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Hydrogen-Bonded Extended Arrays of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core-Containing Clusters

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Site-differentiated solvated clusters of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(MeCN)_{6-n}](SbF_6)_2$ ($n = 4$, *cis* and *trans*; $n = 5$) undergo ligand substitution reaction with isonicotinamide to afford the corresponding amide derivatives, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(\text{isonicotinamide})_{6-n}]^{2+}$ [**1** ($n = 5$); **2** ($n = 4$, *trans*); **3** ($n = 4$, *cis*)]. Retention of stereochemistry in each case was confirmed by ^1H and ^{31}P NMR. The solid-state structures of all three compounds were established crystallographically, which revealed self-complementary hydrogen-bonding interactions between adjacent cluster units. While complex **1** exists as hydrogen-bonded dimers in the solid state, compounds **2** and **3** form one-dimensional chains of clusters bridged by paired hydrogen bonds. It is the rigid stereochemistry of the cluster, combined with the classic crystal engineering motif of complementary N–H···O amide hydrogen bonding, that affords the predictable solid-state structures and dimensionality.

Introduction

Supramolecular chemistry, the "chemistry beyond the molecule", is based on the notion of creating novel structural and functional extended systems using noncovalent interactions between prefabricated molecular or ionic building blocks.[1] Central to the success of this field has been the creative utilization and manipulation of hydrogen-bonding interaction[2] and coordination-driven assembly,[3] among other intermolecular forces.[4] The combination of these two tools is particularly powerful for constructing novel supramolecular species, as evidenced by the recent surge of research activities aiming at the creation of inorganic−organic hybrid materials by assembling metal complexes through hydrogen bonds.[5,6]

We envision an analogous yet possibly more interesting elaboration of this relatively new synthetic approach by making use of molecular metal clusters as building blocks.[7] Structurally, metal clusters offer a number of metal sites for coordination, either exclusively by ligands capable of forming hydrogen bonds or by such ligands in combination with kinetically inert and therefore site-blocking ligands. In the latter case, site-differentiated clusters are produced, and stereospecific supramolecular frameworks built on such

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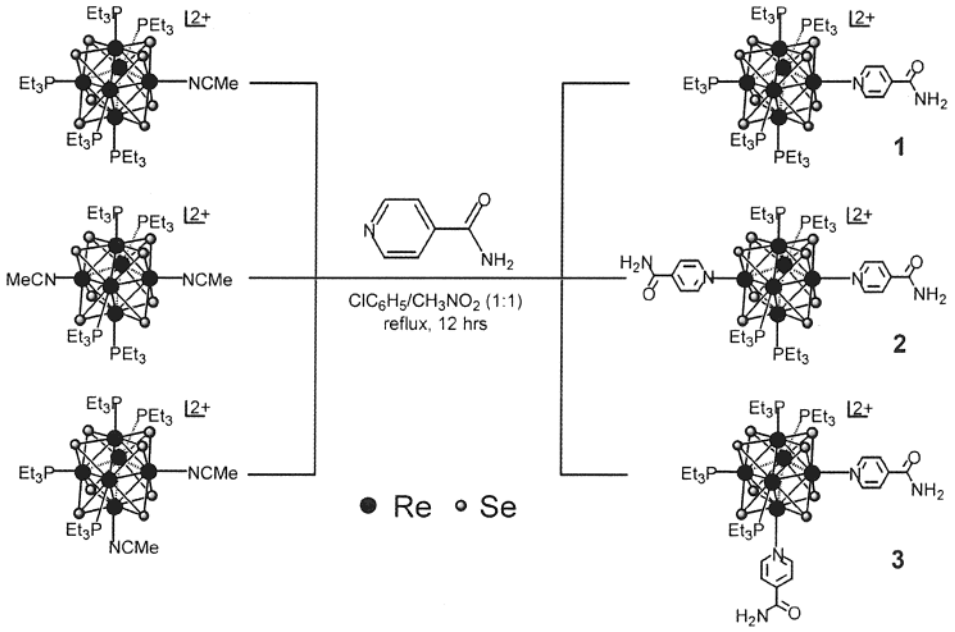
Scheme 1



