of $[Re_6S_8Br_6]^{3-/4-}$ and $[Re_6Se_8I_6]^{3-/4-}$ substitution chemistry have established controlled halide replacement protocols with nonlabile triethylphosphine, generating site-differentiated species $[Re_6Q_8(PEt_3)_{6-n}X_n]^{(2-n)}$ (n = 4–6, Q = S, X = Br; Q = Se, X = I) currently inaccessible with group 6 halide- or technetium(III) analogue clusters. Refluxing DMF solutions of $[Re_6Se_8I_6]^{4-}$ or $[Re_6S_8Br_6]^{4-}$ with triethylphosphine affords nearly all diastereomers of the mixed-ligand clusters $[Re_6Q_8(PEt_3)_{6-n}X_n]^{(2-n)+}$ (n = 4–6, Q = S, Se, X = Br, I). Product mixtures are separable by flash-column chromatography. The rhenium-iodine bond, but not the bond to bromine, is labile to treatment with silver(I) salts in coordinating solvents, allowing access to site-differentiated solvate clusters [145,146]. All of these phosphine-terminated species have been characterized by ^1H- and ^{31}P-NMR spectroscopy and many by X-ray diffraction. The available crystal structures of these and all other rhenium chalcogenide clusters show negligible variation of $[Re_6Q_8]^{2+}$ dimensions with terminal ligands. A smaller series of $[Re_6S_8Cl_nL_{6-n}]^{(2-n)+}$ where L = pyridine, substituted pyridines, or pyrazine, has been reported [147,148]. Again, dehalogenation is achieved by prolonged refluxing in an excess of ligand in DMF.

Chelated hexanuclear type **I** clusters are attainable from $[Re_6Se_8I_6]^{3-}$ and hexamethylene-spaced diphosphine ligands [149]. We restrict the meaning of chelation, in the context of clusters, to dibasic ligands bound to *cis*-neighboring metal sites. Clusters where polydentate ligands chelate a single metal ion are not here considered. The reaction of $Ph_2P(CH_2)_6PPh_2$, abbreviated dpph, with $(Bu_4N)_3[Re_6Se_8I_6]$ in DMF at 100 °C or at reflux, after a few hours, results in a series of chelated clusters $[Re_6Se_8I_{6-2n}(\mu_2\text{-dpph})_n]^{2n-4}$ (n = 1, 2, 3). The fully diphosphine-chelated cluster $[Re_6Se_8(dpph)_3](SbF_6)_2$ was isolated as a racemic mixture from interaction of $Ph_2P(CH_2)_6PPh_2$ with $[Re_6Se_8(MeCN)_6](SbF_6)_2$ in a 2:1 chlorobenzene/DMF mixture. Macrochelation of $Ph_2P(CH_2)_6PPh_2$ to the Re_6 octahedron forms an unusual ten-membered ring, far exceeding in size and conformational pliability the familiar chelates of mononuclear metal centers. $[Re_6Q_8]^{2+}$ exopolyhedral σ-bonding ligands are mainly d_{z^2} in character, and are fixed at 90° to one another (Fig. 10). These orbitals necessitate such long linking elements between bound phosphines. The aliphatic backbone allows phosphorus lone pairs to orient perpendicularly with a minimal steric penalty. This chelation strategy differs from that prevalent in multiply-bonded metal dimers, where much smaller, rigid ligands, such as acetate, bidentately bridge adjacent metal ions, to produce a five-membered ring. In such dimers, the metal-ligand bonding orbitals have δ-symmetry [150,151] and situate parallel to each other, accommodating smaller, inflexible chelators.

A full thermodynamic study of the chelate effect in metal clusters has not appeared. Suffice it to say that the substitutional inertness of the $[Re_6Q_8]^{2+}$ core imparts great kinetic stability to such phosphine-chelated clusters [140]. The generality of this synthesis concept is unsubstantiated, particularly when applied to clusters of the first-row transition metals. Such chelation also differs fundamentally from the cavitand approach to cluster ligation [152], originally conceived for cubane-type $[Fe_4S_4]$ clusters [153]. The cavitand concept relies

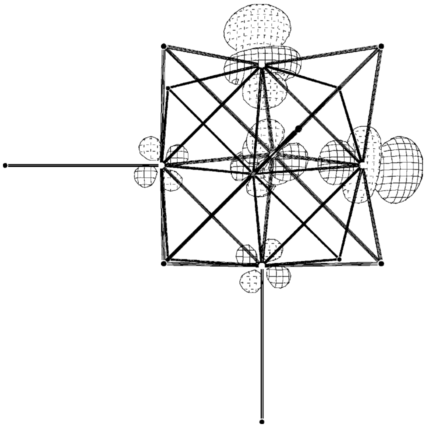


Fig. 10. Extended Hückel HOMO of a hypothetical, *cis*-divacant $[Re_6Se_8I_4]^{2-}$ showing Re–L bonding orbitals on adjacent metal atoms, situated at approximately right angles to each other.

on ligands, specially contrived to capture the Fe_3 face of an $[Fe_4S_4]$ cuboid. The ligand conformation in the bound cluster approximates the lowest-energy conformation of the free base. The cavitand concept has not yet been applied to single clusters of nuclearity exceeding four, but certainly pertains to larger entities.

