

Exploring the Breadth of Terminal Ligands Coordinated in $[\text{Mo}_6\text{X}_8]^{4+}$ - and $[\text{Re}_6\text{Q}_8]^{2+}$ -Based Cluster Complexes



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Abstract This survey provides an overview of the different types of terminal ligands incorporated into molybdenum halide and rhenium chalcogenide cluster complexes. While the incorporation of halide and pseudohalide ligands is prevalent with these systems, this article focuses on the coordination of other nitrogen-, oxygen-, sulfur-, and carbon-donor ligands. Emphasis has been placed on synthetic methodologies and the significance behind coordination of these ligands to discrete cluster complexes.

Keywords Cluster · Ligands · Molybdenum · Rhenium · Synthetic methodology

Honoring the legacy of Marcel Sergent.

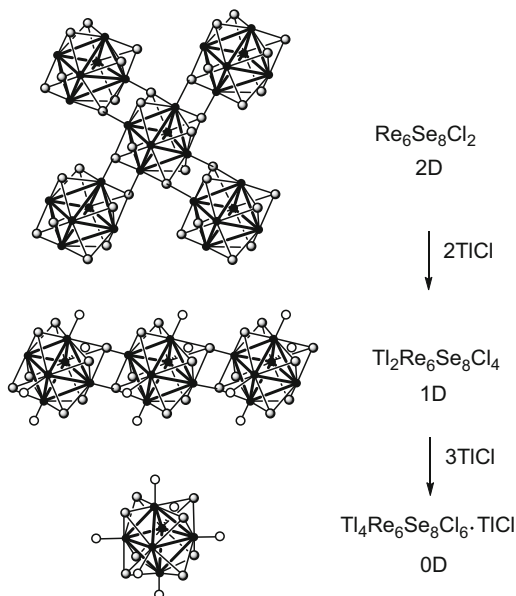
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1 Introduction

The cluster chemistry of molybdenum and rhenium is dominated by polynuclear species having the $[\text{Mo}_6(\mu_3\text{-X})_8]^{4+}$ or $[\text{Re}_6(\mu_3\text{-Q})_8]^{2+}$ core, where X = halogen and Q = chalcogen. These cluster cores contain an octahedron of metal atoms inscribed in a cube of facially bridging heteroatoms. Discrete hexanuclear octahedral clusters are stabilized by six additional terminal or apical ligands (L) leading to molecular systems with the general abbreviated formula of $[\text{Mo}_6\text{X}_8\text{L}_6]^{n+}$ or $[\text{Re}_6\text{Q}_8\text{L}_6]^{n+}$. Although molybdenum(II) halides have been known for many years [1], the field was revolutionized in the 1970s when reports of octahedral metal sulfide clusters appeared in the literature. The discovery of Chevrel phases ($\text{M}'\text{Mo}_6\text{S}_8$) had the most significant impact [2]. The superconducting properties of these ternary molybdenum chalcogenides were discovered early on; further investigations have proven these materials to have numerous other interesting properties, with some of the recent studies examining their potential as cathode materials in rechargeable batteries [3–6]. Not long after the discovery of Chevrel phase materials, reports detailing the preparation of analogous hexanuclear rhenium chalcogenide clusters appeared in the literature [7–9]. However, it was Sergent who pioneered the preparation of rhenium chalcohalide cluster phases and recognized the potential associated with condensing discrete clusters to form higher dimensional materials and how this would enable one to control the physical properties of those materials [10–13]. Cluster excision, the reverse of cluster condensation, is what brought us discrete cluster complexes [14–16]. This process, which is also referred to as dimensional reduction, involves reacting cluster-based materials with simple salts which are able to decrease the bridging interactions, thereby reducing the dimensionality of a material; the dimensional reduction of $\text{Re}_6\text{Se}_8\text{Cl}_2$ is shown in Fig. 1 [17].

Owing to the electronic nature of these 24 electron cluster cores, the regular octahedral geometry and the stereochemical rigidity of these systems (i.e., they are non-fluxional), $[\text{Mo}_6\text{X}_8]^{4+}$ - and $[\text{Re}_6\text{Q}_8]^{2+}$ -containing clusters, are often considered to be larger versions of single metal octahedral complexes. Therefore, research involving these systems has partially been driven by the desire to use these clusters as building blocks in the preparation of novel supramolecular frameworks [18–21]. Efforts to expand on earlier reports detailing the unique photophysical and electrochemical properties displayed by these cluster systems have also been a major driving force [22–26]. In order to take advantage of the unique structural and functional properties associated with these octahedral clusters and design clusters for specific applications, it is necessary to have control over terminal ligand substitution and to have the ability to incorporate a wide variety of ligand types. We present this review in an effort to highlight the progress that has been made toward broadening the scope of terminal ligands coordinated to $[\text{Mo}_6\text{X}_8]^{4+}$ (X = Cl, Br, I) and $[\text{Re}_6\text{Q}_8]^{2+}$ (Q = S, Se) cluster cores. The focus of this account is on the preparation of discrete molybdenum halide and rhenium chalcogenide clusters containing novel terminal ligands, i.e., ligands other than halides or pseudohalides. At times, we refer to applications, reactivity, and physical studies which motivated

Fig. 1 Dimensional reduction of $\text{Re}_6\text{Se}_8\text{Cl}_2$ with TlCl to generate the discrete cluster $\text{Tl}_4[\text{Re}_6\text{Se}_8\text{Cl}_6]\cdot\text{TlCl}$. Adapted with permission from [17] Copyright 2001 American Chemical Society



researchers to pursue these synthetic endeavors. However, the aim of this article is to focus on the synthetic methodologies and significance behind the coordination of these ligands. In addition, it is important to note that this article does not delve into the materials chemistry of these systems (i.e., coordination polymers, nanoparticles, incorporation into organic polymers, etc.), but focuses on discrete systems that can be solubilized. An extensive review of rhenium chalcogenide clusters was published by Batail and coworkers in 2001 [27], and Prokopuk and Shriver published a review on the chemistry of Group 5 and 6 octahedral clusters in 1998 [28]. Our objective is to build on these and other more recent reviews [29–31] and to provide an up-to-date overview without duplicating material summarized in previous accounts.

2 [Re₆Q₈]²⁺-Based Clusters

2.1 Nitrogen-Donor Ligands

2.1.1 Direct Coordination

Over the years, a number of cluster complexes containing neutral N-donor ligands have been prepared, common among these are nitriles and heterocyclic ligands such as pyridine and pyrazine [27]. Acetonitrile was one of the first nitriles to be coordinated by Holm and coworkers [32], by reacting a cluster complex containing one or more terminal halide ligands with silver(I) salts of non-coordinating anions (such as BF_4^- or SbF_6^-) in the presence of excess nitrile. Our group followed a

similar procedure in the preparation of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{NCC}(\text{CH}_3)_3)](\text{SbF}_6)_2$, which contains the sterically bulky trimethylacetonitrile ligand [33]. Nitriles and pyridine are both readily coordinated to the cluster core; however, pyridine is more versatile in that there are numerous commercially available pyridine derivatives which can be used to enhance the functionality of the cluster. For example, Zheng and coworkers utilized 4,4'-dipyridyl and 1,2-bis(4-pyridyl)ethane to bridge $[\text{Re}_6\text{Q}_8]^{2+}$ cluster cores together [34]. Coordination of pyridine-based ligands has been achieved either by following a procedure similar to that used for the coordination of nitriles or by substitution of acetonitrile ligands by different pyridine donor ligands. It is worth mentioning the structural and functional advantages that these octahedral rhenium chalcogenide clusters have in comparison to other high-nuclearity transition metal clusters for the preparation of supramolecular arrays. The rigid (non-fluxional) nature of the cluster core, as well as the ability to site-differentiate the terminal ligands, allows for control over the positioning of ligands and the eventual connectivity between units. That is, these cluster cores can be viewed as building blocks in the design of supramolecular arrays. Key strategies for assembling these clusters into supramolecular arrays include (1) insertion of a cluster cation in place of a single metal center in a metal organic framework, (2) use of ligated clusters with appropriate functionalities to connect to other metal ions in solution ("cluster-as-ligand" approach), and (3) incorporating ligands that can self-assemble through secondary interactions such as hydrogen bonding and π -stacking. Zheng and coworkers have published some micro-reviews summarizing their (and others) contributions to this area [21, 35–37]. More recently, other pyridine-based ligands such as isonicotinic acid and 4-aminopyridine have been utilized to prepare discrete cluster complexes (e.g., *trans*- $[\text{Re}_6\text{S}_8(4\text{-aminopyridine})_4(\text{OH})_2]$ [38] and *cis*- and *trans*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4(\text{isonicotinic acid})_2](\text{SbF}_6)_2$ [39]). The difference between the hydrogen-bonded networks formed when *cis*- and *trans*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4(\text{isonicotinic acid})_2](\text{SbF}_6)_2$ crystallize is shown in Fig. 2; two of the structures shown contain isonicotinate, indicating deprotonation of one of the isonicotinic acid units during crystallization. The successful coordination of six porphyrin rings to the rhenium sulfide and selenide cores emphasizes the increased size of the rhenium chalcogenide cores compared to their single metal counterparts, i.e., $[\text{Re}_6\text{Q}_8(\text{H}_2\text{PyT}_3\text{P})_6]^{2+}$ (Fig. 3, left) and $[\text{Re}_6\text{Q}_8(\text{ZnPyT}_3\text{P})_6]^{2+}$ (Q = S, Se; $\text{H}_2\text{PyT}_3\text{P}$ = 5-(4-pyridyl)-10,15,20-tritolylporphyrin, and ZnPyT_3P = 5-(4-pyridyl)-10,15,20-tritolylporphyrinatozinc (II)) [40]. Electrochemical studies of these and of disubstituted clusters bridged to ruthenium porphyrin complexes (*cis*- and *trans*- $[\text{Re}_6\text{S}_8\text{Cl}_4\{(\mu\text{-bpy})\text{Ru}(\text{CO})(\text{ttp})\}_2]^{2-}$ and *trans*- $[\text{Re}_6\text{S}_8\text{Cl}_4\{(\mu\text{-pyrazine})\text{Ru}(\text{CO})(\text{ttp})\}_2]^{2-}$ (Fig. 3, right) (ttp = tetratolylporphyrin) were undertaken to explore the redox communication between the cluster core and the porphyrin moieties.