cluster units may be anticipated. Furthermore, as compared with mononuclear complexes, cluster-based building blocks are larger in size, and this feature is particularly attractive for making porous structures potentially useful for guest recognition and separation. Functionally, clusters possess many fundamentally distinct properties that are intrinsic to metal−metal bonded species. The incorporation of such building units into an extended system will therefore create new prospects for realizing materials with interesting properties and possibly important applications. Despite such high expectations, there is only one literature precedent,[8,9] to the best of our knowledge, of metal-cluster arrays that are assembled via intercluster hydrogen bonding using *rationally designed* hexamolybdate clusters equipped with oxobenzamide ligands.

In an effort to extend this hydrogen-bonding approach to the creation of novel cluster-based extended systems and ultimately to explore the properties of such supramolecular materials, we have recently designed and synthesized a series of cluster complexes featuring the octahedral, face-capped $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core[10,11] and studied their organization into multicluster arrays via intercluster hydrogen bonding. This cluster may be viewed as an octahedron of rhenium enfolded in a cube formed by the eight face-capping selenides (Scheme 1). We have chosen this particular cluster system for a number of reasons. First of all, unlike their well-known isomorphs of the earlier transition metal-halide/chalcogenides,[12] the hexarhenium clusters are stable to aerobic handling and vigorous synthetic conditions, yet labile enough that multiple-step, solution-phase ligand substitution reactions are easily accomplished. In fact, a series of site-differentiated cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nL_{6-n}](SbF_6)_2$ ($n = 4-6$; L = a coordinating solvent molecule or a pyridyl-based ligand) have been prepared and characterized,[13] whereby the substitutionally inert phosphine ligands serve to protect a number of the rhenium sites and, concomitantly, to enforce the stereochemistry. Derivatives featuring bridged diphosphine ligands have also been re-

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ported.[14] These stereoisomers provide readily modifiable precursors for a broad range of chemistry, demonstrated or anticipated, based on the cluster system. Second, the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters are luminescent, and the luminescence is dependent on the rhenium coordination environment,[15,16] suggesting that one might be able to tune the optical properties of the final assembly. Indeed, the well-behaved chemistry and interesting photophysical properties of these clusters have made them the subject of recent intensive research,[10,11,13−23] with distinct efforts toward cluster-supported extended structures.[13,18−22]

In this report, we describe the preparation, structural characterization, and supramolecular organization of three $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing cluster complexes featuring isonicotinamide ligand(s). Specifically, the design and synthesis of site-differentiated complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(\text{isonicotinamide})_{6-n}]^{2+}$ [$n = 4$ (*cis* and *trans*), 5] are reported. The substitutionally inert phosphine ligands serve to protect four or five of the rhenium sites, while the amide ligand(s) occupy the remaining site(s) via Re−N(pyridyl) coordination. The amide function is capable of complementary hydrogen-bonding interaction and, indeed, leads to supramolecular cluster arrays mediated by intercluster hydrogen bonding. The solid-state structures of the supramolecules, dictated by the stereochemistry of the corresponding cluster building blocks, were established crystallographically.

Experimental Section

Preparation of Compounds. Reagents were of commercial origin and were used as received. Cluster solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(CH_3CN)_{6-n}](SbF_6)_2$ [$n = 4$ (*cis* and *trans*), 5] were prepared according to published procedures.[13] NMR spectra were recorded on a Varian Unity 300 spectrometer in CD_3CN. Chemical shifts of ^{31}P spectra were referenced to 85% H_3PO_4 ($\delta = 0$ ppm, with negative values meaning upfield). Microanalyses (CHN) were performed by Desert Analytics Laboratory, Tucson, Arizona, using samples that had been dried under high vacuum. The formulas reported in the following paragraphs differ from the crystallographic ones by not possessing any crystallization solvent.