The cluster chemistry of rhenium tellurides is extensive and complicated [154,155]; no technetium analogues are known. The most important Re_6 telluride is Re_6Te_{15}, where $[Re_6Te_8]^{2+}$ units are connected by unique, planar Te_7 units [156,157]. This compound self-assembles from a stoichiometric mixture of the elements or by chemical vapor deposition methods. This phase is a starting material for excision reactions leading to derivative clusters (Section 5)

The unusual ligands TeX_2 ($X = Cl, Br$) (Fig. 11) are stabilized by binding apically to the $[Re_6Te_8]^{2+}$ core [158]. In these ligands, tellurium is in the +2 oxidation state. The reaction of rhenium(III) bromide with tellurium affords $[Re_6Te_8(TeBr_2)_6]Br_2$; reaction of Re_6Te_{15} with iodine at 450 °C yields $[Re_6Te_8(TeI_2)_6]I_2$, containing similar TeI_2 ligands with local C_{2v} symmetry [159]. A mixed-core compound $[Re_6Te_6Cl_2(TeCl_2)_2Cl_4]$ results from reaction of $ReCl_5$ with Te at 450 °C; the two μ_3-Cl and the four μ_3-Te ligands are statistically disordered over the cubic core. The phases $Re_6Te_{16}Cl_{18}$ and $Re_6Te_{16}Cl_6$, with extensive intercluster bridging and the unusual chlorotellurato ligands $[Te_8Cl_{18}]^{2-}$, *cyclo*-Te_6, and $TeCl_3^-$, were prepared in a like manner [160].

3. Apparent fragment condensation

An alternative route to larger clusters is apparent fragment condensation, (Scheme 1B) wherein suitably shaped cluster motifs coalesce into higher nuclearity entities with ligand expulsion, in some prearranged fashion [161]. We adopt the qualifier 'apparent' to avoid implying mechanistic certitude in fragment condensation-type reactions. It generally difficult to exclude precursor decomposition reactions whose products may be the true antecedents of higher-nuclearity clusters. None of the apparent fragment condensations that follow has been studied kinetically. Few reproducible condensation-based syntheses of hexa- or higher nuclearity clusters are known.

3.1. Niobium and tantalum

There are no reports of apparent fragment condensation syntheses of higher-nuclearity Nb or Ta clusters, despite numerous (potential) trinuclear cluster precursors [162,163].

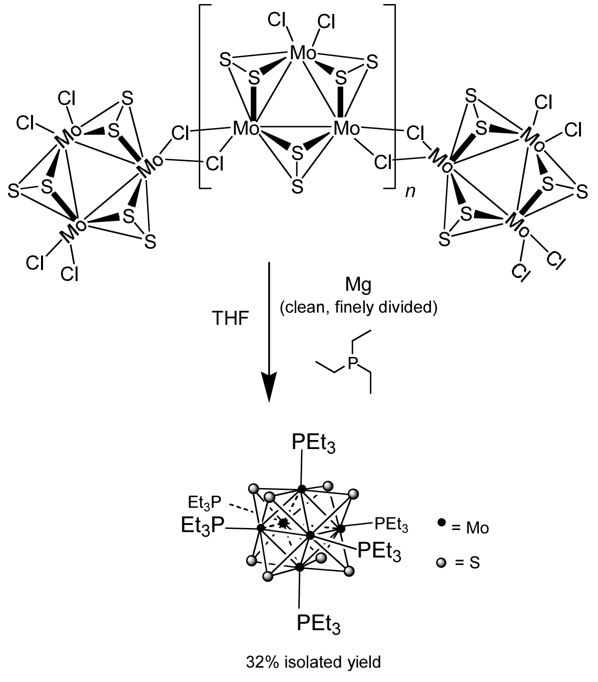
3.2. Molybdenum

Early successes in fragment condensation demonstrated syntheses of $[Mo_6S_8(PEt_3)_6]$, $[Mo_6Se_8(PEt_3)_6]$, and $[W_6S_8(PEt_3)_6]$, the first soluble model clusters of the molybdenum Chevrel phases [164] and their (unknown) tungsten analogues [165].

A high-temperature apparent fragment condensation synthesis of extended solids $A_xMo_6S_8$ has been described. Mixed salts of $[Mo_3S_9]^{3-}$, where the cations are NH_4^+ and a metal ion known to form ternary Chevrel phases, are heated under hydrogen gas at 1000 °C for four hours:

$$2M_p(NH_4)_qMo_3S_9 + (10 - q)H_2 \rightarrow M_{2p}Mo_6S_8 + 10H_2S + 2qNH_3 \quad (12)$$

All side products are gases at room temperature and atmospheric pressure. The solid products are stoichio-



Scheme 3.

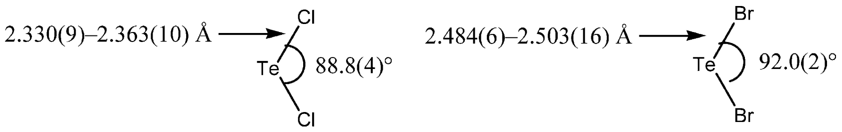


Fig. 11. Structures of TeX_2 ($X = Cl, Br$) ligands found in $[Re_6Te_6Cl_6(TeCl_2)_2]$ and $[Re_6Te_8(TeBr_2)_6]Br_2$, respectively.

metric Chevrel solids, free of side impurities (Mo, MoS_2) that usually accompany ceramic Chevrel phase preparations [166].

