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Supramolecular Architectures Featuring Stereoisomeric Cluster Complexes of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core

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Summary: The $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4L_2]^{2+}$ (both *trans*- and *cis*-isomers) site-differentiated with inert PEt_3 and functional L ligands that are capable of hydrogen bonding or secondary (with respect to primary coordination with the cluster core) metal-ligand coordination interactions have been prepared. The applications of such stereospecific cluster isomers as building blocks for supramolecular construction have been studied. A great variety of multicluster arrays mediated by intercluster hydrogen bonding or cluster ligand coordination with secondary metal ions have been obtained and structurally characterized. The findings from this research clearly establish the superior utility of these novel building blocks for the creation of structurally sophisticated architectures and possibly functional materials

Keywords: hydrogen bonding; metal clusters; metal coordination; self-assembly; supramolecular structures

Introduction

Supramolecular chemistry, the "chemistry beyond the molecule", is based on the notion of creating novel structural and functional extended systems by linking prefabricated molecular or ionic building blocks via intermolecular interactions.[1] The designing principles, i.e. the intermolecular forces, are relatively well understood, and extensive research in the past few decades has produced numerous supramolecular constructs, many of which are not only of consummate structural beauty, but also have interesting and potentially useful properties.[2] Although there are certainly underlying principles and design rules yet to be discovered, further development in the future of this interdisciplinary research field appears to hinge upon our creativity to design novel building blocks in order to manipulate and utilize the known intermolecular forces.

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In light of this observation, over the past few years we have focused our efforts on the development of supramolecular chemistry utilizing metal clusters as building blocks. From a structural viewpoint, the multiple metal sites available in a cluster allow for site-differentiation, that is, selective binding to purpose-specific ligands. Thus, a range of building blocks with systematically varied and rigidly fixed stereochemistry may be realized. The fixed stereochemistry imparts the shape and directionality critical to supramolecular synthesis. From the perspective of creating novel functional materials, metal clusters are attractive because, in addition to the anticipated magnetic, electronic, optical, or catalytic properties inherent to metal complexes, clusters frequently exhibit interesting traits that are unique to metal-metal bonded species.[3] Thus, the efforts to build cluster-supported supramolecular structures are expected to offer many fascinating research problems with potentially significant ramifications.

We have concentrated our efforts on the use as building blocks of hexarhenium chalcogenide clusters featuring the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ (Q = S, Se) core (Figure 1).[4] The research is not only stimulated by the potential applications of metal-chalcogenide clusters for heterogeneous catalysis, photovoltaics, and semiconductor fabrication,[5] it is also conveniently built on their extensive and flexible synthetic chemistry.[6] In this mini-review, the highlights from our efforts will be summarized. In the first section we will elaborate on why these clusters, more specifically those containing the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core, are of special interest in supramolecular construction. We will then illustrate the use of various stereoisomers derived from the common cluster core for the creation of a great variety of supramolecular architectures via either intercluster hydrogen bonding interactions or secondary (with respect to the primary ligand-cluster bonding) metal coordination; cluster complexes serve as ligands for the coordination of single metal ions in the latter. We will conclude with some perspectives in this exciting and rapidly growing research area.

The $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ Clusters: Synthetic and Physical Fundamentals

Soluble molecular clusters of the hexarhenium chalcogenide core are a rather recent development in cluster chemistry.[12] The 24-electron face-capped hexanuclear core can be viewed as an octahedron of rhenium atoms enclosed in a cube formed by substitutionally inert chalcogenide ligands. Using the dimensional reduction protocol,[7] halide-terminated clusters of the general formula $[Re_6(\mu_3\text{-}Q)_8T_6]^{4-}$ (T = Cl, Br, I; Q = S, Se) are obtained from the initial solid-state synthesis.[4c]

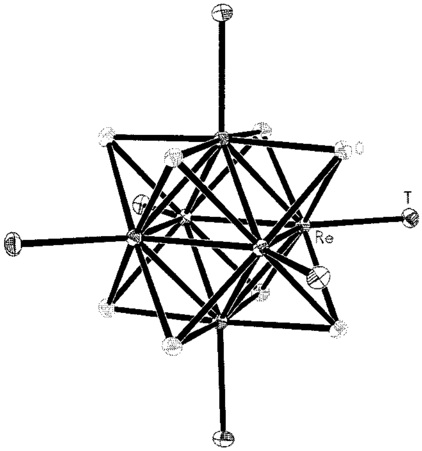


Figure 1. The structure of the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ cluster shown with terminal ligands (T).

