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Novel Concentration-Driven Structural Interconversion in Shape-Specific Solids Supported by the Octahedral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Cluster Core

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A complex containing the face-capped octahedral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core, *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ (**1**), is used as a ditopic ligand with an enforced right angle between the two 4,4′-dipyridyl moieties for the coordination of Cd^{2+} ion. Two coordination polymers, $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4\cdot 21C_4H_{10}O\cdot 21CH_2Cl_2$ (**2**) and $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}\{Cd(NO_3)_3\}](NO_3)\cdot 2C_4H_{10}O\cdot CH_2Cl_2$ (**3**), are obtained. The relative concentration of Cd^{2+} determines which species is isolated, and the conversion of the first structure into the second is demonstrated experimentally.

The chemistry of the face-capped octahedral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing clusters[1−12] has progressed rapidly since the advent of the high-yield solid-state synthesis of the soluble molecular clusters.[2] Holm and co-workers were the first to investigate in a systematic manner the ligand substitution reaction of these clusters. A series of cluster derivatives of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nL_{6-n}](SbF_6)_2$ ($n = 3-6$; L = a coordinating solvent molecule or a pyridyl-based ligand) have been prepared and characterized.[3] Analogous derivatives with bridged diphosphine ligands have also been reported.[4] These clusters have been found, both theoretically[5] and experimentally,[4,6] to possess interesting photophysical characteristics, which may impart unique optical properties to materials containing these cluster components.

In addition to the physical properties and chemical reactivity of the single-cluster complexes, the potential of using these clusters as unique structural and functional building blocks for preparing extended multicluster arrays has also been explored. For example, the octahedral cluster core has been utilized as a focal point to support dendritic architectures[8] as well as a host of cluster-expanded framework solids.[9,10] In addition to the efforts using the symmetric cluster species, our attention has also been directed toward the application of the various stereoisomers of the phosphine-derived (site-differentiated) clusters in a similar role.[3c,11,12] Rather than relying on a single building block, the available stereoisomers form a complete kit of blocks and are therefore more versatile synthons. Furthermore, the fixed geometry of a given cluster derivative lends its shape (e.g., a right angle for a *cis*-isomer) to a final product and serves to direct and limit the structural outcome to a small manifold of possibilities.

Two different approaches have been taken to incorporate these stereospecific (shape-specific) clusters into multicluster structures. In the first approach, reacting a cluster solvate site-differentiated by phosphine ligands with an appropriate polytopic ligand leads to the displacement of the solvent ligands and the formation of an array composed of a number

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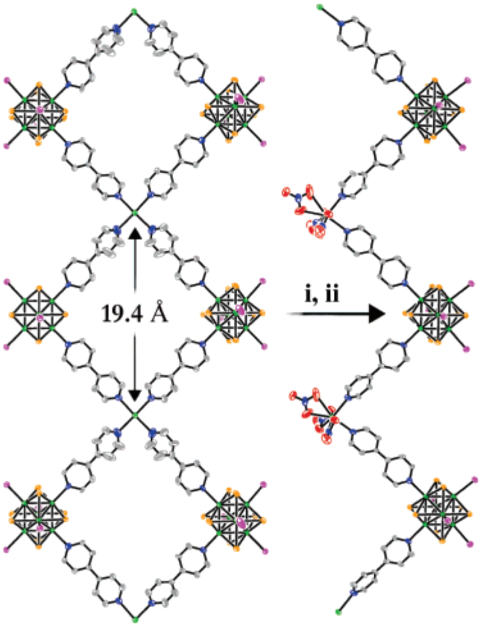

Figure 1. Thermal ellipsoid plots of **2** (left) and **3** (right) rendered at 50% probability. Only the framework structure is shown. Noncoordinated counterions and phosphine phenyl groups of both **2** and **3**, and hydrogen atoms, are removed for clarity. Conversion in two steps: (i) $Cd(NO_3)_2$/CH_3OH; (ii) ether diffusion. Color scheme: C (gray), Cd (green, mononuclear), N (blue), O (red), P (purple), Re (green, cluster), and Se (yellow).

of cluster units covalently linked by the polytopic ligands. Using this methodology, a number of supermolecules of predetermined shapes and dimensions have been realized.[3c,11]

In the second method, clusters are joined via interactions such as hydrogen bonding[12a] and ligand−metal coordination.[12b] Such supramolecular approaches maintain the ease of handling offered by the monocluster species in solution, yet offer the possibility of obtaining crystalline extended solids upon assembly. In this report, we describe the creation of two hybrid cluster−transition metal coordination polymers, wherein Cd^{2+} ions serve to mediate assembly of the shape-specific cluster-based ligands.