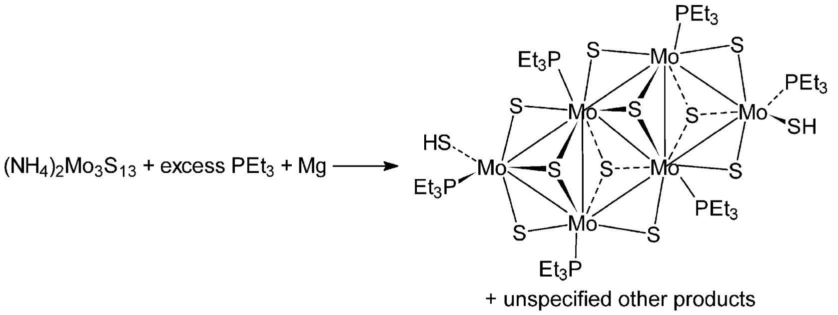
The reaction of $[Mo_3S_4Cl_4(PEt_3)_4(CH_3OH)]$ with clean, finely divided magnesium metal in THF affords the 20-electron cluster $[Mo_6S_8(PEt_3)_6]$ in 30% reported yield [167]. Mo–Mo distances in this compound (2.664 and 2.662 Å) compare closely to the shorter Mo–Mo bond length in (20-electron) Mo_6S_8 (2.698 and 2.862 Å) (estimated errors are not available from the original reference). The trinuclear starting material was prepared in methanol by treatment of $Mo_3S_7Cl_4$ with triethylphosphine [168]. The following sequence was later found [169] to be more efficient (Q = S, Se) (Scheme 3):

$$Mo_3Q_7Cl_4 + 8PEt_3 \rightarrow \text{'}[Mo_3Q_4Cl_4(PEt_3)_5]\text{'} + 3QPEt_3 \tag{13}$$

$$2\text{'}[Mo_3Q_4Cl_4(PEt_3)_5]\text{'} + 4Mg \rightarrow [Mo_6Q_8(PEt_3)_6] + 4MgCl_2 + 4PEt_3 \tag{14}$$

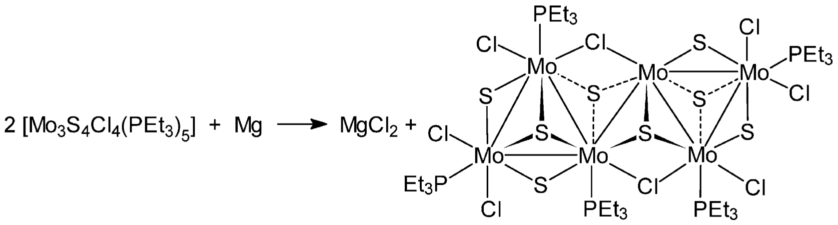
Here, the ill-characterized product of reaction between triethylphosphine and polymeric $Mo_3Q_7Cl_4$ is reduced with magnesium metal in THF. The hexanuclear molybdenum clusters are both oxidizable and reducible by one electron; reduction is achieved with sodium amalgam, with ion exchange to give air-sensitive $(PPN)[Mo_6Q_8(PEt_3)_6]$ (PPN = bis(triphenylphosphine)iminium).

The same research group subsequently reported non-octahedral, raft-type clusters formed under similar conditions. The reaction of $(NH_4)_2[Mo_3S_{13}]$ with triethylphosphine and magnesium in THF afforded the raft-like cluster $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ in 11% yield, which was characterized by X-ray crystallography (Eq. (15)) [170]:



(15)

Reduction of $Mo_3S_4Cl_4(PEt_3)_5$ with Mg in THF at −20 °C gave a different raft, $Mo_6S_8Cl_6(PEt_3)_6$, the structure of which was also determined (Eq. (16)):



(16)

In this latter case, two Mo_3 triangles are joined by a single metal–metal bond, two μ_2-chlorides and one μ_3-sulfide ligand. The stated yield of this cluster is 26%; a selenide analogue was prepared analogously in 11% yield [171]. Attempts to reduce these rafts to octahedral Chevrel-like clusters $[Mo_6Q_6(PEt_3)_6]$ were unsuccessful.

3.3. Tungsten

Tungsten Chevrel phases are unknown, despite many years' effort. Model clusters are available, however, from solution-phase chemistry.

The reaction of W_6Cl_{12} with elemental sulfur at 300 °C gives $W_3S_7Cl_4$ [172], the crystal structure of which was determined [173]. Treatment of this polymeric solid with PEt_3 affords an uncharacterized green product, which when reacted with magnesium in THF, affords brown $[W_6S_8(PEt_3)_6]$ in 10% yield after chromatography [174]. This cluster is isostructural with the molybdenum analogue and likewise suffers reversible one-electron reduction and oxidation.

The fragment condensations of Equations 13 and 14 depend critically on finely divided and clean magnesium. It is noteworthy that the $[W_6S_8(PEt_3)_6]$ synthesis originally proceeded by decomposing hexanuclear clusters in W_6Cl_{12} to the trinuclear fragment $W_3S_7Cl_4$, with recombination to $[W_6S_8(PEt_3)_6]$. This elaborate procedure may have suggested the global ligand replacement reactions described in Part 4.

3.4. *Rhenium chalcogenide clusters*

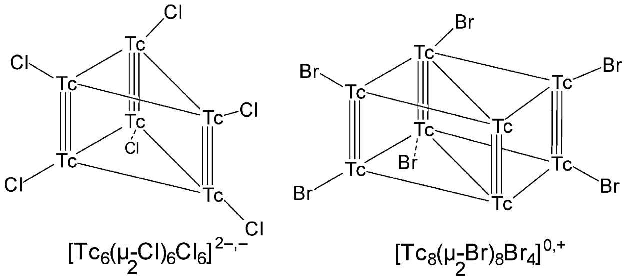
Recent work by Fedorov et al. [175] reports some preparations of $[Re_6Q_{8-n}Br_{6+n}]^{n-4}$ (Q = S, Se) clusters arising from the thermal reaction of Re_3Br_9 with the lead(II) or cadmium chalcogenides. In all cases save one, the interior cores of μ_3-face-bridging ligands are partially halogenated ($n > 0$), no doubt because the starting mixtures were systematically bromide-rich. A condensed cluster, $[Re_9Se_{11}Br_6]^{2-}$, (cf. $[Mo_9Se_{11}]$ core in Fig. 7) was claimed late in 1998, but details are sparse, no yield is reported, and characterization relies solely upon X-ray crystallography, which cannot distinguish Se from Br.