At the heart of the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ (Q = S, Se) system's success is an extremely convenient derivatization (ligand substitution), affording a set of substitutional isomers of the cluster complexes.[6] Specifically, Holm and coworkers found that the six Re(III) sites could be differentiated from one another by reacting the starting $(n\text{-}Bu_4N)_3[Re^{III}_5Re^{IV}(\mu_3\text{-}Q)_8I_6]$ with varying ratios of PEt_3.[6a,b] Depending on the relative ratio of cluster to phosphine, the number of apical halides displaced could be varied from three to six. This was completely unlike any other known molecular cluster system. Instead of cluster decomposition or persubstitution, the phosphine substitution reactions could be executed in a controllable fashion. Citing biological terminology, the process was referred to as site differentiation.

Site differentiation was extremely significant however, as it marked the departure from cluster chemistry in the traditional sense. The phosphine ligands were completely inert once bound to the cluster core, thus fixing the stereochemistry of the system. More importantly, the remaining sites could be dehalogenated conveniently to afford the labile cluster solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_{6-n}(solv)_n]^{2+}$ (solv = MeCN, DMF, DMSO, and pyridine).[6a,8] These solvate sites were subject to further ligand exchange, making the structural possibilities limited only by imagination. The combination of easily controlled ligand exchange, robust cluster core, and large size allowed one to contemplate the synthesis of cluster complexes for more sophisticated purposes than elucidation of fundamental properties, for example, as a basis set of stable, chemically accessible, geometric building blocks for supramolecular construction. Although the use of mononuclear complexes in this role was already commonplace, no cluster system had ever been available in sufficient yields, with sufficient stability and range of stereochemistry, to replace them. With the site differentiated solvates in hand, it was clear that their large size and rigid stereochemistry would make them ideal components of supramolecular constructs.

Beyond the desirable structural characteristics, the extension of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ system to endeavors not normally associated with clusters is supported by a host of potentially useful physical properties. The first of these is the now well characterized luminescence of all $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ cores. Although initially the subject of some debate, it has been conclusively demonstrated that the cluster cores are luminescence. This was predicted by early computational work by Arratia-Perez and coworkers,[9a] and recently, established experimentally by Holm, Nocera, and their coworkers.[9b]

The $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ cluster systems also feature extensive electrochemistry.[6] Like the luminescence, the electrochemistry is acutely sensitive to both inner and apical ligands. Incorporation of electronically bistable cluster complexes into supramolecular systems could result in novel electroactive materials for use in displays and other devices.[10]

Site-differentiated Cluster Complexes – A Set of Stereoisomeric Building Blocks

As alluded to in the above section, site-differentiation, the practice of protecting specific numbers of Re(III) coordination sites with inert phosphine ligands, affords a range of substitutional isomers. The stereochemistry of these isomers forms the geometric basis set of building blocks for construction of cluster-based supramolecules, provided that certain types of functional groups capable of secondary (with respect to primary cluster ligation) intermolecular interactions such as hydrogen bonding and metal-ligand coordination are integrated into the non-phosphine ligand(s). In this way, multicluster arrays mediated by the secondary interactions can be fabricated (Figure 2).