The unique electrochemical and luminescent properties of the $[\text{Re}_6\text{Q}_8]^{2+}$ and $[\text{Mo}_6\text{X}_8]^{4+}$ systems are often cited as reasons behind the sustained interest in these octahedral clusters. The following are examples where functionalized pyridines were used to control the physical properties of the cluster complexes. Guldi and coworkers modified the pyridine ligand with a fullerene in the preparation of a covalently linked donor-acceptor dyad, wherein a rhenium chalcogenide cluster core was the donor

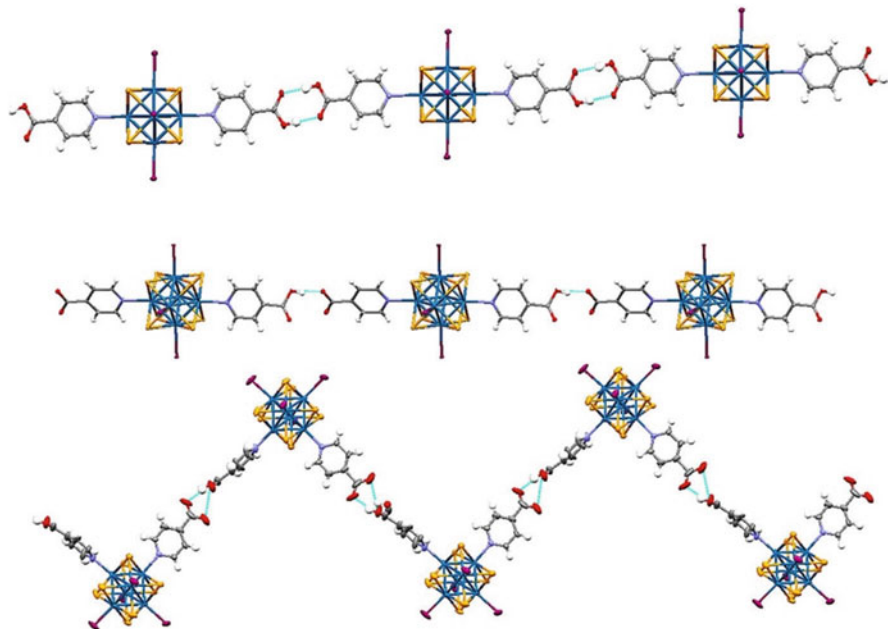


Fig. 2 The structures of *trans*-[Re₆Se₈(PEt₃)₄(isonicotinic acid)₂]²⁺, *trans*-[Re₆Se₈(PEt₃)₄(isonicotinic acid)(isonicotinate)]⁺, and *cis*-[Re₆Se₈(PEt₃)₄(isonicotinic acid)(isonicotinate)]⁺ (top to bottom), where intermolecular hydrogen bonding (blue lines) is observed. Reprinted by permission from Springer Nature Customer Service Centre GmbH [39] Copyright 2015

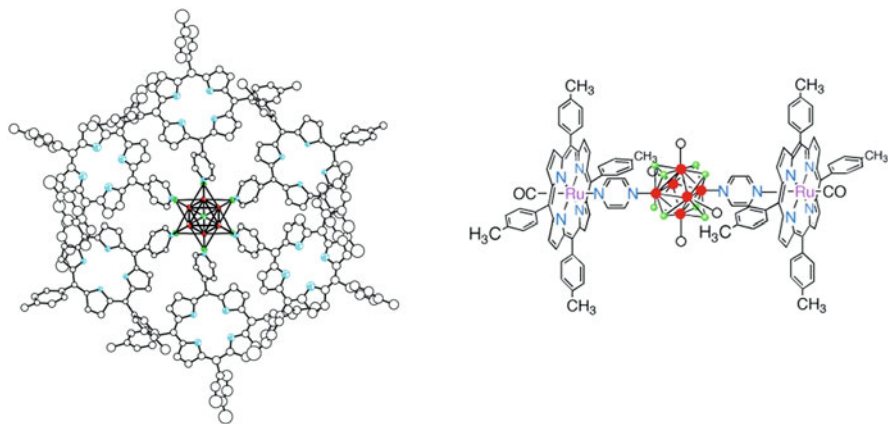
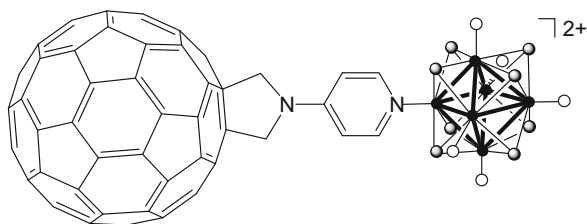


Fig. 3 Structure of [Re₆Se₈(H₂PyT₃P)₆]²⁺ (left) and a schematic structure of [Re₆S₈Cl₄{(μ-pyrazine)Ru(CO)(tp)}₂]²⁻ (right). Reprinted with the permission from [40] Copyright 2002 Wiley-VCH Verlag GmbH & Co

Fig. 4 Visual representation of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(N\text{-pyridyl-3,4-fulleropyrrolidine})]^{2+}$. Reprinted with the permission from [41] Copyright 2010 Wiley-VCH Verlag GmbH & Co



and C_{60} -fullerene the acceptor (Fig. 4) [41]. Such a design was inspired by the multicomponent systems found in natural photosynthetic processes. It is proposed that a light-induced energy transfer from the cluster to the C_{60} -fullerene in the $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(N\text{-pyridyl-3,4-fulleropyrrolidine})]^{2+}$ complex occurs. Another example, published by Kitamura and coworkers, involves fine-tuning the photophysical properties of the rhenium sulfide cluster core by controlling the energy between the $[\text{Re}_6\text{S}_8]^{2+}$ core centered HOMO and the π^* orbital of the ligand. In this example, the phenylpyridine ligand in $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_8\text{Cl}_5(4\text{-phenylpyridine})]$ (obtained by photoirradiation of a MeCN solution of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8\text{Cl}_6]$ in the presence of 4-phenylpyridine) was found to enhance metal-to-ligand charge-transfer emission leading to a longer excited state lifetime [42]. This provides an example of how the synthetic chemistry of these systems has improved in such a way that subtle control over the physical properties of the rhenium chalcogenide clusters is becoming a reality.

In an effort to expand the type of potential organic linkers to rhenium chalcogenide cluster cores, Mironov et al. developed a synthetic route toward the coordination of neutral pyrazole ligands. Heating a mixture of $\text{Cs}_4[\text{Re}_6\text{Q}_8\text{Br}_6]$ ($\text{Q} = \text{S}$ or Se) with 3,5-dimethylpyrazole at 200°C led to the isolation of $[\text{Re}_6\text{Q}_8(3,5\text{-Me}_2\text{PzH})_6]\text{Br}_2 \cdot 2(3,5\text{-Me}_2\text{PzH})$ ($\text{Q} = \text{S}$, Se) [43]. Substitution of the starting material with $\text{Cs}_3[\text{Re}_6\text{Q}_7\text{Br}_7]$ ($\text{Q} = \text{S}$, Se) resulted in the formation of $[\text{Re}_6\text{Q}_7\text{O}(3,5\text{-Me}_2\text{PzH})_6]\text{Br}_2 \cdot 3,5\text{-Me}_2\text{PzH}$ [44]. This is a rare example of a facially bridging ligand undergoing exchange where the oxygen is believed to have come from trace water present in the starting material. These are also the first examples where hot molten ligands were utilized as the reaction medium for a ligand substitution reaction involving octahedral rhenium clusters (i.e., the cluster and ligand are mixed and sealed in a glass ampoule which is then heated past the melting point of the organic ligands). The advantage of this type of synthetic route is discussed by the authors.

Most of the nitrogen-donor ligands mentioned so far have been neutral in charge. However, Brylev et al. reported the direct coordination of anionic benzotriazolate (BTA) ligands. When the hexahydroxo species, $[\text{Re}_6\text{Q}_8(\text{OH})_6]^{4-}$ ($\text{Q} = \text{S}$ or Se), is heated with 1*H*-benzotriazole at 150°C , the products $\text{K}_4[\text{Re}_6\text{S}_8(\text{BTA})_6] \cdot 3.5\text{EtOH} \cdot 4\text{H}_2\text{O}$ and $\text{K}_{2.75}\text{H}_{1.25}[\text{Re}_6\text{Se}_8(\text{BTA})_6] \cdot 3\text{EtOH} \cdot 7\text{H}_2\text{O}$ are isolated [45] (Fig. 5). The latter complex is considered to be a 3:1 mix of $[\text{Re}_6\text{Se}_8(1\text{H-BTA})(\text{BTA})_5]^{3-}$ and $[\text{Re}_6\text{Se}_8(1\text{H-BTA})_2(\text{BTA})_4]^{2-}$ along with the potassium ions and solvate molecules; the weaker electron-accepting ability of the selenide core compared to the sulfide core is believed to be the reason behind the isolation of slightly

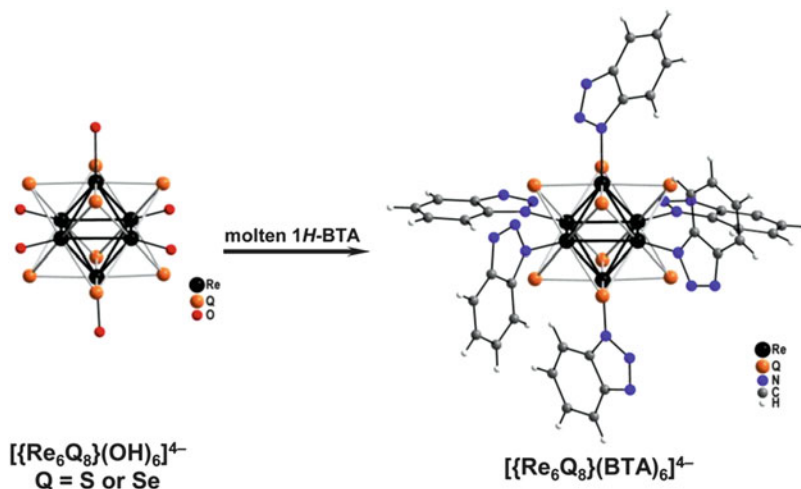


Fig. 5 The formation of $[\text{Re}_6\text{Q}_8(\text{BTA})_6]^{4-}$ from $[\text{Re}_6\text{Q}_8(\text{OH})_6]^{4-}$ and molten 1*H*-benzotriazole (1*H*-BTA). Reprinted with permission from [45] Copyright 2014 American Chemical Society

different formulations. Acidifying aqueous solutions of these complexes leads to the precipitation of $[\text{Re}_6\text{Q}_8(1\text{H-BTA})_4(\text{BTA})_2]$ (Q = S or Se). These clusters represent the first water-soluble rhenium sulfide clusters containing a heterocyclic ligand and were specifically designed to test their potential for biological applications. The authors report that both $\text{K}_4[\text{Re}_6\text{S}_8(\text{BTA})_6] \cdot 3.5\text{EtOH} \cdot 4\text{H}_2\text{O}$ and $\text{K}_{2.75}\text{H}_{1.25}[\text{Re}_6\text{Se}_8(\text{BTA})_6] \cdot 3\text{EtOH} \cdot 7\text{H}_2\text{O}$ were taken up by human cells and at the same time did not show any acute cytotoxic effects [45]. In addition, photophysical properties suggest that these complexes could have applications in bioimaging or photodynamic therapy. Also, the incorporation of BTA ligands shows a marked stability over the carboxylate-containing clusters (*vide infra*) in that the BTA ligands do not exchange with water over an extended period of time.

2.1.2 Formation of Novel Ligands via Small Molecule Activation

Small molecule activation is frequently associated with catalytic processes whereby substrates undergo transformation during their association with a metal center. It is well known that metals can alter the chemistry of coordinated ligands, yet metal reactivity is often selective making it challenging to predict which of these transformations will be achieved by a given complex. Of interest to this review is that rhenium chalcogenide cluster cores have been proven to be strong Lewis acids. In fact, they are strong enough to activate small molecules to undergo transformations either faster or under milder conditions (or both) than what would be required if the molecule was not coordinated to the cluster. Unlike so many other Lewis acidic centers, the rhenium chalcogenide clusters are relatively stable upon exposure to air and water, making them potentially attractive alternatives to other, less robust,

systems. It is important to note that, as of yet, there are no reported examples of catalysis by a rhenium chalcogenide cluster core (i.e., examples where more than one equivalent of substrate is transformed at a given time). The ability of rhenium chalcogenide clusters to activate small molecules has enabled species such as nitriles, coordinated to the $[\text{Re}_6\text{Se}_8]^{2+}$ core, to be converted into unique ligands, thereby expanding the number and type of ligands incorporated into these supraoctahedral cluster complexes. Here we discuss the application of this synthetic methodology toward the coordination of unique terminal N-donor ligands. Rhenium chalcogenide clusters are known to be substitutionally inert, normally requiring heat and extended reaction times for reaction to occur. One attractive feature of small molecule activation is that novel ligands can often be incorporated under milder conditions. Here we discuss reactions in which different anionic and neutral nucleophiles attack nitriles coordinated to the $[\text{Re}_6\text{Se}_8]^{2+}$ core.