Ibers et al. [176] have lately reported the synthesis of $[Re_6Se_8(CN)_6]^{4-}$ from a cubane-type rhenium telluride cluster. The reaction of $[Re_4Te_4(TeCl_2)_4Cl_8]$ [177], KSeCN, and NH_4Cl in acetonitrile, superheated to 300 °C, afforded crystalline $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$ after 3 days. The organic cation is acetamidinium. One such preparation afforded a 50% yield based on rhenium, but this corresponded to 7 mg of product. Replacement of telluride ligands by selenide is precedented in Re_6 clusters [201]. The reaction necessitates the reduction of rhenium(IV) to rhenium(III) and of selenium in $SeCN^-$ to Se^{2-}. The authors suppose Te^{2-} to be the reductant, but tellurium-containing products are not identified. This conversion of an Re_4 core to an Re_6 cluster appears to be unprecedented. The reaction is not easily classified; although we include it with apparent fragment condensations, it could qualify as a spontaneous self-assembly or global ligand substitution. The authors emphasize the solubilizing tendencies of superheated acetonitrile in 'the facile breakup of the $[Re_4Te_4]^{8+}$ core,' [176].

3.5. *Halide clusters of technetium and rhenium*

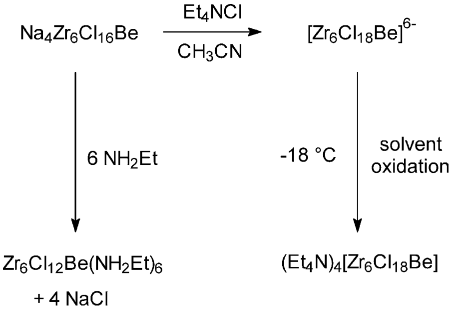
A limited range of higher nuclearity clusters (six or more metals) clusters is known for Tc [178,179] and Re halides; for these compounds the chemistry is complicated. Although the starting materials for these aggregates are mononuclear, we include these clusters under the heading of apparent fragment condensation because they are more naturally considered as linked cohorts of multiply-bonded metal–metal dimers. The reduction of $(Me_4N)TcCl_6$ or $(Me_4N)TcO_4$ by elemental hydrogen under pressure (3–8 MPa) at 140–220 °C in an autoclave affords black crystals, consisting of a mixture of $(Me_4N)_3[Tc_6(\mu_2\text{-}Cl)_6Cl_6]Cl_2$ and $(Me_4N)_2[Tc_6(\mu_2\text{-}Cl)_6Cl_6]$. Yields are unstated. Both clusters are D_{3h}-symmetric trigonal prisms with rectangular faces bounded by two Tc≡Tc triple bonds (2.21 Å, $[Tc_6(\mu_2\text{-}Cl)_6Cl_6]^-$; 2.16 Å, $[Tc_6(\mu_2\text{-}Cl)_6Cl_6]^{2-}$) and approximately single bonds along triangular faces (2.57 Å, $[Tc_6(\mu_2\text{-}Cl)_6Cl_6]^-$; 2.70 Å, $[Tc_6(\mu_2\text{-}Cl)_6Cl_6]^{2-}$) [180], Fig. 12. The bonding in these compounds has been analyzed [181] within the extended Hückel approximation, which indicates that $[Tc_6Cl_{12}]^{2-}$ may be oxidizable by up to two electrons [182].

A mixture of octanuclear technetium clusters is obtained from the reaction of $HTcO_4$ or H_2TcBr_6 at 140–160 °C in concentrated hydrobromic acid in an autoclave [183]; two of the characterized products are $[H(H_2O)_2][Tc_8(\mu_2\text{-}Br_8)_8Br_4]Br$ and $[Tc_8(\mu_2\text{-}Br_8)_8Br_4]Br\cdot 2H_2O$; this mixture was originally misformulated as a single phase composed of the latter [184]. Both compounds were characterized by X-ray crystallography, and consist of four Tc≡Tc bonds within a face-sharing trigonal biprism.



Edge-bridging ligands omitted for clarity.

Fig. 12. Skeletal structures of halide-bridged technetium clusters.



Scheme 4. Adapted from Ref. [188].

A few occurrences of analogous trigonal prismatic rhenium halide clusters have emerged. The salt formulated [185] as $(CH_3CON(CH_3)_2)(H_3O)_n[Re_6Br_{14}]$, of unknown charge, transforms into $(C_{10}H_{13}O_2)_2[Re_6Br_{14}]$ upon treatment with acidified acetylacetone [186]; the organic cation is the dimer of acetylacetone, and the fate of the starting cation is unknown. Crystallographic analysis of this compound reveals both triple (mean 2.265 Å) and single Re–Re bonds (mean 2.650 Å).

4. Excision

A review of cluster excision reactions before 1990 is available [187]. We consider here developments since that time.

4.1. Interstitially stabilized zirconium halide clusters

Excision from extended solids is an efficient conduit to centered Zr_6-halide clusters. The most easily excisable clusters are those where intercluster linkages are fewest. The earliest efforts disclosed solubilization of $Na_4Zr_6Cl_{16}Be$ with ethylamine or chloride ion [188] as in Scheme 4. Cluster reduction accompanies reaction with Et_4NCl in acetonitrile to give undetermined oxidation products. Later work extended Zr_6 excision chemistry with PEt_3, and with cryptands for phases having alkali-metal counterions. Clusters encasing larger interstitials, such as Fe, are more reactive. A possible cause is the expanded Zr_6 core, which better exposes the metal vertices to attacking nucleophiles. Excising the Zr_6 core (in the absence of redox) increases Zr–Z distances by ~ 0.015 Å for Z = C, Fe. Oxidative excision of $Rb_5Zr_6Cl_{18}B$ (14-electron) to yield $(Ph_4P)_4Zr_6Cl_{18}B\cdot(Ph_4P)_2ZrCl_6$ increases the Zr–B distance by 0.035 Å, consistent with elimination of a bonding electron [188].