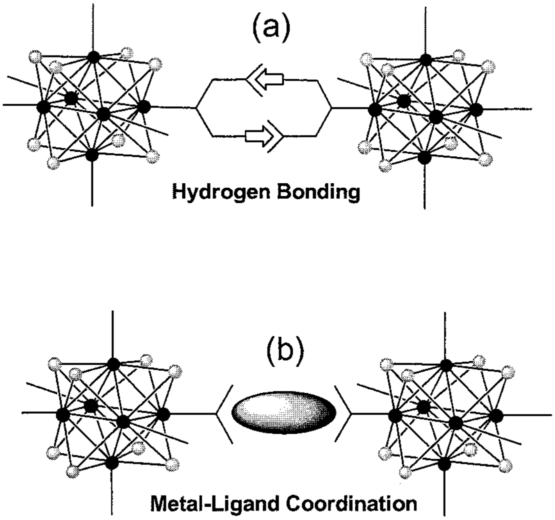
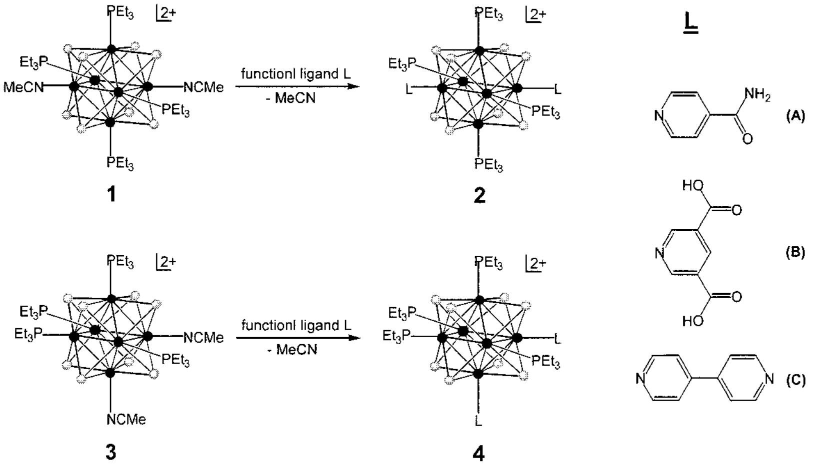


Figure 2. Schematic demonstration of hydrogen bonding (a) and metal-ligand coordination (b) interactions for mediating the assembly of multicluster arrays.

As will be elaborated fully in the following sections, the fixed stereochemistry of the phosphine-protected clusters acts as the primary structure-directing element in the synthetic process. Moreover, the wider displacement of ligands relative to their mononuclear counterparts minimizes structural ambiguity due to mononuclear complex flexibility.[11] Consequently *structural predictability* will be greatly enhanced. Furthermore, both the intercluster hydrogen bonding and the "cluster complex-as-ligand" approaches maintain the ease of handling offered by the monocluster species in solution yet offer the possibility of obtaining crystalline samples, frequently in the form of single crystals, of the supramolecular materials when assembled in the solid state.

Functional site-differentiated cluster complexes have thus been designed and synthesized (Scheme 1). In the first (**2A**, **2B**, **4A**, and **4B**), a complex is formed with ligands (isonicotinamide, for example) that bear functional groups capable of intermolecular hydrogen bonding. In the second (**2C** and **4C**), a cluster complex features ligands (4,4'-dipyridyl, for instance) that possess free coordinating atoms potentially exploitable for secondary metal coordination. The corresponding stereospecific acetonitrile solvates (**1** and **3**) can be readily prepared by deiodination of the respective iodo complexes with $AgSbF_6$ in the presence of MeCN.



Scheme 1. Syntheses of site-differentiated $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster complexes featuring inert PEt_3 ligands and ligands (L) capable of either hydrogen bonding (**A** and **B**) or ligand-metal coordination (**C**) interactions.

The Hydrogen Bonding Approach to Supramolecular Architectures

The hydrogen bond is not only one of the strongest intermolecular forces but has the added advantage of being directional. By using the site-differentiated cluster complexes as the hydrogen-bonding basis, the geometric and dimensional control of the cluster is added to the directionality of the hydrogen bond. We have prepared a number of site-differentiated cluster complexes with hydrogen bonding-capable ligands.[12-14] The solid-state structures of several of these clusters have been established crystallographically, revealing aesthetically pleasing and rather sophisticated hydrogen bonded supramolecular arrays of cluster building blocks. As an example, the supramolecular structure of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2](SbF_6)_2$ (**2A**, Scheme 1),[12] each amide unit engages in a pair of self-complementary hydrogen bonding to two neighboring clusters, generating an infinite, one-dimensional chain featuring the cluster units and the cluster-linking hydrogen bonds (a, Figure 3).