The cluster building block of interest is *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ (**1**), prepared by reacting *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(CH_3CN)_2](SbF_6)_2$[3a] with an excess of 4,4′-dipyridyl. There is an enforced right angle between the two dipyridyl ligands, each with one of its N atoms coordinated to the cluster, leaving the other available for further metal coordination. A 1:1 (molar) mixture of **1** in CH_2Cl_2 and $Cd(NO_3)_2$ in methanol was subjected to ether diffusion, resulting in thick plate-shaped crystals.[13] The product is readily soluble in alcoholic solvents but, in stark contrast to **1**, insoluble in CH_2Cl_2. Crystallographic analysis[14] revealed that this compound (**2**), formulated as $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4\cdot 21C_4H_{10}O\cdot 21CH_2Cl_2$, forms a one-dimensional chain of corner-sharing squares (left, Figure 1) in the solid state. Each shared corner is a single octahedrally coordinated Cd^{2+} ion, bound in the equatorial plane by four pyridyl nitrogens and axially by two $\eta^1\text{-}NO_3^-$ ligands. The unshared corners are formed by the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters. The chains of squares extend along the *b* direction. Adjacent chains are stacked along *c* with a slippage of the chains in the *b* and *c* directions.

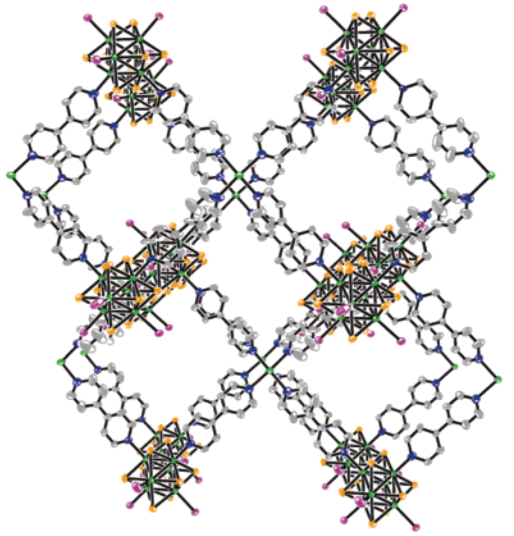

Figure 2. Packing diagram of **2** showing the channel structure. The channel-occupying counterions and solvent molecules, Cd^{2+}-coordinating nitrato ligands, and the phenyl groups of the phosphine ligands are removed for clarity. Color scheme: C (gray), Cd (green, mononuclear), N (blue), P (purple), Re (green, cluster), and Se (yellow).

Serendipitously, this packing results in large channels (Figure 2) that pass through the center of the squares, at roughly 40° from the $b-c$ bisector and at a constant *a* of 0.25 or 0.75, connecting one square with its neighbor at an upper or lower value of *b*. Smaller cross channels about the Cd^{2+} link all channels into one large area. Perhaps most interesting, however, is the observed cluster/Cd^{2+} ratio. Although pains were taken to ensure a 1:1 ratio, the structure exhibits a 2:1 cluster/Cd^{2+} ratio.

Because of this unexpected result, we sought to probe what effects, if any, the cluster/Cd^{2+} ratio had on the final outcome by reacting **1** with a large excess of the Cd^{2+} salt. Compound **3**, formulated as $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}\{Cd(NO_3)_3\}](NO_3)\cdot 2C_4H_{10}O\cdot CH_2Cl_2$, was isolated quantitatively.[13] The solid-state structure of **3** (right, Figure 1) is a one-dimensional zigzag chain, featuring repeating units of $\{[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2][Cd(NO_3)_3]\}^-$.[14] As with compound **2**, 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

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(13) No specific precautions were taken to exclude air or moisture in preparing compounds **2** and **3**. Complex **2**: $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4\cdot 21C_4H_{10}O\cdot 21CH_2Cl_2$. Dropwise addition of a solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.045 mmol; 14 mg) in a minimum of methanol to a dichloromethane solution of **1** (160 mg, 0.045 mmol) generated an orange solution, to which vapor diffusion of diethyl ether afforded red plate-shaped crystals in quantitative yield. Anal. Calcd for **2** (dried under vacuum to remove solvent) $C_{184}H_{152}N_{10}CdF_{24}O_6P_8Re_{12}Sb_4Se_{16}$: C, 29.86; H, 2.07; N, 1.89. Found: C, 29.81; H, 1.96; N, 2.05. Complex **3**: $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}\{Cd(NO_3)_3\}](NO_3)\cdot 2C_4H_{10}O\cdot CH_2Cl_2$. This compound was synthesized in an identical manner, except that $Cd(NO_3)_2\cdot 4H_2O$ was added in excess (over 100-fold) from a saturated methanol solution. Anal. Calcd for **3** (dried under vacuum) $C_{92}H_{76}N_8CdO_{12}P_4Re_6Se_8$: C, 31.84; H, 2.21; N, 3.23. Found: C, 31.82; H, 2.25; N, 3.29. Synthesis of **3** from **2**: Crystals of **2** were dissolved in methanol to yield an orange-red solution to which a large excess (over 100-fold) of $Cd(NO_3)_2\cdot 4H_2O$ in methanol was added. Diffusion with diethyl ether resulted in red plate-shaped crystals of **3** in quantitative yields.

one pyridyl axial and one equatorial (N−Cd−N bond angle of 87.2°). The remaining three sites are occupied by η^2-NO_3^- ligands.