Hughbanks and coworkers have, for several years, reported success in excising Zr_6 clusters with molten salts. Specifically, the room-temperature ionic melt formed from aluminum chloride and 1-ethyl-2-methylimidazolium chloride (ImCl) readily solubilizes $Zr_6(\mu_2\text{-}Cl)_{12}Cl_6(Z)$ species. These melts can be rendered acidic or basic, according to the ratio of $AlCl_3$ to ImCl: melts rich in $AlCl_3$ are Lewis acidic; in ImCl, basic [189,190].

The reaction of $Rb_5Zr_6Cl_{18}B$ with 2:1 (mol/mol) ImCl:$AlCl_3$ affords a solid formulated (by crystallography) as $Im_5Zr_6Cl_{18}B\cdot CH_3C_6H_5\cdot 2CH_3CN$ in ca. 50% yield [191]. However, this reaction is not a true excision, inasmuch as the starting phase contains independent, nonbridged molecular clusters.

Dissolution of the extended solid $K[Zr_6Cl_{15}C]$ in basic ImCl/$AlCl_3$ is a genuine excision process, liberating $[Zr_6Cl_{18}C]^{4-}$, with three terminal chlorides per cluster supplied by the melt. Voltammetric, NMR, and absorption measurements are all supportable in these room-temperature ionic liquids. The cluster $[Zr_6Cl_{18}C]^{4-}$ oxidizes reversibly at $E_{1/2} = 0.23$ V versus Al/Al^{3+} in the ionic liquid [192], and exhibits a ^{13}C-NMR singlet at $\delta = 458.0$ ppm [193]. The $[Zr_6Cl_{18}C]^{4-}$ absorption spectrum blue-shifts as the melt becomes more acidic.Recently, the N-centered cluster $[Zr_6Cl_{18}N]^{3-}$ was isolated [194] as the bis(triphenylphosphine)iminium salt. Heating an acetonitrile solution of PPNCl with the network solid $Zr_6Cl_{15}N$ afforded $(PPN)_3[Zr_6Cl_{18}N]$ in 30% isolated yield; this corresponds to 100 mg product. $Zr_6Cl_{15}N$ exhibits the same intercluster connectivity pattern as $Na_2Zr_6Cl_{15}B$; all six exocluster chlorides bridge with neighboring clusters to form a three-dimensional network. The boride phase is more readily dissolved, liberating clusters at room temperature in acetonitrile. The nitride phase requires heating in the same solvent with an excess of chloride. Xie and Hughbanks [194] attribute this contrast to differing apical Zr–Cl bond strengths, as reflected by the shorter Zr–Cl distances (2.594(3) Å) in $Zr_6Cl_{15}N$ vs. that of $Na_2Zr_6Cl_{15}B$ (2.681(6) Å). Evidently, these authors do not consider the solvation of Na^+ in acetonitrile to be decisive.

The cyclic voltammogram of $(PPN)_3[Zr_6Cl_{18}N]$ was measured, and the one electron-reduced cluster $[Zr_6Cl_{18}N]^{4-}$ can be prepared by reaction with Decamathylcobaltocene [194].

The two-dimensional network $Li_2Zr_6Cl_{15}Mn$ is insoluble in common organic media, but dissolves in basic chloroaluminate melts, affording an olive-colored solution having a ^{55}Mn-NMR resonance ($I = 5/2$, 100% abundance) at δ 5605 ppm. Acidification with $AlCl_3$ changes the solution color to pink, and the ^{55}Mn-NMR resonance shifts to $\delta = 5260$ ppm; the composition of the pink substance is unknown [193].

The ^{57}Fe Mössbauer spectra of $Zr_6Cl_{14}Fe$, $LiZr_6Cl_{15}Fe$, and $KZr_6Cl_{15}Fe$ exhibit the most negative isomer shifts hitherto recorded, ranging from $\delta = -0.953$ to -0.946 mm s^{-1} at 295 K. These observations are rationalized in terms of favorable overlap of the Fe 4s orbital with the A_{1g} combination of Zr_6 d_{z^2} orbitals; an alternative interpretation, that the oxidation state of the central iron is +6, was deemed implausible [195].

Recently, Hughbanks and coworkers have described the excision and isolation of centered zirconium clusters in aqueous media [196]. It is essential that these aqueous solutions be acidic for the clusters' stability.

4.2. Molybdenum

Fedorov and coworkers [197] have published excision reactions of the $[Mo_6Se_8]^0$ core of the Chevrel phases in a potassium cyanide melt at 650 °C, in 56% yield:

$$Mo_6Se_8(s) + 7KCN(l) \rightarrow K_7[Mo_6Se_8(CN)_6] + \text{uncharacterized products} \quad (17)$$

Here, the product 21-electron cluster is one-electron reduced from the starting Chevrel phase. The potassium salt dissolves in water to give a deep blue solution, and the cluster is quasi-reversibly oxidized to $[Mo_6Se_8(CN)_6]^{6-}$ at $E_{1/2} = 0.39$ V versus SCE. The generality of this method, when applied to other Chevrel phases, including condensed cluster phases, remains to be seen.