The *cis* cognate of **2A**, *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2]^{2+}$ (**4A**, Scheme 1),[12] also features one-dimensional infinite chains of clusters in the solid state, which display a zigzag topology due to *cis*- displacement of the isonicotinamide ligands (b, Figure 3). This zigzag arrangement results in the chains fitting together to form sheets of chains (not shown). The lamellae are apparently stabilized by hydrophobic interdigitation of the phosphine groups between layers. The formation of a hydrogen-bonded square was not realized, probably due to the otherwise thermodynamically disfavored porous structure and packing thereof.

Using *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3(\text{isonicotinamide})_3](SbF_6)_2$,[13] prepared by reacting *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3(MeCN)_3](SbF_6)_2$ with excess isonicotinamide, attempts have also been made to generate a discrete, hydrogen-bonded cluster cube, featuring eight corner-occupying cluster units and twelve edges of paired hydrogen bonds. Instead of a cube however, the cluster complexes form three-dimensional channels by packing such that the isonicotinamide cluster faces form the inner walls of the channels (top, Figure 4). The channels are stitched together by weaker, non-complementary hydrogen bonds from the "equatorial" amides in adjacent clusters along the channel axis (bottom, Figure 4). The very bulky and hydrophobic PPh_3 cluster faces form the outer walls. The structure may be stabilized by the clear separation of the relatively polar hydrogen bonding faces from the hydrophobic PPh_3, which subsequently engage in extensive π-π interactions with neighboring channels.

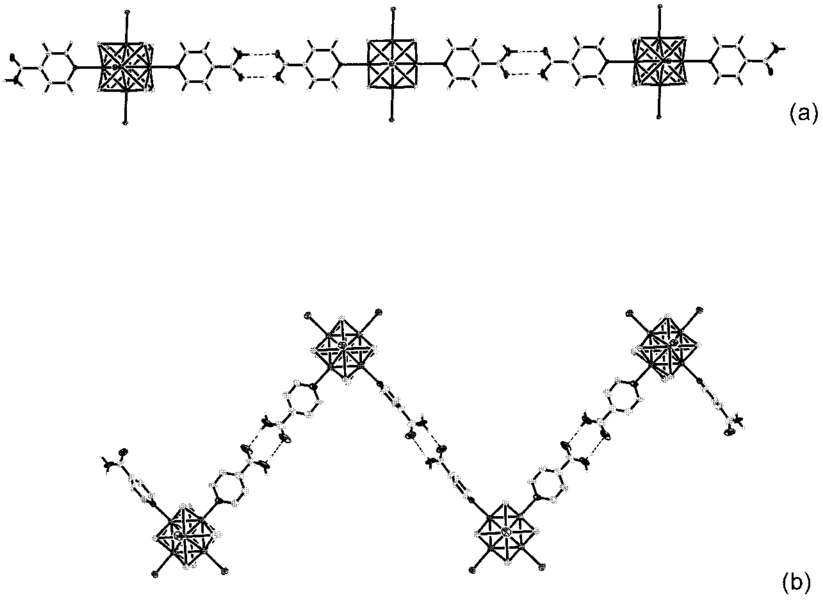


Figure 3. ORTEP views (50% ellipsoids) of hydrogen-bonded arrays of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters [a(**2A**) and b(**4A**)].