In 2007, we discovered that inorganic azides, such as NaN_3 , react with the acetonitrile ligand in $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{NCCH}_3)](\text{BF}_4)_2$ to form tetrazolate complexes [46]. Coordination of acetonitrile to the Lewis acidic rhenium selenide cluster core activates the ligand to undergo a $[2 + 3]$ cycloaddition with N_3^- within minutes at room temperature to form $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(1,5\text{-methyltetrazolate})]^+$. This cycloaddition was classified as “click chemistry” due to the mild conditions, rapid reaction time, high yield, and purity of the product generated. This is the first click reaction reported for this family of clusters. Electrochemical studies enabled the determination of an electronic parameter (E_L) for a tetrazolate ligand and demonstrated that Lever’s method can be applied to higher-nuclearity clusters. Cyclic voltammetric studies also revealed an unusual oxidative decomposition process indicating formation of the starting nitrile complex after accessing the $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(1,5\text{-methyltetrazolate})]^{2+/+}$ couple. That same year, Orto et al. published the formation of imino ester complexes generated when simple alcohols react with analogous acetonitrile complexes [47]. Zheng recently summarized this chemistry, where hydrogen bonding of the alcohol with the bridging selenide ligands on the cluster core is proposed to explain the predominant formation of the Z-isomer [48].

This click chemistry was extended to a series of benzonitrile clusters, $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{N}\equiv\text{CC}_6\text{H}_4\text{Y})](\text{BF}_4)_2$ ($\text{Y} = -\text{H}, -\text{NH}_2, -\text{NO}_2, -\text{OMe},$ and $-\text{COCH}_3$), and the electrochemical, substitution chemistry and reactivity with inorganic azides were investigated [49]. Figure 6 shows click reactions involving $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{N}\equiv\text{CR})]^{2+}$ and various nucleophilic groups. These coordinated benzonitriles also undergo cyclization; however, only the N2 isomers are isolated, e.g., $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(2,5\text{-phenyltetrazolate})](\text{BF}_4)$ was the sole product isolated when $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{N}\equiv\text{CC}_6\text{H}_5)](\text{BF}_4)_2$ was reacted with NaN_3 [46, 49]. This is in contrast to the reaction with coordinated acetonitrile, which forms the N1 isomer at room temperature and a 50/50 mixture of isomers upon heating, demonstrating how the steric size of the nitrile substituent influences the coordination mode of the tetrazolate ring (Fig. 7). Although changing the *para* substituent on the phenyl ring had negligible impact on the redox potentials of these clusters, it did impact the rates of substitution of the coordinated nitriles. Heating $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(1,5\text{-methyltetrazolate})]^+$ (or $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(2,5\text{-phenyltetrazolate})]^+$)

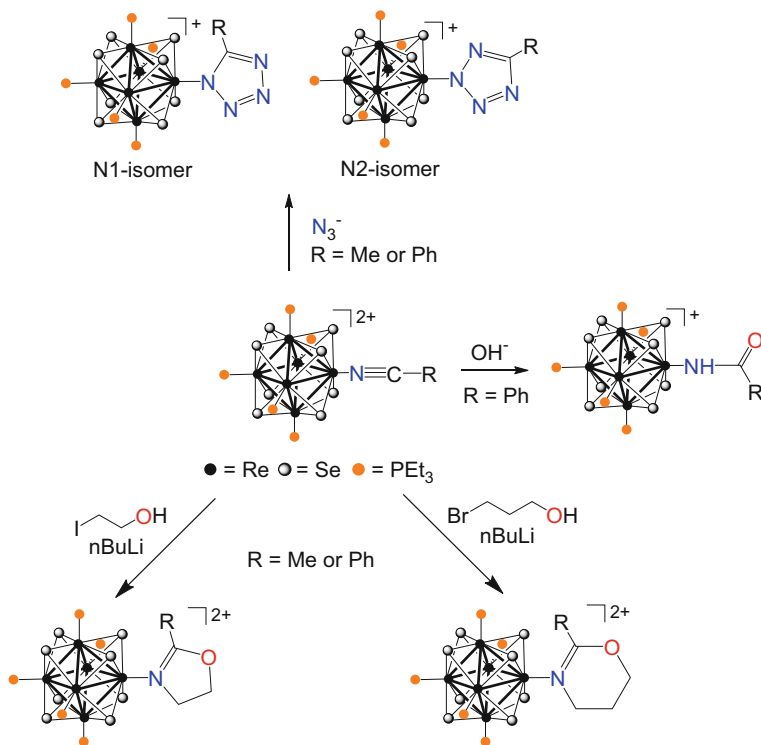


Fig. 6 Schematic diagram showing some of the click chemistry facilitated by the [Re₆Se₈]²⁺ cluster core, formation of tetrazolate, oxazoline, and oxazine rings in addition to formation of a carboxamide ligand

with a strong acid in CH₃CN leads to the release of 5-methyltetrazole (or 5-phenyltetrazole) and formation of the nitrile complex, [Re₆Se₈(PEt₃)₅(NCCH₃)]²⁺, indicating potential for catalysis. Disubstituted tetrazoles could also be generated using alkylating agents such as MeI and BnBr. Even when starting with a single tetrazolate isomer (N1 or N2), mixtures of 1,5- and 2,5-disubstituted tetrazoles were formed, and potential mechanisms for this isomerization process were discussed. It is interesting to note that nitriles coordinated to the rhenium selenide cluster core do not click with organic azides, instead, substitution and subsequent photodecomposition leads to the formation of cluster imino complexes. Zheng discusses this reaction in greater detail in a recent account [48].

Our group also reported the formation of heterocyclic triazolate ligands. Like the formation of tetrazolate ligands, the triazolates were also prepared via a click reaction. However, the triazolates were formed when coordinated azides react with free alkynes [50]. Three different triazolate cluster complexes were synthesized, [Re₆Se₈(PEt₃)₅(4,5-bis(methoxycarbonyl)-1,2,3-triazolate)](BF₄) (Fig. 8), [Re₆Se₈(PEt₃)₅(4-methoxycarbonyl-5-(1-propanol)-1,2,3-triazolate)](BF₄), and

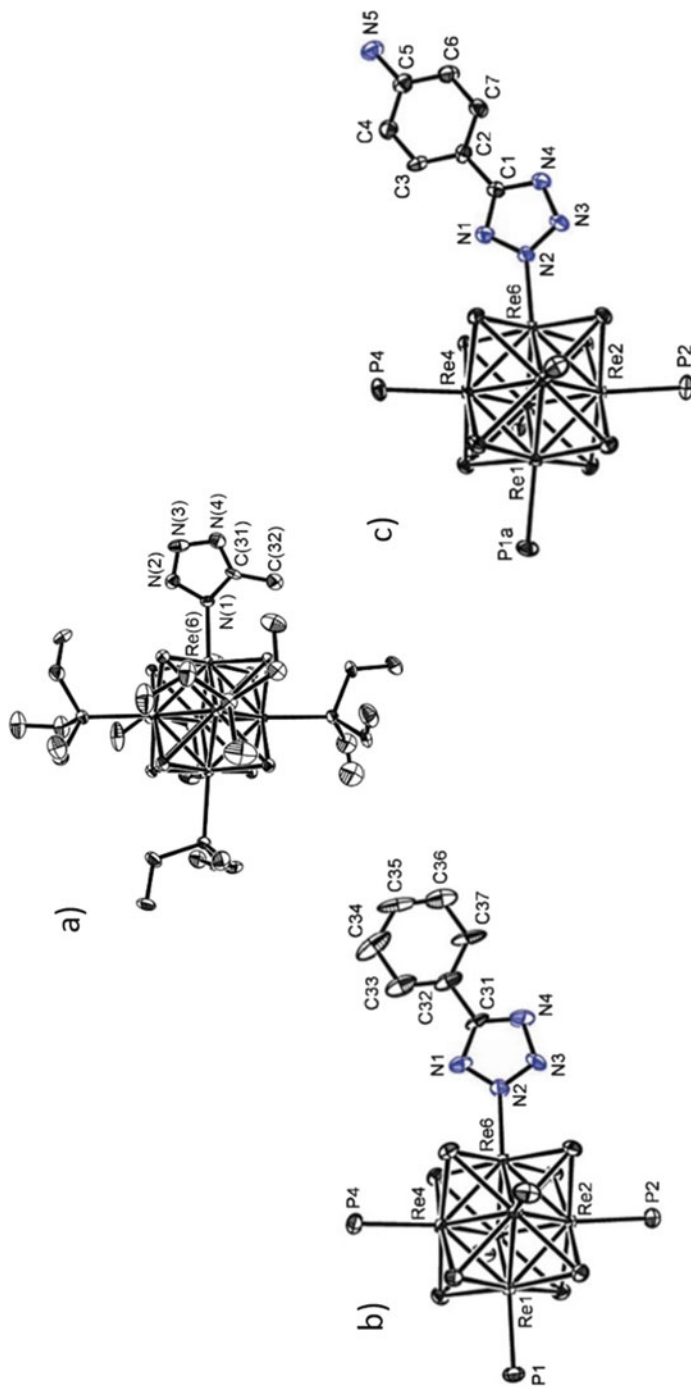
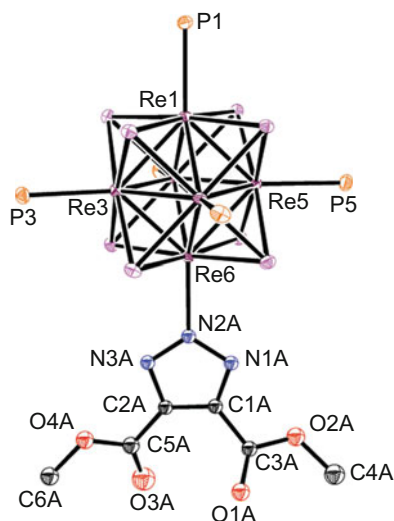


Fig. 7 Structures of (a) $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(1,5\text{-methyltetrazolate})]^+$, (b) $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(2,5\text{-phenyltetrazolate})]^+$, and (c) $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(2,5\text{-}p\text{-aminophenyltetrazolate})]^+$. (a) [46]—Reproduced by permission of The Royal Society of Chemistry. (b, c) Reprinted with permission from [49] Copyright 2012 American Chemical Society

Fig. 8 Structure of [Re₆Se₈(PEt₃)₅(4,5-bis(methoxycarbonyl)-1,2,3-triazolate)]⁺. [50]—Reproduced by permission of The Royal Society of Chemistry



cis-[Re₆Se₈(PEt₃)₄(4,5-bis(methoxycarbonyl)-1,2,3-triazolate)₂]. The latter complex demonstrates that these clusters can promote multiple azide moieties to undergo heterocyclic ring formation. Reaction of the triazolate complexes with electrophilic reagents such as methyl iodide and benzyl bromide leads to the formation of free triazoles as well as the halide containing cluster complexes, e.g., [Re₆Se₈(PEt₃)₅X]⁺ (X = I, Br).

In addition to reacting with simple alcohols, nitriles coordinated to the rhenium selenide cluster core also react with ammonia (Fig. 9). Specifically, addition of ammonia to coordinated nitriles in [Re₆Se₈(PEt₃)₅(MeCN)](BF₄)₂ and *cis*- and *trans*-[Re₆Se₈(PEt₃)₄(MeCN)₂](BF₄)₂ leads to quantitative conversion to the corresponding acetamide complexes, [Re₆Se₈(PEt₃)₅(HN=C(NH₂)CH₃)](BF₄)₂, and *cis*- and *trans*-[Re₆Se₈(PEt₃)₄(HN=C(NH₂)CH₃)₂](BF₄)₂, respectively [51]. As observed with the addition of alcohols to coordinated nitriles, the *Z*-isomer of the acetamide cluster is favored. Amidine ligand removal is achieved through reaction with trifluoroacetate, which generates acetamidinium trifluoroacetate along with the starting nitrile complex.