In related work, Hughbanks et al. [198] have reported the synthesis of $K_6[Mo_6Se_8(CN)_5]$, a solid-state, straight-chain polymer of Mo_6Se_8 clusters bridged by cyanide ligands. Four different preparative routes to this compound were discovered, which involve (formal) excision of clusters from Mo_6Se_8, decomposition of the infinite cluster KMo_3Se_3, or self-assembly from Mo and $MoSe_2$; all of these reactions take place in molten potassium cyanide over 36 hr. The resulting polymeric phase, which is prepared in 75–85% yield, was characterized by single-crystal X-ray diffraction, IR and EPR spectroscopies, and magnetic susceptometry. The $[Mo_6Se_8]^-$ unit possesses 21 metal–metal bonding electrons and is paramagnetic, but antiferromagnetism is absent despite intimate cyanide-bridging. This observation is rationalized in terms of an extended Hückel calculation, which indicates that overlap between the $[Mo_6Se_8]^-$ HOMO (e_g in O_h) and the CN^- π^* orbitals is symmetry-forbidden.

4.3. Rhenium

Excision chemistry has been explored for the rhenium(III) selenide halide phases $Re_6Se_5Cl_8$ (1D) and $Re_6Se_6Cl_6$ (2D), where all intercluster linkages are bridging chlorides. The reaction of one-dimensional $Re_6Se_5Cl_8 \equiv Re_6(\mu_3\text{-}Se)_5(\mu_3\text{-}Cl)_3Cl_4Cl_{2/2}$ with Pr_4NCl in acetonitrile gives an 80% yield of $(Pr_4N)[Re_6Se_5Cl_9]$, which contains discrete clusters. The reaction of the two-dimensional $Re_6Se_6Cl_6 \equiv Re_6(\mu_3\text{-}Se)_6(\mu_3\text{-}Cl)_2Cl_2Cl_{4/2}$ with Pr_4NCl under the same conditions yields $(Pr_4N)_2[Re_6Se_6Cl_8]$ in 78% yield. This salt is also obtainable from reaction of $(Pr_4N)[Re_6Se_5Cl_9]$ with Li_2Se in THF; the yield is 57%. The phase $Re_6Se_7Cl_4$, where clusters are connected in three dimensions, defies excision with a variety of reagents [199].

Excision reactions in sodium- or potassium cyanide melts have more recently been investigated for Re_6Te_8-phases. The reaction of Re_6Te_{15} with molten KCN affords discrete hexa(cyanide) clusters in a nonredox process at 600 °C [200]:

$$Re_6Te_{15}(s) + 6KCN(l) \rightarrow K_4[Re_6Te_8(CN)_6] + K_2Te_n + (7-n)Te \quad (18)$$

If elemental selenium is included in the melt, mixed telluride-selenide clusters are obtained, as confirmed by ^{77}Se and ^{125}Te-NMR [201]. Ion exchange with various cations is possible. In the case of $Ba_2Re_6Te_8(CN)_6 \cdot 12H_2O$, noncoordinated water molecule migration was studied by ^1H-NMR in a temperature range from −140 °C to the decomposition point at 120 °C [202].

5. Global ligand replacement

5.1. Zirconium

The reaction of $Zr_6Br_{14}Fe$, an extended solid phase, with a 1-methyl-3-ethylimidazolium chloride/aluminum chloride melt produces the $[Zr_6Cl_{18}Fe]^{4-}$ ion in unspecified yield [203]. An analogous reaction occurs with chloride salts in acetonitrile solution. These observations bespeak the generality of excision methods, and imply that the distinction between excision and ligand substitution reactions is arbitrary.

5.2. Molybdenum alkoxide clusters

The oldest documented global ligand replacement of a hexanuclear cluster dates from 1968 [204]. The reaction of Mo_6Cl_{12} with an excess of sodium methoxide in methanol, upon refluxing, yields $Na_2[Mo_6Cl_8(OMe)_6]$ as a yellow crystalline material. An analogous cluster, $Na_2[Mo_6Br_8(OMe)_6]$ is obtained from Mo_6Br_{12}. Under more forcing conditions, pyrophoric $Na_2[Mo_6(\mu_3\text{-}OMe)_8(OMe)_6]$ is isolated as a brown solid. This compound has been characterized by ^1H-NMR and IR spectroscopy. An ethoxide analogue was prepared, but was not obtained pure. The crystal structure [205] reveals that the Mo–Mo bonds in $[Mo_6(OMe)_{14}]^{2-}$ are markedly shorter than in the $[Mo_6Cl_{14}]^{2-}$ cluster (2.536(8) vs. 2.620(10) Å) [206]. Reasons for this contraction were not discussed. No reaction chemistry of the $[Mo_6(OMe)_{14}]^{2-}$ entity has been described.

5.3. Molybdenum and tungsten chalcogenide clusters

Difficulties with fragment condensation approaches prompted investigations of other routes to molecular Mo_6Q_8 clusters. The coincidence that both Mo_6Cl_{12} and Mo_6S_8 contain type **I** hexanuclear clusters suggested molybdenum(II) chloride as a Chevrel-phase precursor. The reaction of Mo_6Cl_{12} with NaSH and NaOBu in a 4:1 butanol/pyridine mixure, followed by prolonged extraction in methanol (to remove NaCl) gives an amorphous phase. The amorphous substance, formulated as '$Mo_6S_7Cl(pyridine)_x$,' on further treatment with NaSH, in the same solvent mixture, gives another amorphous solid, '$Mo_6S_8(pyridine)_{\sim 4}$.' This solid is slightly soluble in pyridine, and pure $[Mo_6S_8(pyridine)_6]$ can be obtained by recrystallization from pyridine solutions. Various other amines can be coordinated to the Mo_6S_8 core by refluxing the second phase or its derivatives in the neat amine for one to three days. These $[Mo_6S_8L_6]$ clusters were characterized by X-ray diffraction, ^{1}H-NMR, infrared and Raman spectroscopy, and X-ray photoelectron spectroscopy [207].