The chain structure of **3** can be formally considered to be derived from **2** by replacing the cluster on one side of the squares with a nitrato ligand. Indeed, as confirmed by crystallographic determination of cell parameters, complex **3** was isolated from the reaction of complex **2** with an excess of $Cd(NO_3)_2$ in a methanolic solution upon ether vapor diffusion.[13] The extended structure of **2** is presumably disintegrated in a highly polar solvent like methanol into the component cluster complex and Cd^{2+}; otherwise, the rigid polymeric arrays should exhibit limited solubility. Thus, the formation of a particular polymeric structure may be rationalized in terms of two competing thermodynamic forces: the optimization of crystal density/close packing of the multicluster arrays and the maximization of Cd^{2+}-pyridyl coordination. Specifically, the fused square, representing a compromise between optimal Cd^{2+} coordination and structural density, is the favored structure when the concentration of the cluster complex and that of the Cd^{2+} salt are comparable. In the presence of excess Cd^{2+}, however, the balance shifts to favor close packing, thus affording the zigzag chain that still exhibits the same skeletal arrangement of Cd^{2+} and cluster ligands.

In summary, two closely related polymeric cluster assemblies mediated by Cd^{2+} ions have been obtained. The conversion of one of these coordination polymers, the fused-square structure (**2**), into the other, the zigzag chain (**3**), has been demonstrated experimentally. In both structures, the cluster complexes serve as dimensionally expanded and shape-specific ligands. The rigid geometry of the *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$ ligand limits the number of possible architectures that may be generated with such rationally designed building blocks. The formation of the extended structure is nevertheless dependent as well on the coordination of the secondary metal ions. Conceivably, it is the *balance* between the thermodynamic forces of the close packing of the polymeric chains and the coordination of Cd^{2+} that is ultimately responsible for the formation of a particular structure. The results thus suggest that these site-differentiated cluster derivatives are unique and powerful building blocks for the creation of novel cluster-supported supramolecules and possibly useful materials.

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Supporting Information Available: Crystallographic data in CIF format for the structures of **2** and **3**; thermal ellipsoid diagrams of **2** and **3** showing the complete coordination sphere of Cd^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal data (**2**): $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4 \cdot 21C_4H_{10}O \cdot 21CH_2Cl_2$. Monoclinic, space group *I*2/*a* (No. 15), $a = 36.949(2)$ Å, $b = 19.4415(13)$ Å, $c = 42.134(3)$ Å, $\beta = 102.6240(10)°$, $V = 29535(3)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.7767 cm^{-1}; $D_{calcd} = 2.377$ g cm^{-3}, crystal dimensions 0.3 × 0.3 × 0.1 mm^3. $T = -100$ °C. R1 = 0.0703, wR2 = 0.1212, and GOF = 0.918 for all 15483 reflections, 1116 parameters, and 1465 restraints. Final electron density difference map: 1.492 e$^-$/Å^3 and −2.224 e$^-$/Å^3 0.97 Å from Re5 and 1.32 Å from H5a, respectively. While data were collected to 0.8 Å resolution, significant diffraction did not extend beyond 1.0 Å, and data beyond that limit were rejected. After completing the initial structure solution, it was found that 40% of the cell volume was filled with disordered solvent which could not be modeled as discrete molecules. Analysis of this solvent void using Platon (Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.) gave a volume of 12404 Å^3/cell. From this point on, atoms in the region were removed, and the solvent region was refined as a diffuse contribution without specific atom positions using the Platon module SQUEEZE (van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.). The solvent contribution amounted to 6763 electrons per cell. Crystal data (**3**): $[\{Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}\{Cd(NO_3)_3\}](NO_3) \cdot 2C_4H_{10}O \cdot CH_2Cl_2$. Triclinic, space group *P*1 (No. 2), $a = 18.4029(10)$ Å, $b = 18.5309(9)$ Å, $c = 19.1906(10)$ Å, $\alpha = 99.1660(10)°$, $\beta = 117.9960(10)°$, $\gamma = 91.0700(10)°$, $V = 5671.9(5)$ Å^3, $Z = 2$, μ(Mo Kα) = 0.9291 cm^{-1}; $D_{calcd} = 2.169$ g cm^{-3}, crystal dimensions 0.2 × 0.2 × 0.05 mm^3. $T = -100$ °C. R1 = 0.0887, wR2 = 0.0961, and GOF = 0.858 for all 21093 reflections, 1180 parameters, and 619 restraints. Final electron density difference map: 1.988 e$^-$/Å^3 and −1.411 e$^-$/Å^3 1.05 Å from Re1 and 0.22 Å from O4B, respectively. After completing the initial structure solution, it was found that 20% of the cell volume was filled with disordered solvent which could not be modeled as discrete molecules. One site probably contained dichloromethane, while the remaining sites were probably diethyl ether. Analysis of this solvent void using Platon (Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.) gave a volume of 1295 Å^3/cell. From this point on, atoms in the region were removed, and the solvent region was refined as a diffuse contribution without specific atom positions using the Platon module SQUEEZE (van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.). The solvent contribution amounted to 252 electrons per cell. Data for both structures were collected using a Bruker SMART 1000 CCD based area detector diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Structures were solved with direct methods followed by Fourier synthesis using Bruker's SHELXTL (v. 5.0) software package.