Most recently, we published a report detailing the reaction of coordinated nitriles with hydroxide and haloalcohols in the presence of *n*BuLi [52]. Reaction of [Re₆Se₈(PEt₃)₅(benzotrile)](BF₄)₂ with an aqueous solution of KOH at room temperature led to the formation of [Re₆Se₈(PEt₃)₅(phenylcarboxamide)]⁺ (Fig. 10). In addition, heterocyclic oxazine and oxazoline formation occurs when [Re₆Se₈(PEt₃)₅(NCPh)](BF₄)₂ and [Re₆Se₈(PEt₃)₅(NCCH₃)](BF₄)₂ undergo reaction with BrCH₂CH₂CH₂O⁻ and ICH₂CH₂O⁻ (generated in situ). The incorporation of four new heterocyclic ligands was achieved by these reactions; these include 2-methyloxazoline, 2-phenyloxazoline, 2-methyloxazine, and 2-phenyloxazine. Of

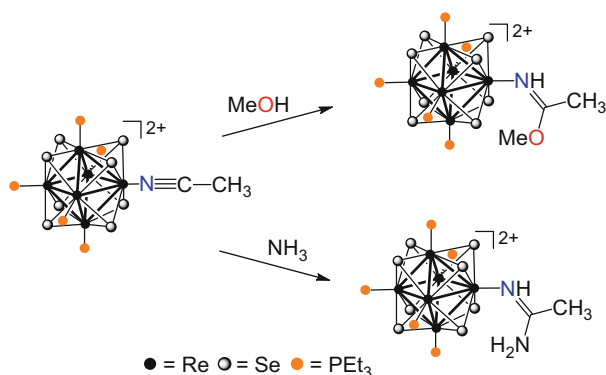


Fig. 9 Schematic diagram showing the reaction of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{NCMe})]^{2+}$ with methanol to form an imino ester ligand and with ammonia to form an acetamidine ligand

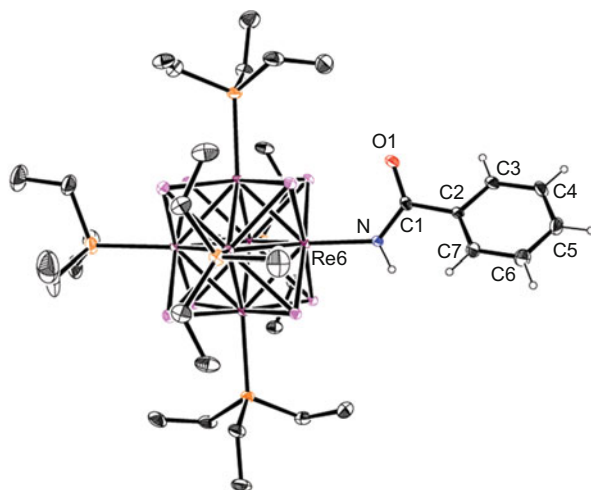


Fig. 10 Structure of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{phenylcarboxamide})]^+$. [52]—Reproduced by permission of The Royal Society of Chemistry

interest is that isolation of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(2\text{-phenyloxazine})](\text{SbF}_6)_2$ could only be achieved in the absence of light. Exposure of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(2\text{-phenyloxazine})]^{2+}$ to ambient light at room temperature led to the expulsion of 2-phenyloxazine; this represents the first time ligand removal has occurred without the addition of other reagents and under such mild conditions. Heat and UV light were shown to facilitate ligand removal of the other oxazine and oxazoline rings, and the relative strength of all four heterocyclic ligands was reported as phenyloxazine < phenyloxazoline < methyloxazine < methyloxazoline. This ranking indicates that ligand strength is dependent on both steric and electronic factors. As with some of the ligand removal studies already mentioned, the formation of the starting nitrile cluster complexes is

observed upon ligand removal indicating the potential for catalytic activity. These examples demonstrate the versatility of small molecule activation in the generation of cluster complexes containing novel ligands.

2.2 Oxygen- and Sulfur-Donor Ligands

Preparation of the first hexaqua rhenium chalcogenide cluster, $[\text{Re}_6\text{S}_8(\text{H}_2\text{O})_6]^{2+}$, was reported in 1998 [53], and a couple of years later, reports of mixed aqua/hydroxo cluster complexes appeared. The first of these, $[\text{Re}_6\text{Se}_8(\text{H}_2\text{O})_4(\text{OH})_2] \cdot 12\text{H}_2\text{O}$, was generated via the reaction of $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{Se}_8\text{I}_6]$ and aqueous NaOH [54]. Reports of the hexahydroxo complexes, $\text{K}_4[\text{Re}_6\text{Se}_8(\text{OH})_6] \cdot 8\text{H}_2\text{O}$ and $\text{K}_4[\text{Re}_6\text{S}_8(\text{OH})_6] \cdot 8\text{H}_2\text{O}$, followed; these were prepared from the chalcogenides, $\text{Re}_6\text{Q}_8\text{Br}_2$ [55]. As with so many of the single metal aqua/hydroxo complexes, the nature of the ligands is dependent on pH. A study involving the dependence of formulation and spectroscopic properties of $\text{K}_4[\text{Re}_6\text{Se}_8(\text{OH})_6] \cdot 8\text{H}_2\text{O}$ and $\text{K}_4[\text{Re}_6\text{S}_8(\text{OH})_6] \cdot 8\text{H}_2\text{O}$ as a function of pH led to the formation of $\text{K}_2[\text{Re}_6\text{Se}_8(\text{H}_2\text{O})_2(\text{OH})_4] \cdot 2\text{H}_2\text{O}$, $[\text{Re}_6\text{S}_8(\text{H}_2\text{O})_4(\text{OH})_2] \cdot 12\text{H}_2\text{O}$, $[\text{Re}_6\text{S}_8(\text{H}_2\text{O})_6][\text{Re}_6\text{S}_8\text{Br}_6] \cdot 10\text{H}_2\text{O}$, and $[\text{Re}_6\text{Se}_8(\text{H}_2\text{O})_4(\text{OH})_2]$ [56]. A number of these aqua/hydroxo cluster complexes have been characterized via X-ray crystallography, and the data show extensive hydrogen-bonding interactions in the solid state. In fact, a comparison of the structures of $[\text{Re}_6\text{Se}_8(\text{H}_2\text{O})_4(\text{OH})_2]$ [56] and $[\text{Re}_6\text{Se}_8(\text{H}_2\text{O})_4(\text{OH})_2] \cdot 12\text{H}_2\text{O}$ [54] emphasizes how much the hydration of these complexes can influence the solid-state structure. Brylev et al. also studied the chemical and spectroscopic properties of these compounds in solution and were able to describe the equilibrium that takes place as pH is varied [56]. There are also examples of complexes containing mixed terminal ligands, hydroxide/water with ligands such as cyanide (or cyanide bridging to another metal complex), or pyridine-based ligands (e.g., $[\text{Re}_6\text{Se}_8(\text{CN})_4(\text{OH})_2]^{4-}$ and $[\text{Re}_6\text{S}_8(\text{OH})_2(4,4'\text{-bipyridine})_4]$) [38, 57]. A unique feature of these complexes is that they often display an extensive array of hydrogen bonding to the coordinated aqua or hydroxo ligands as well as to waters of solvation.

The hydroxo ligands are reported to be relatively labile in that they can be readily substituted by halides; they can also act as bridging ligands in the formation of coordination polymers with Group 2 metal ions [55, 58]. Carboxylate coordination to the rhenium chalcogenide cluster cores is not as common as with $[\text{Mo}_6\text{X}_8]^{4+}$ clusters but has been achieved via the reaction of the aforementioned hydroxide-containing clusters with free carboxylic acids. The first reported example of carboxylate coordination involved an amphiphilic diblock copolymer, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{CH}_2\text{CONH-GlyPheLeuGlyPheLeu-COO}^-$, with a carboxylate terminus. This was coordinated to the rhenium sulfide cluster core forming $\text{K}_4[\text{Re}_6\text{S}_8(\text{OH})_5(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{CH}_2\text{CONH-GlyPheLeuGlyPheLeu-COO})]$. This long-chain carboxylate was designed to improve cellular uptake, and studies comparing $\text{K}_4[\text{Re}_6\text{Q}_8(\text{OH})_6] \cdot 8\text{H}_2\text{O}$ (Q = S or Se) and $\text{K}_4[\text{Re}_6\text{S}_8(\text{OH})_5(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{CH}_2\text{CONH-GlyPheLeuGlyPheLeu-COO})]$ were tested for cellular

uptake and toxicity with HeLa cells (human cervical epithelial adenocarcinoma cells) [59]. Notably, both $K_4[Re_6S_8(OH)_6] \cdot 8H_2O$ and $K_4[Re_6S_8(OH)_5(CH_3O(CH_2CH_2O)_{12}CH_2CONH-GlyPheLeuGlyPheLeu-COO)]$ were found to permeate cell walls and populate the cytoplasm and nucleus. The absence of acute cytotoxic properties at low concentrations indicates that there is potential for using rhenium sulfide clusters for diagnostic or therapeutic agents; however, as noted below, the stability of rhenium chalcogenide carboxylates in aqueous solution limits the applicability of carboxylate-containing clusters.

Hexacarboxylate clusters were obtained when hexahydroxo clusters were utilized as starting materials. For example, reaction of $M_4[Re_6S_8(OH)_6] \cdot 8H_2O$ ($M = K^+$ or Cs^+) with formic acid leads to the generation of $M_4[Re_6S_8(HCOO)_6]$ ($M = K^+$ or Cs^+). Figure 11 shows the structure of $Cs_4[Re_6S_8(HCOO)_6]$. 1H NMR studies of $K_4[Re_6S_8(HCOO)_6]$ in D_2O indicate a small amount of free formate is present upon immediate dissolution, the resonance for which increases in intensity over time (weeks) [60]. Studies in H_2O indicate that additional further substitutions occur, leading to the eventual precipitation of $[Re_6S_8(H_2O)_4(OH)(HCOO)]$. In order to better understand the ligand substitution chemistry of the hexahydroxo species, reactions involving $[Re_6Q_8(OH)_6]^{4-}$ with different pyridine ligands were undertaken [61]. Reaction with 4-*t*-butylpyridine (TBP) led to the formation of *trans*- $[Re_6Q_8(TBP)_4(OH)_2]$. It is believed that the bulky *t*-butyl groups prevent

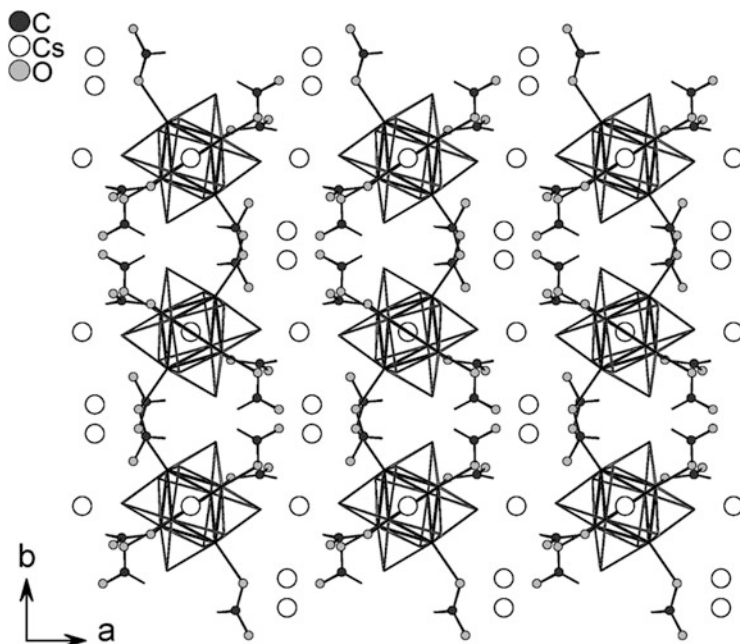


Fig. 11 The crystal structure of $Cs_4[Re_6S_8(HCOO)_6]$ is shown to have an alternation of cationic and anionic layers parallel to the bc plane. Reprinted with permission from [60] Copyright 2009 American Chemical Society

aggregation and allow for a clean substitution to take place. Unlike substitution of the halide ligands in $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ with triethylphosphine, site-differentiation appears to favor formation of the neutral species, which precipitate from the aqueous reaction mixture. The authors comment on how this can be used as a general procedure for the formation of *trans*- $[\text{Re}_6\text{Q}_8\text{L}_4(\text{OH})_2]$ (L = a neutral ligand) clusters. Of interest here is that reaction of *trans*- $[\text{Re}_6\text{Q}_8(\text{TBP})_4(\text{OH})_2]$ with derivatives of 3,4,5-trihydroxybenzoic acid (or gallic acid) leads to the formation of *trans*- $[\text{Re}_6\text{Q}_8(\text{TBP})_4(3,4,5\text{-trismethoxybenzoate})_2]$ and *trans*- $[\text{Re}_6\text{Q}_8(\text{TBP})_4(3,4,5\text{-tris(octyloxy)benzoate})_2]$; these gallic acid derivatives were utilized in attempts to generate mesomorphic materials [61]. All of the reported carboxylate ligands act as monodentate ligands.