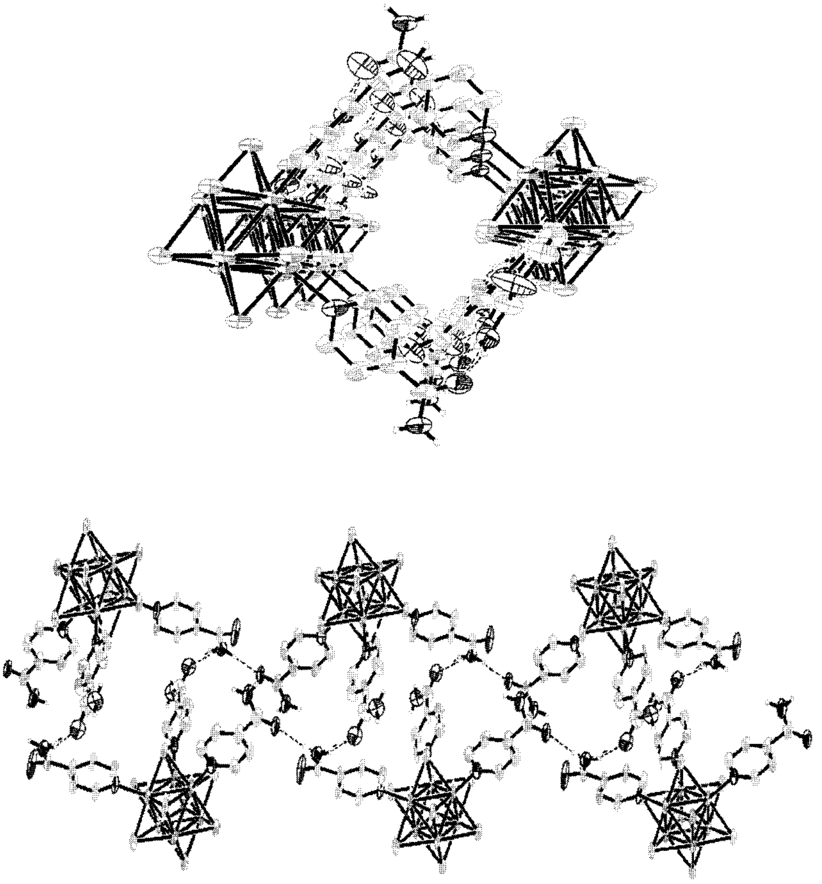


Figure 4. An ORTEP view (50% ellipsoids) of the extended hydrogen-bonded structure of *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3(\text{isonicotinamide})_3](SbF_6)_2$. Triphenylphosphine ligands are removed for clarity.

Encouraged by the success in generating hydrogen bonded-supramolecular cluster arrays, cluster complexes **2B** and **4B** (Scheme 1) were prepared, in efforts to explore new modes of generating hydrogen bonded networks supported by cluster stereoisomers.[14] The non-phosphine ligand, namely 3,5-pyridinedicarboxylic acid (**B**), bares two hydrogen bonding donor (D) and acceptor (A) groups placed at 120E from each other on the pyridyl ring. The DA groups are subject to a variety of different hydrogen bonding modes. The combined effect of the increased number of hydrogen bonding DA units per molecule, and the increased variability of the hydrogen bonding modes, is to reduce the influence of the cluster stereochemistry over the final self-assembled architecture. Thus, the resultant hydrogen bonded arrays should reflect a synergy between cluster and ligand geometry, possibly affording novel structure and function not possible with only one component dominating the self-assembly process.

The solid-state structure and supramolecular arrangement of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(3,5\text{-pyridinedicarboxylic acid})_2](SbF_6)_2$ (**2B**) have been established by crystallographic analysis (Figure 5).[14] The centroid of the cluster sits on an inversion center. The unique 3,5-pyridinedicarboxylic acid ligand is bound to a Re(III) center via the pyridyl nitrogen atom. Applying the inversion operator reveals that the 3,5-pyridinedicarboxylic acid ligands, including the carboxylic acid moieties, are virtually coplanar with the plane of four Re atoms that includes the two to which they are bound. The inversion related carboxylic acid groups undergo complementary hydrogen bonding with the neighboring sets. Interestingly, the second acid group on each ligand does not participate in any hydrogen bonding. Instead, the acid group extends into a small space between the chains and appears to be in close contact with a selenium atom on a neighboring cluster, as well as a hydrogen atom of that cluster's PEt_3 ligands. As the ligands are *trans*-coordinated to Re(III) sites, and only one of the two sets per ligand engage in hydrogen bonding, these carboxylic acid moieties may be considered *trans*-related across the complex. The result of this *trans-ligand, trans-acid* arrangement is the formation of zigzag hydrogen bonded cluster polymers.