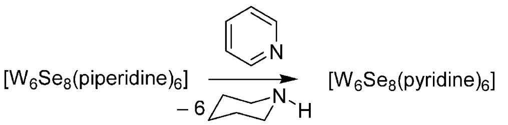
Global ligand replacement chemistry is more extensively developed for tungsten than for any other element. The experimental conditions involved closely parallel those for molybdenum sulfide clusters. The reaction of W_6Cl_{12} with NaSH and NaOBu in a 1:12:6 ratio in refluxing pyridine gives $[W_6S_8(\text{pyridine})_6]$ in high yield:

$$\begin{aligned} W_6Cl_{12} &+ 8NaSH + 6\ \text{pyridine} \\ &+ 4NaOBu \rightarrow [W_6S_8(\text{pyridine})_6] + 12NaCl \\ &+ 4BuOH + 2H_2 \end{aligned} \tag{19}$$

The tungsten sulfide complex precipitates as red microcrystals. Magnetic susceptometry measurements indicate a singlet ground state of this 20-electron cluster. Attempts to decomplex pyridine, either thermally or with Lewis acids, failed to produce a ‘tungsten Chevrel phase.’ Intractable, noncrystalline solids resulted, and it is unclear if the W_6 cluster survived the reaction conditions [208].

A different protocol yields the selenide homologues, where Na_2Se is the chalcogen source [209]. The product is the 20-electron cluster $[W_6Se_8L_6]$ (L = pyridine, piperidine). Yields are 74% for $[W_6Se_8(\text{piperidine})_6]$ and 56% for $[W_6Se_8(\text{pyridine})_6]$. The cause of the four-electron oxidation of the W_6 cluster (from 24-electron W_6Cl_{12}) is unknown. X-ray photoelectron spectroscopy of the product found elemental tungsten, which may originate from disproportionation of an unstable 24-electron cluster.

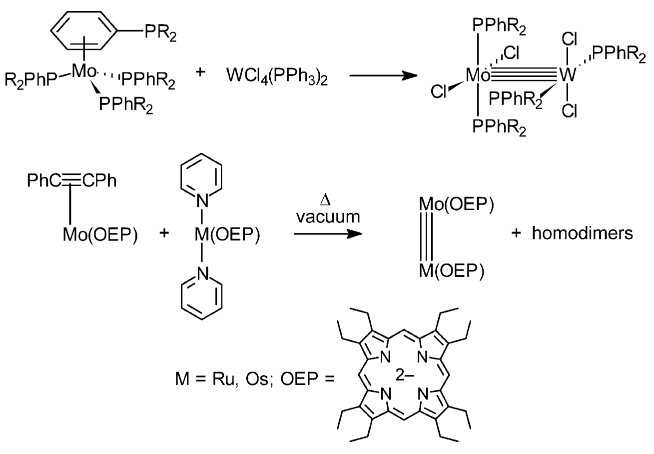
Quantitative substitution of piperidine for pyridine occurs over 1 day, on standing in neat pyridine:



(20)

However, the hexa(pyridine) cluster is indefinitely stable to an analogous treatment with piperidine.

Reaction of W_6Cl_{12} with Na_2Te or a mixture of Na_2Te and Na_2Te_2 in pyridine gives the solvated $[W_6Te_8(\text{pyridine})_6]$ cluster in 88% yield; the corresponding reaction in piperidine is unclean, and no yield was declared, despite recovery of $[W_6Te_8(\text{piperidine})_6]$ single crystals. A reduced cluster $[Na(\text{pyridine})_6][W_6Te_8(\text{pyridine})_6]$ was isolated and characterized crystallographically, but no yield was stated and pyridine loss impeded quantitative elemental analysis [210,211].



Scheme 5.

5.4. Cyanide-terminated Re_6 clusters

The reaction of Re_6Te_{15} with 8 equiv. molten KSCN at 500 °C for 24 h afforded a solid product, which was washed with ethanol and then dissolved in an aqueous solution of CsCl of unreported concentration. Solvent evaporation at 30 °C produces red-brown crystals of $Cs_3K[Re_6S_8(CN)_6]$ in unspecified yield. X-ray diffraction analysis indicates that the crystals were a mixture of compounds, with some μ_3-bridging positions retaining tellurium. Refinement of the structure indicates the approximate composition $K_{0.78}Cs_{3.22}Re_6S_{7.40}Te_{0.60}(CN)_6$ [212].

Phases $K_4[Re_6S_{8-y}Te_y(CN)_6]$, of intermediate composition, are prepared by similar methods, and have been examined by X-ray crystallography. No clear relationship exists between unit cell parameters and tellurium content [213].

6. Conclusion and prospects

Early transition metal clusters continue to attract large numbers of researchers. Their enduring fascinations are their exoticism, their complexity, and a potential for discovery that still exceeds the numerous achievements reviewed above. New developments begin at the level of cluster preparation; Corbett’s dictum, ‘First comes the synthesis,’ [26] is axiomatic.

The prevailing synthetic avenues [16] to early transition element clusters are four: spontaneous self-assembly, fragment condensation, excision, and ligand substitution. Of these, the most efficient is self-assembly; the rest are ‘last resorts’ available when self-assembly approaches fail, as with tungsten analogues of Chevrel clusters. Opportunities in cluster chemistry are varied and challenging; certainly, the most daunting is adding to the modest arsenal of workable synthetic routes to early transition metal clusters.

More immediate prospects include the following.

6.1. More sophisticated self-assembly processes

Spontaneous self-assembly reactions usually employ simple starting materials, often elemental metals, metal halides, and metal chalcogenides. Investigations of low-valent metal compounds with labile ligands, such as arenes, olefins, and acetylenes, may bear fruit. Such compounds are indeed useful for heterometal quadruple bond formation [8,214–216], Scheme 5 [217].