The only example of sulfonate ligand coordination is that of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{OTs})](\text{OTs})$; this was prepared from the reaction of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5\text{I}]\text{I}$ with silver(I) *p*-toluenesulfonate (OTs^-) [62]. Sulfonate ligands are traditionally weakly coordinating; therefore, this complex was prepared to be utilized as a starting material for the preparation of other cluster complexes. A few rhenium chalcogenide clusters containing alkoxide ligands have been reported, but they are not well studied. The synthesis and X-ray structures of the mono-alkoxide complexes, $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{OMe})](\text{PF}_6)$ and $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{OPh})](\text{PF}_6)$, were reported [63, 64]. The methoxy complex was prepared from $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{py})](\text{PF}_6)_2$ and NaOMe, while the phenoxy complex was prepared via reaction of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{OMe})](\text{PF}_6)$ with phenol. The only other known alkoxide complex is $(\text{Bu}_4\text{N})_4[\text{Re}_6\text{S}_8(\text{OC}_6\text{H}_4\text{NO}_2)_6]$ which was reported as a private communication (S. Nagashima, private communication, Cambridge structural database, 2018).

2.3 Carbon-Donor Ligands

Cyanide is by far the most common terminal C-donor ligand that has been incorporated into hexanuclear $[\text{Re}_6\text{Q}_8]^{2+}$ -based cluster compounds [27]. However, since CN^- is typically considered a pseudohalide, we will not delve into this area any further. Here, we will focus on studies involving more traditional organometallic ligands such as carbonyls and carbenes. Numerous examples of transition metal cluster carbonyls have been reported in the literature, so many in fact that there are books dedicated to the topic [65]. Thus, it is somewhat surprising that there are so few examples of organometallic octahedral clusters.

Zheng et al. prepared the first examples of organometallic rhenium chalcogenide clusters by coordinating CO to the $[\text{Re}_6\text{Se}_8]^{2+}$ core. The synthesis involved reacting $[\text{Re}_6\text{Se}_8(\text{PET}_3)_x\text{I}_{6-x}]^{x-4}$ ($x = 4$ and 5) with AgSbF_6 in a methylene chloride solution saturated with CO to generate $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{CO})](\text{SbF}_6)_2$ and *cis*- and *trans*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4(\text{CO})_2](\text{SbF}_6)_2$, respectively [66, 67]. Of interest is that the CO stretching frequency, $\nu(\text{CO})$, shifts to lower wavenumbers upon coordination. This was surprising at first since it was originally believed that the highest occupied molecular orbitals (HOMOs) of $[\text{Re}_6\text{Se}_8]^{2+}$ did not have the appropriate orientation for back donation to CO. Computational studies revealed that backbonding from the

cluster core is possible; however, the majority of the electron density (approximately 50%) comes from the nearby selenide ligands. In terms of reactivity of the coordinated carbonyl, it was mentioned that methyl lithium does react with $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{CO})](\text{SbF}_6)_2$ to form the corresponding acyl complex; as of yet, there are no reports discussing conversion of this acyl complex into a carbene. A more detailed summary of these studies has been published [48].

Incorporation of carbene ligands, another important organometallic ligand, into transition metal clusters is quite limited in comparison with the chemistry of single metal complexes. Our group has begun to investigate the viability of carbene containing rhenium chalcogenide clusters. In 2015, we reported the preparation and study of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{SIMes})](\text{OTs})_2$, *trans*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{SIMes})_2](\text{OTs})_2$, and $[\text{Re}_6\text{S}_8(\text{PEt}_3)_2(\text{IMes})_2\text{Cl}_2]$ (SIMes = 1,3-bis(dimesityl)imidazol-4,5-dihydro-2-ylidene and IMes = 1,3-bis(dimesityl)imidazol-2-ylidene) (Fig. 12) [68]. These represent the first examples of hexanuclear cluster complexes containing a carbene ligand of any type (*N*-heterocyclic carbene, Fischer or Schrock). $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{OTs})](\text{OTs})$ was initially used as the starting material for the preparation of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{SIMes})]^{2+}$. However, we later found that SIMes was strong enough to replace the iodo ligand in $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]^+$. This is the only example of substitution of a $[\text{Re}_6\text{Q}_8]^{2+}$ coordinated halide where substitution did not require the use of heat, silver(I) salts, or photoirradiation. NHCs are considered spectator ligands, and as such the chemistry of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{SIMes})](\text{OTs})_2$ was limited. The advantage of $[\text{Re}_6\text{S}_8(\text{PEt}_3)_2(\text{IMes})_2\text{Cl}_2]$ is that there is potential for further reactivity of the halide ligands. The Re-C bond lengths averaged about 2.22 Å, slightly longer than the Re-CO bond lengths reported by Zheng and coworkers (average of 2.04 Å) in the carbonyl-containing clusters discussed above. We are currently in the process of investigating the possibility of incorporating other types of carbene ligands into these cluster complexes. Our group has also prepared the isonitrile cluster complex, $[\text{Re}_8\text{Se}_8(\text{PEt}_3)_5(\text{C}\equiv\text{NPh})](\text{SbF}_6)_2$ [69]. We are in the process of conducting X-ray crystal structure analyses as well as investigating the physical properties of this newly prepared species.

3 $[\text{Mo}_6\text{X}_8]^{4+}$ -Based Clusters

3.1 Nitrogen-Donor Ligands

Shriver and coworkers reported the reaction of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{OTf})_6]$ ($\text{OTf} = \text{CF}_3\text{SO}_3^-$) with 4,4'-bipyridine in the preparation of microporous xerogels and with 4-vinylpyridine in the preparation of polymeric materials [70, 71]. However, the first discrete molybdenum halide cluster complex containing a non-pseudohalide N-donor ligand to be isolated was reported about 10 years later by Perrin and Astruc and coworkers; $[\text{Mo}_6\text{Br}_8\text{L}_6](\text{OTf})_4$ (L = pyridine, 4-*t*-butylpyridine, 4-vinylpyridine, and a new dendronic pyridine derivative 3,3'- $\{\text{CH}_2\text{O}p\text{-C}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3\}_2\text{py}$) were synthesized via the reaction of the corresponding

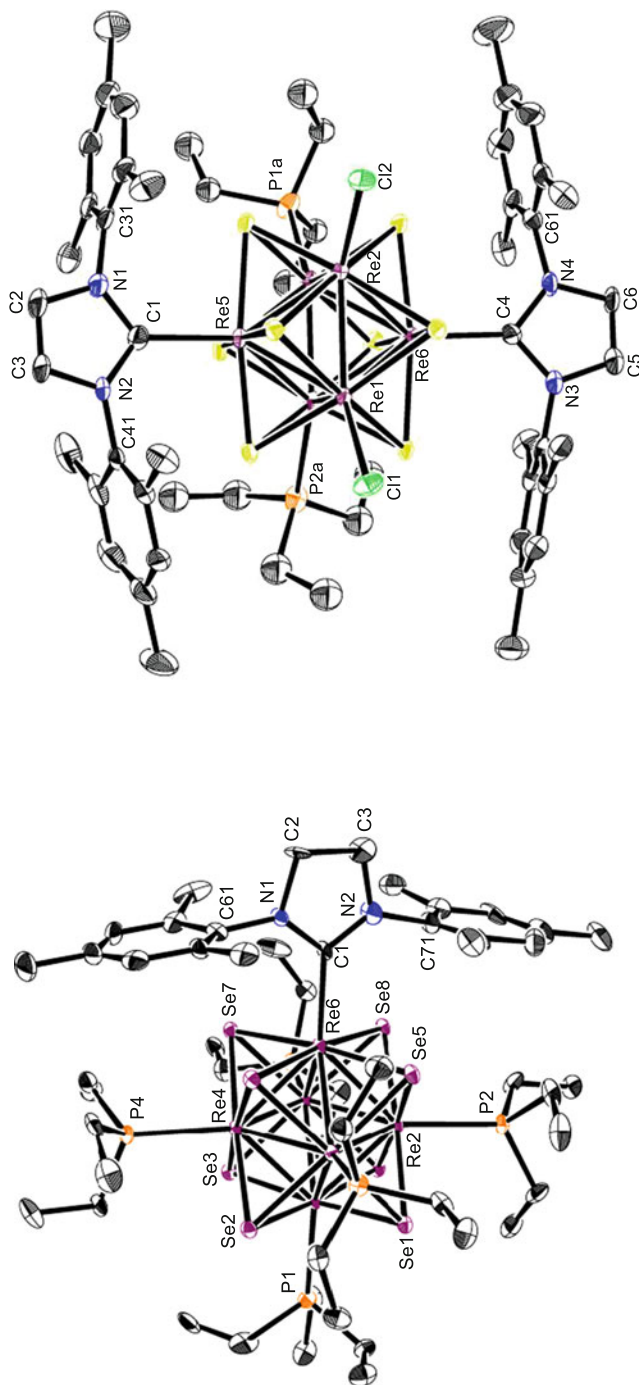


Fig. 12 Structures of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{SIMes})]^{2+}$ (left) and $[\text{Re}_6\text{S}_8(\text{PEt}_3)_2(\text{IMes})_2\text{Cl}_2]$ (right) [68]. Reproduced by permission of The Royal Society of Chemistry

hexatriflate cluster with an excess of the given pyridine ligand [72]. Another report details the synthesis of the iodo-based clusters $[\text{Mo}_6\text{I}_8\text{L}_6](\text{OTf})_4$ ($\text{L} = \text{pyridine}, 4\text{-}t\text{-butylpyridine}, 4\text{-vinylpyridine}$) and $(\text{Bu}_4\text{N})[\text{Mo}_6\text{Br}_{13}\text{L}]$ ($\text{L} = 4\text{-}t\text{-butylpyridine}, 4\text{-vinylpyridine}, \text{and pyridine-based dendrons}$) [73]. $[\text{Mo}_6\text{Br}_8(\text{py})_6](\text{OTf})_4$ is only sparingly soluble in organic solvents making it somewhat challenging to work with. In addition, stability studies indicate that while $[\text{Mo}_6\text{Br}_8(\text{py})_6](\text{OTf})_4$ is stable in air and acetone, even in the presence of light, the complex decomposes in methanol and in water [72]. As was seen with the rhenium chalcogenide clusters, the advantage of incorporating pyridine-based ligands is that cluster functionalization can be achieved simply by utilizing substituted pyridines. For example, the organometallic pyridine ligands $[\text{Ru}(\text{Cp}(\text{PPh}_3)_2(\eta^1\text{-C}\equiv\text{C-4-pyridinyl}))]$ and 1-ferrocenyl-2-(4-pyridinyl)acetylene were incorporated through reaction with $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8(\text{OTf})_6]$ leading to the formation of light-sensitive clusters surrounded by organometallic fragments (Fig. 13) [73, 74]. Cluster-cored dendrimers were also prepared through the reaction of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{OTf})_6]$ ($\text{X} = \text{Br}$ or I) or $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_{13}(\text{OTf})]$ with a variety of monopyridine dendrons. Based on the extensive chemistry of rhenium chalcogenide clusters containing pyridine-based ligands, it is somewhat surprising that there are not more examples of pyridine containing molybdenum halide clusters; this could be due to issues of solubility as well as stability issues of these cluster complexes.