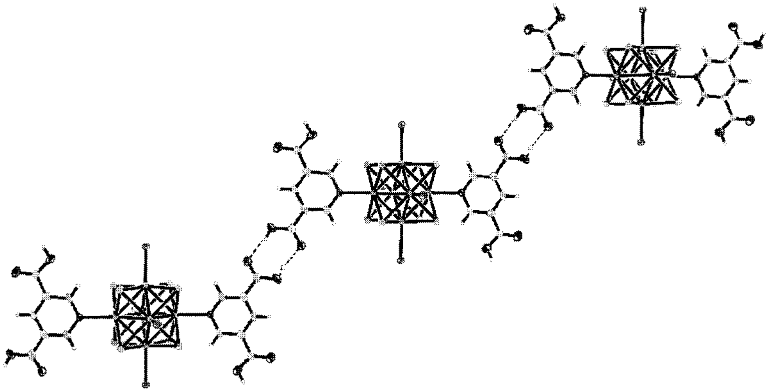


Figure 5. An ORTEP view (50% ellipsoids) of the extended hydrogen-bonded structure of *trans*-[$Re_6(\mu_3\text{-}Se)_8(PEt_3)_4$(3,5-pyridinedicarboxylic acid)$_2$]$(SbF_6)_2$ (**2B**, Scheme 1). Ethyl groups of the triphenylphosphine ligands are removed for clarity.

The "Cluster Complex-as-Ligand" Approach to Supramolecular Architectures

Using cluster complexes as ligands to direct secondary metal ion coordination represents the second half of our noncovalent cluster assembly paradigm. With the demonstration of the synthesis of hydrogen bonded arrays directed and supported by the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster stereoisomers, we were confident that the cluster core would be ideal in the role of "cluster complex-as-ligand". As compared with traditional organic ligands, complex ligands offer two distinct advantages. The first and most obvious is the that a complex ligand will bring its own physicochemical properties to the ensemble, offering the tantalizing prospect of creating materials with desirable properties such as magnetic, catalytic, and photo- and electrochemical activity. Second, the geometric preferences of a given complex ligand allow the realization of building blocks with shapes not trivially nor cheaply generated with purely organic molecules. As such, more sophisticated structures may be anticipated relative to traditional coordination polymers and oligomers. Admittedly, the coordination to a naked metal ion sacrifices some of the directionality and predictability of a hydrogen bonded linkage, the large size and rigid displacement of cluster-supported ligands are likely to ameliorate some of the potentially complicating factors associated with self-assembly (e.g. packing forces, ligand flexibility).

As a proof-of-concept first step, we synthesized *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ (**2C**, Scheme 1) and studied its coordination with a number of transition metal ions.[15] This cluster complex features two *trans*- disposed 4,4'-dipyridyl ligands; each of the pyridyl ligands coordinates the cluster core with one N atom, while leaving the other available for potential coordination to secondary metal ion. In effect, the complex is an expanded pyridyl-based ditopic ligand that can be used in lieu of purely organic equivalents to mediate the self-assembly of extended metal ion arrays.

Isomorphous linear coordination polymers based on *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ and $Co(NO_3)_2$ (**2C•Co**) and $Cd(NO_3)_2$ (**2C•Cd**) have been obtained and structurally characterized. Compound **2C•Co** is the first complex synthesized in the series of linear polymers (Figure 6). It features a repeat unit consisting of a single *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(4,4'\text{-dipyridyl})_2]$ unit bound to a Co^{2+} ion via the open nitrogen of a single 4,4'-dipyridyl ligand. The Co^{2+} ion is bound to a second pyridyl nitrogen from the next repeat unit. Charge is balanced by a single SbF_6^- counterion located near the cluster and three nitrato ligands bound to the Co^{2+} ion. The polymer formed by this repeat unit has significant curvature between the Re atom coordinated to one end of the 4,4'-dipyridyl ligand and the Co^{2+} unit at the other. The curvature is the result of the summation of small shifts from linearity at each individual bond between the two metals, and is a feature shared with its Cd^{2+} cognate. The curvature results in the polymers forming sinusoidal chains of modest amplitude. Adjacent chains have the cluster and cadmium units shifted with respect to one another, leading to alternating layers of opposing “phases” and an overall lamellar structure in the solid state with each layer composed of parallel polymer chains.