A method much like this was used to prepare $[Cr_6Te_8(PEt_3)_6]$ from bis(2,4-dimethylpentadienyl)chromium(0) [84] and $[W_6I_8]^{4+}$-phases from $W(CO)_6$ [98] (vide supra); other applications are conceivable. The two leading issues in improving self-assembly approaches are selectivity toward clusters over other products and generality for a range of metals.

Long and collaborators [89] have described a gas-phase reactor modified to allow cocondensation of vaporized metal-chalcogenide particles and volatile ligands. Clusters self-assemble in the vapor or on the reactor walls, and are protected by capping ligands. Upon cooling, they deposit on the vessel walls. This strategy yielded discrete, polynuclear sulfides of chromium ($[Cr_6S_8(PEt_3)_6]$), iron ($[Fe_4S_4(PEt_3)_4]$), cobalt ($[Co_6S_8(PEt_3)_6]$), nickel ($[Ni_4S_4(PEt_3)_8]$), and copper ($Cu_6S_4(PEt_3)_4$, $Cu_{12}S_6(PEt_3)_8]$). Two new copper selenide species, $[Cu_{26}Se_{13}(PEt_3)_{14}]$ and $[Cu_{70}Se_{35}(PEt_3)_{21}]$ were also prepared. The authors state that most such reaction runs afford mixtures of clusters. Isolated yields are not reported, except for the copper species; $[Cu_{12}S_6(PEt_3)_8]$ and $[Cu_{26}Se_{13}(PEt_3)_{14}]$ were each recovered in quantities exceeding 200 mg. Long states on his website that the use of resistive heating (as opposed to laser ablation) is an essential part of the preparative concept. The generality of this promising method remains to be seen. Arguably its most enticing prospect is controlling the major deposition product by varying the reaction conditions, especially the heating and cooling temperatures.

6.2. Water activation

The challenging four-electron oxidation of water to dioxygen has stimulated worldwide efforts to devise a suitable, robust catalyst [218,219]. The microscopic reverse of this process is catalyzed by the cluster solid $Ru_2Mo_4Se_8$ [220,221]:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad (21)$$

$Ru_2Mo_4Se_8$ contains 24-electron type **I** clusters, isoelectronic with $[Mo_6Cl_{14}]^{2-}$ and $[Re_6S_8Cl_6]^{4-}$. The utility of these soluble, hydrolytically stable species for water oxidation (possibly coupled to their triplet excited states) is uncharted.

6.3. Supramolecular chemistry

Use of clusters in supramolecular chemistry [222] and in microporous framework solids is an attractive prospect [223]. At least three research groups [224,225] have utilized $[Re_6Q_8(CN)_6]^{4-}$ clusters as bases for new, expanded Prussian blue-type framework solids [226] and other extended networks [227]. Recent work has described xerogels composed of $[Mo_6Cl_8]^{4+}$ clusters bridged by 4,4′-bipyridine. Triflate counterions are believed to occupy intercluster voids. These substances are prepared from $[Mo_6Cl_8(OTf)_6]^{4-}$, and have been characterized by infrared and Raman spectroscopy, emission and UV–vis absorption spectroscopy, and X-ray powder diffraction, but not by single-crystal diffraction methods [228].

A recent innovation uses cobalt clusters of the type $[Co_6Q_8(PR_3)_6]$ ($Q = S$, Se) as pillaring agents in lamellar sulfides [229,230]. Mixture of $[Co_6Q_8(PR_3)_6]$ and exfoliated suspensions of $LiMoS_2$ causes flocculation of bulk MoS_2 where the cobalt cluster has intercalated. A 1:6 $[Co_6S_8(PPh_3)_6]$: $LiMoS_2$ loading causes an interlayer expansion of 15.3 Å relative to undoped MoS_2. The resulting composites are more catalytically active than commercial sulfided $Co–Mo/Al_2O_3$ for the hydrodesulfurization of benzothiophene. It is believed that the pillaring action of the intercalated cluster exposes more catalytically active sites in the MoS_2 layer, enhancing its capacity. A similar intercalation strategy has been tested with $[Fe_6S_8(PEt_3)_6]^{2+}$ intercalation into TaS_2 [231,232].

6.4. Other potential applications

Recently, Nocera and coworkers [233] have demonstrated the use of $[Mo_6Cl_{14}]^{2-}$ clusters, embedded in fiber-optic cables, as dioxygen sensors. This application derives from the triplet-triplet annihilation of the $[Mo_6Cl_{14}]^{2-}$ excited state by O_2. In separate work, this quenching was shown to proceed by an energy-transfer mechanism, with formation of singlet oxygen, as confirmed by reaction with 1-methylcyclohexene [234]. Demas et al. [235] have discussed the potential use of similar, noncluster triplet emitters, including their application in blood-gas quantification. Tungsten(II) halide- and rhenium(III) chalcogenide clusters may be similarly adaptable, and we note that the luminescence quantum yields of some tungsten(II) iodide clusters more than double that of $[Mo_6Cl_{14}]^{2-}$ (ϕ_{em} $[W_6I_{14}]^{2-}$: 0.40; ϕ_{em} $[Mo_6Cl_{14}]^{2-}$: 0.19, in acetonitrile, room temperature) [234].

The fitness of transition element clusters for medical X-ray contrast imaging is occasionally discussed [98,236]. Such clinical applications are limited, above all, by the toxicity of many heavy-metal species. Suitable ligand design might alleviate metallocluster toxicity. Perhaps dendritic ligands [237,238] can render clusters biocompatible: dendrimer-ligated $[Mo_6Cl_8]^{4+}$ clusters were recently isolated by Gorman et al. [239] and related $[Re_6Se_8]^{2+}$ species were reported by Zheng and co-workers [240,241]. The use of water-solubilizing dendrimer ligands is an appealing extension of this chemistry.

We conclude that the future of early transition metal cluster chemistry warrants an optimistic outlook.

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