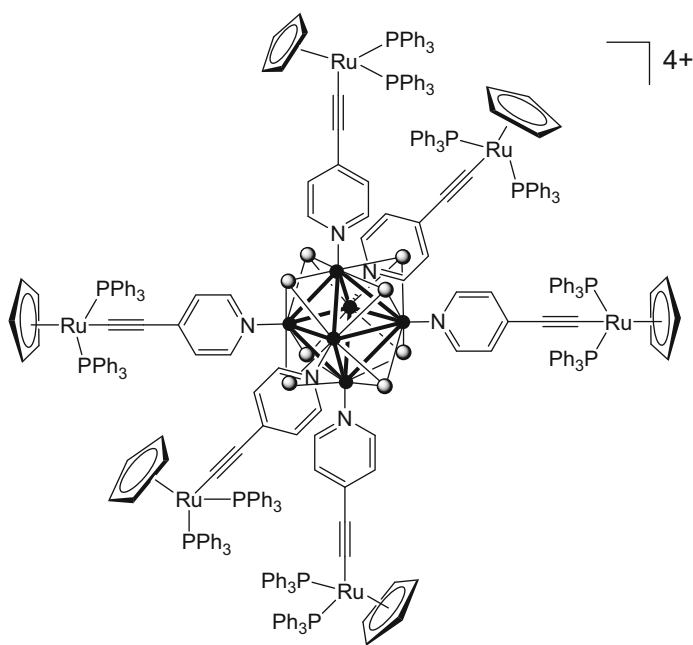


Fig. 13 Visual representation of $[\text{Mo}_6\text{Br}_8(\mu\text{-py-C}\equiv\text{C-RuCp}(\text{PPh}_3)_2)_6]^{4+}$. Adapted with permission from [73] Copyright 2006 American Chemical Society

3.2 Oxygen- and Sulfur-Donor Ligands

Carboxylate ligands have become the most widely incorporated apical ligand in molybdenum halide cluster complexes. The most common synthetic route used to prepare carboxylate-containing cluster complexes involves the reaction of (Bu₄N)₂[Mo₆X₁₄] (X = Cl, Br, I) with silver(I) carboxylates, where the removal of the terminal halogens and precipitation of silver halide salts drives the reaction to completion. One disadvantage of this synthesis is that commercially available functionalized carboxylates are limited; therefore, these often need to be synthesized as well. Another popular route for the molybdenum iodide clusters uses Na₂[Mo₆I₈(OMe)₆] and free carboxylic acids. The key advantage to this method is that the methanol by-product that is generated upon reaction is easily removed, simplifying the purification process. In the studies discussed here, both synthetic methods have been utilized. The first example of a carboxylate-containing [Mo₆X₈]⁴⁺ cluster complex was that of (Bu₄N)₂[Mo₆Cl₈(CF₃COO)₆], which was prepared from the starting hexahalide cluster and silver(I) trifluoroacetate [75]. Attempts at substituting the trifluoroacetate ligands of [Mo₆Cl₈(CF₃COO)₆]²⁻ with sodium acrylate resulted in an incomplete substitution and the isolation of a mixture of complexes, i.e., (Bu₄N)₂[Mo₆Cl₈(CF₃COO)_{6-n}(CH₂=CHCOO)_n]. A study of a series of molybdenum halide complexes containing the heptafluorobutyrate (C₃F₇COO⁻) ligands was significant in that it led to the discovery that (1) the cluster containing bridging iodide ligands, i.e., (Bu₄N)₂[Mo₆I₈(C₃F₇COO)₆] (Fig. 14, left), possessed enhanced photophysical properties compared to the corresponding molybdenum chloride and bromide clusters and (2) modifying the terminal ligands can improve the photophysical performance of these luminescent cluster complexes [76]. These findings motivated Kirakci and coworkers to prepare the trifluoroacetate iodo cluster, (Bu₄N)₂[Mo₆I₈(CF₃COO)₆] (Fig. 14, right), and to conduct a comparative study

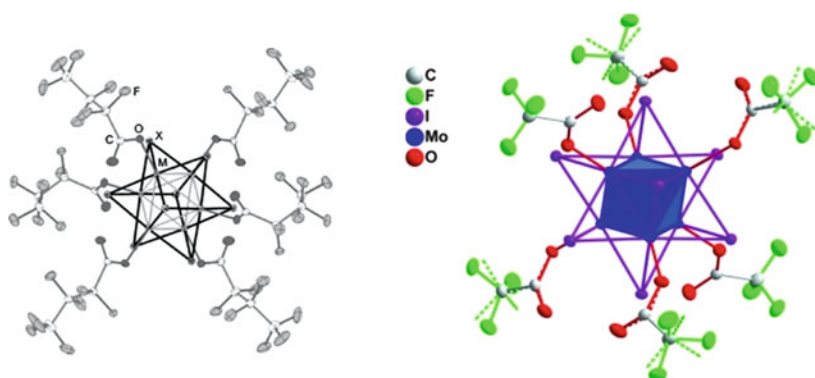


Fig. 14 Structures of [Mo₆Cl₈(C₃F₇COO)₆]²⁻ (left). Reproduced from [76] with permission from The Royal Society of Chemistry and [Mo₆I₈(CF₃COO)₆]²⁻ (right). Reprinted with permission from [77] Copyright 2012 Wiley-VCH Verlag GmbH & Co

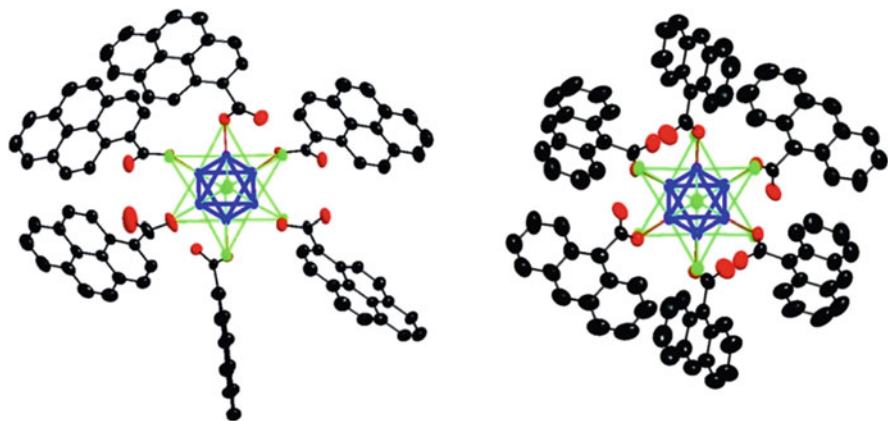


Fig. 15 Structures of $[\text{Mo}_6\text{I}_8(\text{pyrene-COO})_6]^{2-}$ (left) and $[\text{Mo}_6\text{I}_8(\text{anthracene-COO})_6]^{2-}$ (right). Reprinted with permission from [79] Copyright 2014 Wiley-VCH Verlag GmbH & Co

of the redox and excited state properties of the following six complexes, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{CF}_3\text{COO})_6]$ and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_{14}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [77, 78]. The data show that both $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8(\text{CF}_3\text{COO})_6]$ and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{CF}_3\text{COO})_6]$ display long excited state lifetimes and high yields of singlet oxygen formation. However, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{CF}_3\text{COO})_6]$ is unique in that it has an extremely high quantum yield ($\phi_{\text{em}} = 1$, or 100% efficient) and a narrower emission band than the other complexes. This comparative study led to the conclusion that pairing terminal carboxylate ligands with the $[\text{Mo}_6\text{I}_8]^{4+}$ core optimizes the luminescent properties of these clusters. However, hexanuclear molybdenum clusters typically display relatively low molar absorption coefficients, which is a disadvantage in that higher concentrations would be needed for a reasonable response in an application setting. In order to address this issue, aromatic carboxylates, which could potentially act as an antenna and transfer their absorbed energy to the cluster core for a brighter luminescence, were incorporated. Reaction of $\text{Na}_2[\text{Mo}_6\text{I}_8(\text{MeO})_6]$ with carboxylic acids of anthracene and pyrene led to the formation of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{pyrene-COO})_6]$ and $(\text{Ph}_4\text{P})_2[\text{Mo}_6\text{I}_8(\text{anthracene-COO})_6]$ (Fig. 15) [79]. Grafting strongly absorbing chromophores such as anthracene and pyrene to the carboxylate ligand did increase molar absorption coefficients; however, there was a marked decrease in the quantum efficiency of the $(\text{Ph}_4\text{P})_2[\text{Mo}_6\text{I}_8(\text{anthracene-COO})_6]$ complex indicating the fine balance required in tuning the luminescent properties of these systems.

In an effort to develop the applications of these clusters, adamantane carboxylate was coordinated to the molybdenum iodide cluster core. The synthesis of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{adamantane-COO})_6]$ (from $\text{Na}_2[\text{Mo}_6\text{I}_8(\text{MeO})_6]$ and adamantane-1-COOH) was published along with its incorporation into films and nanoparticles [80]. This complex is reported to be the first radioluminescent octahedral complex capable of X-ray-induced singlet oxygen, making it the first in a new class of nanoscintillators with potential applications in X-ray-induced photodynamic therapy. The ability of these clusters to generate singlet oxygen upon excitation means

that they could have practical applications for oxygen probing or singlet oxygen sensitization in biological systems. However, their low stability in water at physiological pH leads to the formation of aqua-hydroxo complexes, which have been known to be toxic once aggregated. Kirakci and coworkers explored the idea of utilizing ligands that form inclusion complexes with macrocycles which would provide a hydrophobic environment for the cluster. This led to the formation of molybdenum clusters containing *closo*-dicarbaborane C-carboxylates: Na₂[Mo₆I₈(1-OOC-1,2-*closo*-C₂B₁₀H₁₁)₆], Na₂[Mo₆I₈(1-OOC-1,7-*closo*-C₂B₁₀H₁₁)₆], and Na₂[Mo₆I₈(1-OOC-1,12-*closo*-C₂B₁₀H₁₁)₆] all of which have an affinity for a β -cyclodextrin polymer [81]. The physical properties of the β -cyclodextrin polymer containing Na₂[Mo₆I₈(1-OOC-1,7-*closo*-C₂B₁₀H₁₁)₆] were investigated, and potential applications discussed. Another example involves the coordination of a benzoate ligand containing a diphenylphosphino moiety at the *para* position, i.e., Na₂[Mo₆I₈(OOC₆H₄PPh₂)₆] (Fig. 16). Although sterically crowded, the phosphorus atom is still able to donate to another metal center enabling the formation of coordination polymers. Kirakci and coworkers took advantage of this property in designing coordination polymers with palladium that were capable of catalyzing cross-coupling reactions [82].