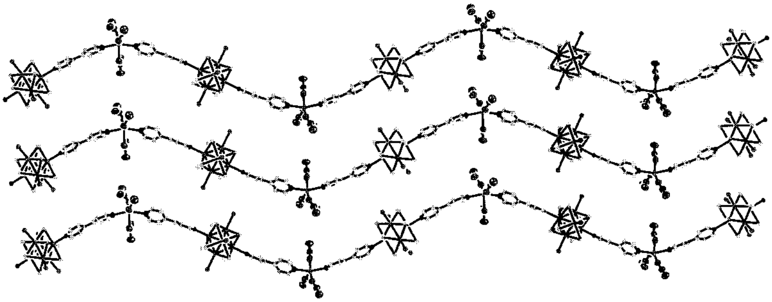


Figure 6. One layer of the Co^{2+}-mediated cluster assembly **2C•Co** shown with ethyl groups, hydrogen atoms, unbound counterions, and solvent omitted for clarity.

Using Zn^{2+} as the secondary metal ion, a chemically very similar coordination polymer (**2C•Zn**) was obtained. Structurally however, it is quite distinct (Figure 7). The repeat unit is essentially the same as **2C•Co** and **2C•Cd** except that the $N_{pyridyl}$-Zn^{2+}-$N_{pyridyl}$ coordination mode is *cis-* with respect to the Zn^{2+} ion, with an average $N_{pyridyl}$-Zn^{2+}-$N_{pyridyl}$ angle of 88<. The effect of this coordination mode is to produce pseudo-linear zigzag polymer chains, rather than the sinusoidal polymers of **2C•Co** and **2C•Cd**. Indeed, one might consider the zigzag motif the canonical limit of the curvature observed in the previous structures: The relatively rigid 4,4'-dipyridyl ligand can only accommodate a certain amount of distortion before adopting the *cis-* configuration about the secondary metal ion. The relative contributions of electronic, steric, and packing energetics that result in a given configuration remain speculative, however. As in the previous two structures, the zigzag polymers form layers of parallel chains, but the layers are interpenetrated. In the spaces between chains in a given sheet, chains forming the penetrating layer run roughly normal to the plane of the sheet. This packing mode results in the formation of small channels that pass through the crystal in the *b* direction between neighboring Zn^{2+} sites (not shown).

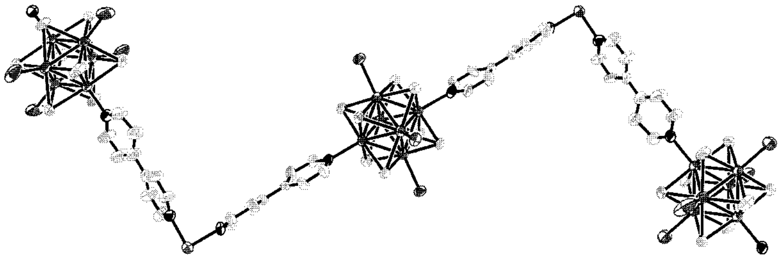


Figure 7. A single chain of the Zn^{2+}-mediated cluster assembly (**2C•Zn**). Ethyl groups, protons, counterions, and solvent omitted for clarity.

The linear polymers **2C•Co**, **2C•Cd**, and **2C•Zn** are aesthetically pleasing supramolecules and serve as excellent proofs-of-concept for the utility of cluster expanded "big-bpy" type ligands. The second motif was inspired by our original work with molecular squares[16] and was intended to increase structural and functional sophistication in a rational way. By using *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-}dipyridyl)_2](SbF_6)_2$ (**4C**, Scheme 1), a ligand equipped with an enforced right angle between the two dipyridyl ligands, we hoped to realize a very large molecular square with **4C** forming the corners.

An unexpected product was produced upon ether diffusion into a 1:1 (molar) mixture of **4C** in dichloromethane and $Cd(NO_3)_2$ in methanol. As revealed by crystallographic analysis, the product, formulated as $\{[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-}dipyridyl)_2]_2[Cd(NO_3)_2]\}(SbF_6)_4$ (**4C•Cd1**) exhibits a 2:1 cluster/Cd^{2+} ratio and forms a one-dimensional chain of corner-sharing squares (left, Figure 8) in the solid state.[17] Each shared corner is a single octahedrally coordinated Cd^{2+} ion, bound in the equatorial plane by four pyridyl nitrogens and axially by two η^1-NO_3^- ligands. The unshared corners are formed by the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters.