Table 1. Crystal Data[a] and Structure Refinement for Complexes **1**−**3**

	[**1**](SbF$_6$)$_2$	[**2**](SbF$_6$)$_2$	[**3**](SbF$_6$)$_2$
formula	$C_{37}H_{83}Cl_2F_{12}N_2OP_5Re_6Sb_2Se_8$	$C_{40}H_{83}Cl_2F_{12}N_7O_8P_4Re_6Sb_2Se_8$	$C_{44.5}H_{93}ClF_{12}N_4O_4P_4Re_6Sb_2Se_8$
fw	3018.18	3205.29	3127.94
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	1	2
a, Å	14.5249(11)	11.790(2)	15.515(2)
b, Å	14.7424(11)	12.944(3)	15.736(2)
c, Å	20.537(2)	13.471(3)	19.451(3)
α (deg)	92.955(2)	77.20(3)	75.958(2)
β (deg)	106.210(2)	72.18(3)	69.934(2)
γ (deg)	115.1720	76.15(3)	60.681(2)
V, Å^3	3747.6(5)	1875.6(7)	3873.3(9)
ρ_{calcd}, Mg m^{-3}	2.675	2.838	2.682
μ, mm^{-1}	14.478	14.462	13.964
θ range	1.63 to 29.09	2.10 to 26.37	1.12 to 25.03
R1,[b] wR2[c]	0.0612, 0.1218	0.0278, 0.0596	0.0528, 0.1265

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 170 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|(F_o)^{1/2}$.

$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\text{isonicotinamide})](SbF_6)_2$ (1). To a solution of 26 mg (9.0 μmol) of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)](SbF_6)_2$ in 5 mL of chlorobenzene/nitromethane (v/v 1:1) was added isonicotinamide (20× excess) as a solid. The mixture was stirred and refluxed for 12 h to afford an orange solution. The solvent was evaporated, and the residue was extracted using dichloromethane and water. The organic phase was dried over anhydrous $MgSO_4$, and the product was obtained as an orange-red powder after removal of solvent (20.5 mg, yield: 79%). ^1H NMR: 0.95−1.17 (m, $5CH_3$), 2.12 (q, $1CH_2$), 2.23 (q, $4CH_2$), 6.43 (broad s, amide 1H), 7.00 (broad s, amide 1H), 7.57 (d, pyridyl 2H$^\beta$), 9.40 (d, pyridyl 2H$^\alpha$). ^{31}P NMR: −19.5 ($4PEt_3$), −23.0 ($1PEt_3$). Anal. Calcd for $C_{36}H_{81}N_2F_{12}OP_5Re_6Se_8Sb_2$: C, 14.68; H, 2.92; N, 1.06. Found: C, 14.74; H, 2.78; N, 0.96.

***trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2](SbF_6)_2$ (2).** Prepared in a manner similar to **1** except that *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CH_3CN)_2](SbF_6)_2$ was used in place of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)](SbF_6)_2$ (Yield: 75%). ^1H NMR: 1.15 (q, CH_3), 2.31 (q, CH_2), 6.42 (broad s, amide 1H), 7.00 (broad s, amide 1H), 7.55 (d, pyridyl 2H$^\beta$), 9.30 (d, pyridyl 2H$^\alpha$). ^{31}P NMR: −16.7. Anal. Calcd for $C_{36}H_{72}N_4F_{12}O_2P_4Re_6Se_8Sb_2$: C, 14.48; H, 2.47; N, 2.00. Found: C, 14.72; H, 2.47; N, 1.91.

***cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2](SbF_6)_2$ (3).** Prepared in a manner similar to **1** except that *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CH_3CN)_2](SbF_6)_2$ was used in place of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)](SbF_6)_2$ (Yield: 72%). ^1H NMR: 1.08−1.20 (m, CH_3), 2.23 (q, CH_2), 2.35 (q, CH_2), 6.48 (broad s, amide 1H), 7.06 (broad s, amide 1H), 7.64 (d, pyridyl 2H$^\beta$), 9.57 (d, pyridyl 2H$^\alpha$). ^{31}P NMR: −20.4, −17.5. Anal. Calcd for $C_{36}H_{72}N_4F_{12}O_2P_4Re_6Se_8Sb_2$: C, 14.48; H, 2.47; N, 2.00. Found: C, 14.46; H, 2.28; N, 1.86.