Multiple cluster complexes containing a wide variety of carboxylate ligands have been prepared and studied in order to learn how to gain better control over these various factors. Two series of molybdenum clusters, (Bu₄N)₂[Mo₆I₈(RCOO)₆] (RCOO⁻ = acetate, pivalate, α -furancarboxylate, benzoate, 3,5-dimethylbenzoate, perfluorobenzoate, 3,5-dinitrobenzoate, 1-naphthoate, and perfluoropropionate) and (Bu₄N)₂[Mo₆Br₈(RCOO)₆] (RCOO⁻ = acetate, pivalate, α -furancarboxylate, 3,5-dimethylbenzoate, perfluorobenzoate, 3,5-dinitrobenzoate, 1-naphthoate, 4-nitrobenzoate, 4-cyanobenzoate, 3,5-dimethylbenzoate, and 4-methoxybenzoate), were synthesized and fully characterized and their structural, electrochemical, and

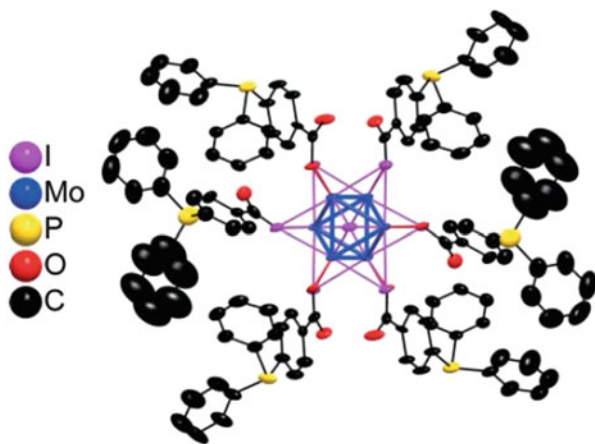


Fig. 16 Structure of [Mo₆I₈(OOC₆H₄PPh₂)₆]²⁻. Reprinted with permission from [82] Copyright 2016 Wiley-VCH Verlag GmbH & Co

photophysical properties investigated [83–86]. The dependence of some of these properties on the pK_a s of the carboxylic acids and how this dependence can be used to tune the redox, spectroscopic, and luminescent properties is discussed. It is worth noting that with increasing knowledge of how terminal ligands can be used to tune the physical properties of the octahedral molybdenum clusters and with a variety of carboxylate ligands available, researchers have started to design materials which incorporate these carboxylate-containing clusters for specific applications. We provide a few references as an example of some research in this area [87–90], but since this review is focused on discrete/soluble cluster systems, we will not describe these studies in further detail.

There are examples of molybdenum halide clusters containing alkoxide ligands, although this area of research is not as well developed as that of the carboxylate ligands. In an effort to utilize $[\text{Mo}_6\text{X}_8]^{4+}$ clusters as building blocks in the generation of supramolecular arrays, Shriver and coworkers utilized the 4-hydroxybenzamide to prepare $\text{Na}_2[\text{Mo}_6\text{Cl}_8(\text{OC}_6\text{H}_4\text{CONH}_2)_6]$ [91]. The addition of 2.2.2-cryptand to the reaction mixture leads to the crystallization of $(\text{cryptNa})_2[\text{Mo}_6\text{Cl}_8(\text{OC}_6\text{H}_4\text{CONH}_2)_6]$, which is described as a hydrogen-bonded organic-inorganic network. In trying to prepare hybrid dendrimers that could potentially take advantage of the interesting electrochemical and photophysical properties of the molybdenum halide cluster core, Gorman and coworkers also incorporated phenolate-based ligands in the preparation of dendrimers. Different focally substituted phenol dendrons, containing 0–2 hyperbranches, were prepared and then coordinated to the $[\text{Mo}_6\text{Cl}_8]^{4+}$ cluster core [92]. This synthesis involved reacting $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{OMe})_6]$ with different dendrons, where the methoxide ligand is believed to deprotonate the incoming substituted phenols. The structure of the $[\text{Mo}_6\text{Cl}_8(p\text{-methoxyphenolate})_6]^{2-}$ anion is shown in Fig. 17; this is the cluster containing the zero-hyperbranched ligand. These cluster dendrimers are reported as having the potential to be utilized for catalysis and for potentially controlling electron transfer. In a separate study, Méry et al. incorporated dendronic phenolate ligands $(\text{OC}_6\text{H}_4\text{C}\{\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Fc}\}_3)$ to the $[\text{Mo}_6\text{Br}_8]^{4+}$ core generating an octadecylferrocenyl dendrimer which is able to recognize the biologically important adenosyl triphosphate di-anion (ATP^{2-}) [74]. Two nitrophenolate cluster complexes, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(4\text{-nitrophenolate})_6]$ and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(2,4\text{-dinitrophenolate})_6]$, were prepared by Sokolov and coworkers in an effort to test the luminescent properties of another $[\text{Mo}_6\text{I}_8]^{4+}$ cluster containing terminal ligands with different electronic properties [93]. These were prepared from $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_{14}]$ using silver salts of 4-nitrophenolate and 2,4-dinitrophenolate. The resulting cluster complexes were shown to have high molar absorption coefficients, indicative of a strong ligand-cluster electronic interaction; this is believed to impact the intensity of the emission band. Although these complexes are also strong emitters, their quantum yields and excited state lifetimes do not match those of some other molybdenum iodide clusters, such as $[\text{Mo}_6\text{I}_8(\text{C}_3\text{F}_7\text{COO})_6]^{2-}$ [76] and as $[\text{Mo}_6\text{I}_8(\text{CF}_3\text{COO})_6]^{2-}$ [77].

The preparation of sulfonate complexes has been driven by the desire to prepare cluster complexes with weakly coordinating ligands that can be used as starting materials in the preparation of other cluster complexes. Shriver prepared triflate

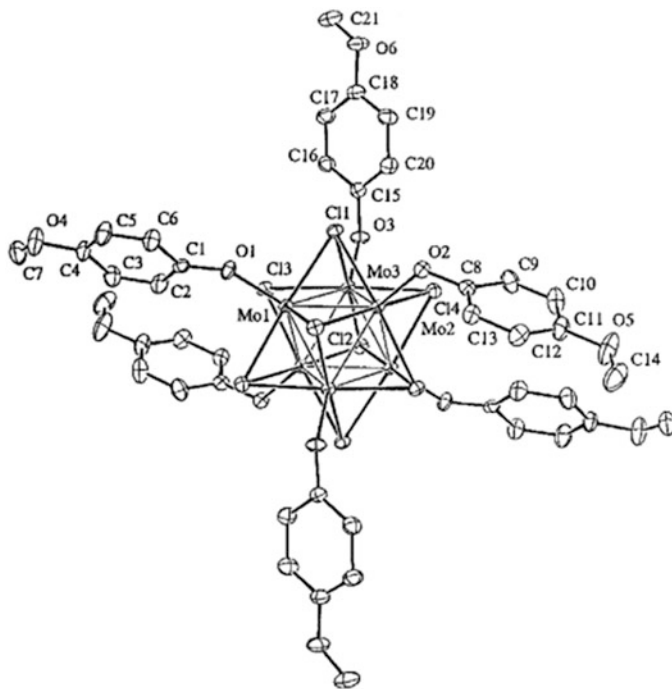


Fig. 17 Structure of $[\text{Mo}_6\text{Cl}_8(\text{OC}_6\text{H}_4\text{OCH}_3)_6]^{2-}$. Reproduced from [92] with permission from The Royal Society of Chemistry

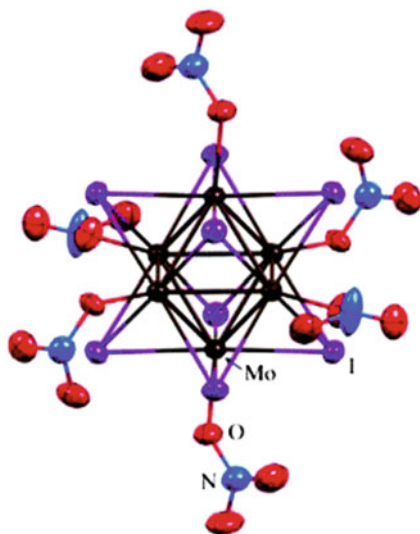
(⁻OTf) and tosylate (⁻OTs) cluster complexes, i.e., $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{OTf})_6]$ and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{OTs})_6]$ and conducted ligand substitution studies [28, 94]. More recently the complete series of molybdenum halide hexatosylate (⁻OTs) and hexabzenesulfonate (PhSO_3^-) complexes were synthesized and structurally characterized, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{OTs})_6]$ and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{PhSO}_3)_6]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [95, 96]. These were prepared in acetone by reacting silver(I) tosylate, or silver(I) benzenesulfonate, with the hexahalide clusters, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_{14}]$, and both the electrochemical and photophysical properties of these clusters were investigated. The latest study in this area reports the preparation and study of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{OTf})_6]$ along with some tungsten halide cluster complexes containing triflate ligands [97]. Cyclic voltammetric studies show that substitution of the terminal halide ligands for sulfonate ligands increases the stability of the cluster complex toward oxidation. In addition, the iodo-bridged clusters, $[\text{Mo}_6\text{I}_8(\text{sulfonate})_6]^{2-}$, show superior luminescent properties (longer excited state lifetimes and higher quantum yields) compared with $[\text{Mo}_6\text{X}_8(\text{sulfonate})_6]^{2-}$ ($\text{X} = \text{Br}, \text{Cl}$) as was observed with the molybdenum clusters containing carboxylate ligands. However, there are issues with the long-term stability of the sulfonate containing

cluster complexes in solution, indicating clusters containing these ligands are better suited as precursors in the coordination of more strongly donating ligands.

Nitrate (NO_3^-) and nitrito (ONO^-) ligands have also been coordinated to molybdenum halide cluster cores. The hexasubstituted complexes that have been isolated include $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{NO}_3)_6]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [98, 99] and $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_8(\text{NO}_2)_6]$ ($\text{X} = \text{Cl}$ and Br) [98]. These were all prepared from $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{X}_{14}]$ and either AgNO_3 or AgNO_2 , and X-ray structural data was reported for $\text{A}_2[\text{Mo}_6\text{X}_8(\text{NO}_3)_6]$ ($\text{A} = \text{Bu}_4\text{N}$ or AsPh_4 ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $(\text{PPh}_4)_2[\text{Mo}_6\text{Cl}_8(\text{NO}_2)_6]$. Figure 18 shows the structure of the $[\text{Mo}_6\text{I}_8(\text{NO}_3)_6]^{2-}$ anion. The structural data indicates O-bound coordination for all species, and IR spectroscopy confirmed O-bound coordination of the nitrito ligands. Photophysical measurements of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{NO}_3)_6]$ show that it has the highest quantum yield and longest excited state lifetime of any previously reported metal cluster complex with an exclusively inorganic ligand environment. Not surprisingly, however, the nitrate ligands are similar to the sulfonate ligands in that they are reported to be labile making these complexes potentially useful precursors. The authors demonstrated this by using the hexanitrate cluster to incorporate the $[\text{Mo}_6\text{I}_8]^{4+}$ cluster core into thiol-functionalized polystyrene microspheres [99].