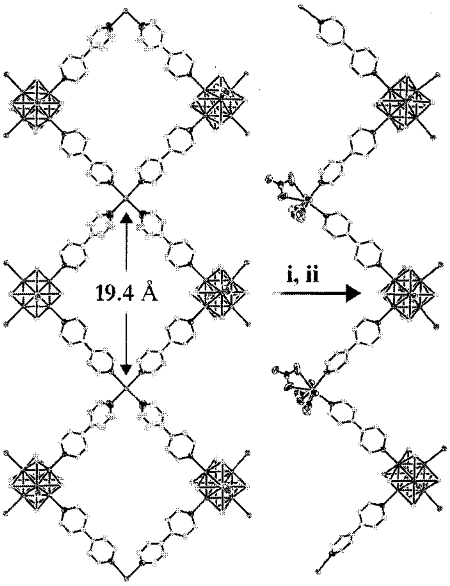


Figure 8. Thermal ellipsoid plots of **4C•Cd1** (left) and **4C•Cd2** (right) rendered at 50% probability. Only the framework structure is shown. Conversion in two steps: (i) $Cd(NO_3)_2/CH_3OH$; (ii) ether diffusion.

A complex of a 1:1 cluster/Cd^{2+} ratio was subsequently attempted and obtained by reacting **4C** with a large excess of the Cd^{2+} salt. The product, formulated as $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}\{Cd(NO_3)_3\}](NO_3)$ (**4C•Cd2**) is a one-dimensional zigzag chain in the solid state (right, Figure 8). As with **4C•Cd1**, the chains clearly reflect the geometric constraint imposed by the cluster ligands, but also show flexibility at the Cd^{2+} site. The coordination environment about the Cd^{2+} ion is distorted trigonal bipyramidal, with one pyridyl axial and one equatorial (N-Cd-N bond angle of 87.2°). The remaining three sites are occupied by $\eta^2\text{-}NO_3^-$ ligands. Though disappointing, the outcome was not too surprising as the polymeric structure is indeed the more likely product when considered from a crystal energetics perspective.

Curiously, the chain structure of **4C•Cd2** can be formally considered to be derived from **4C•Cd1** by replacing the cluster on one side of the squares with a nitrato ligand. Indeed, as confirmed by crystallographic determination of cell parameters, complex **4C•Cd2** was isolated from the reaction of complex **4C•Cd1** with an excess of $Cd(NO_3)_2$ in a methanolic solution upon ether vapor diffusion. However, the extended structure of **4C•Cd1** is presumably disintegrated in a highly polar solvent like methanol into the component cluster complex and Cd^{2+} prior to their re-assembly, with the additional $Cd(NO_3)_2$, into the zigzag chain of **4C•Cd2**.

Conclusions

The purpose of the research is the development of synthetic methodologies necessary to bring the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ system out of the limited sphere of fundamental cluster chemistry and into general synthetic applicability. The significance of this research is born of its novelty – but not the trite observation that no one has done such an investigation before. Rather, the research is significant because no other inorganic system, cluster or otherwise, exhibits the same range of reactivity, durability, and physicochemical activity that makes the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ system so useful. Specifically, we have explored the uses of site-differentiated cluster complexes featuring secondary functionality placed at the ends of pyridyl based-ligands as expanded and stereospecific building blocks for supramolecular construction. These secondary functions are moieties capable of hydrogen bonding or metal ion coordination. The cluster's versatility in this role is manifested in the variety of beautiful architectures obtained and the facile change of synthetic paradigms necessary to achieve these results. Although we have explored a range of structural types and their synthetic methods, often with interesting and unexpected results, we are only at the beginning of a very exciting journey. It is obvious that Nature still has a few tricks up in her sleeve, but the complete set of building blocks available from the cluster basis, combined with the adaptability to any assembly mode, will no doubt make the task of uncovering these secrets considerably easier.

Acknowledgements

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