Two phosphine oxide ligands were coordinated in the synthesis of $[\text{Mo}_6\text{Cl}_8(\text{OPEt}_3)_2\text{Cl}_4]$ and $[\text{Mo}_6\text{Cl}_8(\text{OP}(n\text{Pr})_3)_2\text{Cl}_4]$ [100]. These complexes were prepared in a manner similar to how the analogous phosphine clusters, $[\text{Mo}_6\text{Cl}_8(\text{PR}_3)_2\text{Cl}_4]$, were prepared [101], by reaction of $\text{Mo}_6\text{Cl}_{12}$ with the corresponding phosphine oxides. Reactivity studies show that the coordinated phosphine ligands in $[\text{Mo}_6\text{Cl}_8(\text{PR}_3)_2\text{Cl}_4]$ ($\text{R} = \text{Et}$ or $n\text{Pr}$) were susceptible to oxidation by H_2O_2 as well as by Me_3NO . The reaction with Me_3NO was surprising since even free phosphines do not react with this oxidant; it is likely that the Lewis acidic cluster

Fig. 18 Structure of $[\text{Mo}_6\text{I}_8(\text{NO}_3)_6]^{2-}$.
Reproduced from [99] with permission from The Royal Society of Chemistry



core facilitates oxidation of the coordinated phosphine ligand by Me_3NO . To the best of our knowledge, this is the only example where coordination to a molybdenum halide cluster core significantly alters the reactivity of a ligand in this manner.

The instability of the $[\text{Mo}_6\text{X}_{14}]^{2-}$ ($\text{X} = \text{Cr}, \text{Br}, \text{I}$) anions to hydrolysis is well known and has been discussed previously [28]. However, there are two hydrolysis studies that are worth mentioning. The first involves the structural characterization of three new molybdenum iodide cluster, $[\text{Mo}_6\text{I}_8(\text{OH})_4(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ ($n = 2, 12, 14$) [102]. These were obtained by controlled hydrolysis of $[\text{K}(\text{diglyme})(\text{NCCCH}_3)_2][\text{Mo}_6\text{I}_{14}]$ in sodium borate buffer solutions. All three complexes show extensive hydrogen bonding in their solid-state structures as observed with many of the rhenium chalcogenide clusters containing hydroxo/aqua ligands. The second report describes the unexpected formation of the first oxo-bridged dimer of a molybdenum halide cluster. During the recrystallization of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{N}_3)_6]$ out of acetone/diethyl ether, crystals of a minor by-product, $(\text{Bu}_4\text{N})_4[(\text{Mo}_6\text{I}_8(\text{N}_3)_5)_2\text{O}]$, also formed and were structurally characterized [103]. Although the authors have not been able to optimize the synthesis of $(\text{Bu}_4\text{N})_4[(\text{Mo}_6\text{I}_8(\text{N}_3)_5)_2\text{O}]$, this study is significant in pointing out the viability of oxo-bridged molybdenum halide clusters.

The first example of sulfur-donor ligand coordination is that of thiophenol coordinated in $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{SPh})_6]$. Two synthetic procedures were reported, reaction of $\text{Na}_2[\text{Mo}_6\text{Cl}_8(\text{OMe})_6]$ with thiophenol or reaction of $\text{Mo}_6\text{Cl}_{12}$ with NaSPh [104]. The authors utilized this complex in analyzing Raman spectroscopic data of a series of $[\text{M}_6\text{X}_8\text{Y}_6]^{2-}$ clusters ($\text{M} = \text{Mo}, \text{W}$; $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$). Thiolate ligands are an important class of ligands in the chemistry of iron-sulfur clusters; therefore, in an effort to explore the chemistry of thiolate ligands coordinated to molybdenum chloride clusters, we prepared a series of thiolate-containing clusters $[\text{Mo}_6\text{Cl}_8(\text{SR})_6]^{2-}$ ($\text{SR}^- = \text{ethanethiolate}, n\text{-butylthiolate}, \text{benzylthiolate}, 3\text{-indolylthiolate}$) [105]. The structures of $(\text{PPN})_2[\text{Mo}_6\text{Cl}_8(\text{SEt})_6] \cdot \text{Et}_2\text{O}$ and $(\text{PPh}_3\text{Me})_2[\text{Mo}_6\text{Cl}_8(\text{SBn})_6] \cdot 2\text{NO}_2\text{CH}_3$ were reported (Fig. 19). At a time when it was thought that only the donor ligand would affect the photophysical properties, we demonstrated that the thiolate substituent also impacted these properties [106]. The reaction of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{SEt})_6]$ with other thiols leads to thiolate ligand substitution, i.e., reaction of $[\text{Mo}_6\text{Cl}_8(\text{SEt})_6]^{2-}$ with benzythiol leads to the formation of $[\text{Mo}_6\text{Cl}_8(\text{SBn})_6]^{2-}$. $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_8(\text{SEt})_6]$ also undergoes reaction with electrophilic reagents such as MeI and HCl . This reactivity is reminiscent of the chemistry of thiolate ligands coordinated to iron-sulfur clusters, indicating that the molybdenum chloride core does not alter the reactivity of thiolate ligands as was observed with coordinated phosphine ligands [100]. The only example of thiolate ligand coordination to the molybdenum iodide core is that of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{SC}_6\text{F}_4\text{H})_6]$, which was reported by Fedin and coworkers. As discussed above, the molybdenum bromide and iodide clusters with fluorinated carboxylates show long excited state luminescence in the red region; therefore, there was interest in examining fluorinated thiolate ligands. $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{SC}_6\text{F}_4\text{H})_6]$ was synthesized from the reaction of $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_{14}]$ and silver(I) 2,3,5,6-tetrafluorothiolate [107]; unlike the series of molybdenum chloride thiolate complexes, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_8(\text{SC}_6\text{F}_4\text{H})_6]$ shows improved luminescence compared to $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_{14}]$.

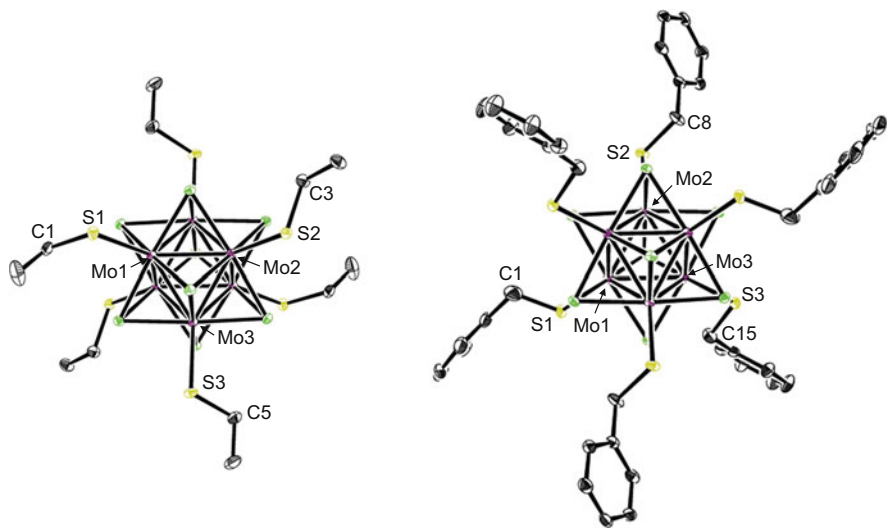
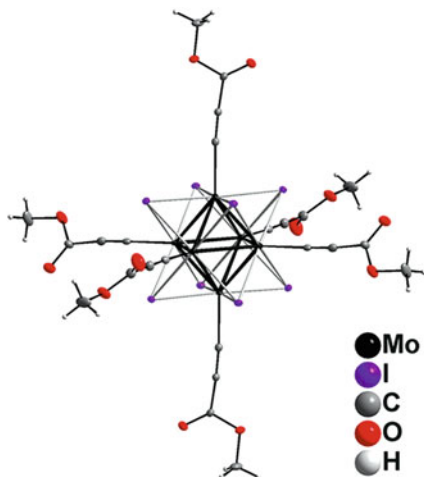


Fig. 19 Crystal structure of $[\text{Mo}_6\text{Cl}_8(\text{SEt})_6]^{2-}$ (left) and $[\text{Mo}_6\text{Cl}_8(\text{SBn})_6]^{2-}$ (right). Reprinted with permission from [105] Copyright 2008 American Chemical Society

3.3 Carbon-Donor Ligands

The first non-pseudohalide C-donor ligands coordinated to a $[\text{Mo}_6\text{X}_8]^{4+}$ cluster core were alkyl ligands; these were prepared using alkylaluminum reagents [28, 101]. In 1997, Saito reported the structures of two additional organometallic cluster complexes, *trans*- $[\text{Mo}_6\text{Cl}_8(\text{PnBu}_3)_2(\text{CH}_2\text{Ph})_4]$ and *trans*- $[\text{Mo}_6\text{Cl}_8(\text{PnBu}_3)_2(\text{phenylethynyl})_4]$. Both of these were prepared from *trans*- $[\text{Mo}_6\text{Cl}_8(\text{PnBu}_3)_2\text{Cl}_4]$ undergoing reaction with solutions of tribenzylaluminum or tris(phenylethynyl)aluminum [108]. More recently, Sokolov and coworkers synthesized $[\text{Mo}_6\text{I}_8(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$, the first fully organometallic molybdenum halide cluster complex [109]. This complex was prepared from $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{I}_{14}]$, silver(I) triflate, and methyl propiolate ($\text{HC}\equiv\text{CC}(\text{O})\text{OMe}$) in the presence of triethylamine. The authors note that they were unsuccessful in preparing the analogous molybdenum bromide and chloride clusters using the same synthetic route. Crystals of $(\text{PPh}_4)_2[\text{Mo}_6\text{I}_8(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]$ were obtained (Fig. 20) and the structure reported. This cluster is highly luminescent, and although it has a shorter excited state lifetime and lower quantum yield in comparison to $[\text{Mo}_6\text{I}_8(\text{C}_3\text{F}_7\text{COO})_6]^{2-}$, it is also a good candidate for singlet oxygen generation or luminescent O_2 sensors.

Fig. 20 Crystal structure of [Mo₆I₈(C≡CC(O)OMe)₆]²⁻. Reprinted with permission from [109] Copyright 2013 American Chemical Society



4 Summary and Perspectives

As detailed in this chapter, the type and scope of terminal ligands coordinated to octahedral cluster cores have greatly increased over the past 20 years. Key advancements in the chemistry of rhenium chalcogenide clusters include the expansion of pyridine-based ligands toward the functionalization of these cluster complexes and the discovery of small molecule activation facilitated by the [Re₆Se₈]²⁺ cluster core. Both of these have greatly expanded the variety of N-donor ligands coordinated to hexanuclear rhenium clusters, which are better stabilized by nitrogen-donor ligands. The most significant development involving molybdenum halide cluster complexes was the discovery that molybdenum iodide clusters containing fluorinated carboxylate ligands (e.g., trifluoroacetate and heptafluorobutyrate) possess exceptional photophysical properties. The fact that carboxylate ligands form stable clusters, and that incorporation of these clusters into materials does not diminish their luminescent properties, makes them ideal moieties for a wide variety of applications such as sensing, imaging, photocatalysis, and photodynamic therapy, to name a few.

Looking forward, although there has been substantial progress in expanding the breadth of terminal ligands coordinated to these cluster cores, there is substantial room for growth. The variety of nitrogen- and oxygen-donor ligands still does not match the type and scope of ligands incorporated into single metal coordination complexes, and carbon- and sulfur-donor ligands are underexplored. The potential applications of these systems keep growing as we learn more about the luminescent properties of these systems and how to develop octahedral cores as building blocks in the preparation of larger complexes and supramolecular arrays. Understanding how to incorporate different apical ligands, and how these ligands can be used to tune the spectral, photophysical, and electrochemical properties of these systems, is

what will make incorporating clusters into devices, and commercially available materials, a reality. We look forward to seeing both the fundamental and applied chemistry of molybdenum halide and rhenium chalcogenide clusters develop even further in future years.

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