X-ray Structure Determinations. X-ray crystallographic data are summarized in Table 1. Red plate-shaped crystals of **1** and **3** were grown from corresponding dichloromethane solutions upon

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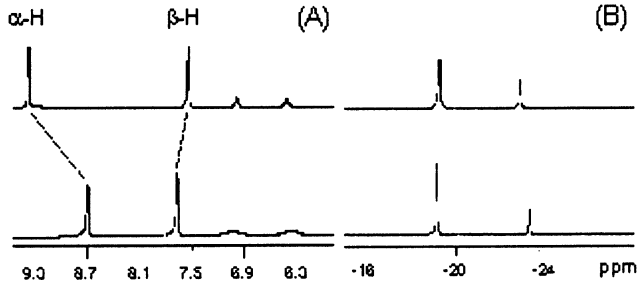

Figure 1. (A) ^{1}H NMR signals of the isonicotinamide ligand in complex **1** (top) and the corresponding resonances of the free ligand (bottom). (B) ^{31}P NMR spectrum of complex **1** (top) and that (bottom) of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$, the corresponding nitrile precursor.

vapor diffusion of diethyl ether at room temperature, while red block-shaped crystals of **2** were obtained analogously starting from a mixed solution of dichloromethane and nitromethane. Data 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. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they were bonded and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom.

Results and Discussion

Synthesis and Characterization of Cluster Complexes. In this work, we sought the synthesis, structural characterization, and supramolecular organization of a series of site-differentiated cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(\text{isonicotinamide})_{6-n}]^{2+}$ [**1** ($n = 5$); **2** ($n = 4$, *trans*); **3** ($n = 4$, *cis*)]. The targeted complexes were prepared via the reaction of the corresponding acetonitrile solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(MeCN)_{6-n}](SbF_6)_2$ with excess isonicotinamide in a refluxing mixture of chlorobenzene/nitromethane (1:1) (Scheme 1). In a representative synthesis, reacting $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ with an excess of isonicotinamide afforded $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\text{isonicotinamide})](SbF_6)_2$ (**1**), the first member of the series, in good yields after straightforward workup. Microanalysis (CHN) is in agreement with the proposed stoichiometry. Several lines of spectroscopic evidence support the molecular structure and stereochemistry of **1**. Specifically, upon the formation of **1**, the ^{1}H NMR resonance of the coordinated nitrile of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$, the starting solvate, disappears, indicating the displacement of the bonded solvent molecule. This is corroborated by the emergence of a signal at 9.40 ppm (Figure 1A) which is attributed to the α-H of the coordinated pyridyl moiety and is significantly downfield-shifted from the corresponding resonance of free isonicotinamide at 8.70 ppm. Also clear from Figure 1 is the noticeable but less dramatic shift of the β-H signal. The two magnetically nonequivalent amide protons, appearing as broad singlets at $\delta = 6.43$ and 7.00 ppm, respectively, are also revealed by ^{1}H NMR. The ^{31}P NMR spectrum of **1** is unsophisticated, showing two ^{31}P resonance peaks at -19.5 and -23.0 ppm, respectively, in a relative ratio of 4:1 characteristic of a pentaphosphine-substituted species (Figure 1B). The corresponding signals of the starting nitrile solvate appear at -19.1 and -23.3 ppm, respectively. Complex **1** is readily soluble in dichloromethane, acetonitrile, and other common polar organic solvents to yield orange-red solutions.

Encouraged by the successful isolation and supramolecular organization of **1**, we hoped to extend the cluster-supported hydrogen bonding to the next level of complexity. By placing the amide ligands at rhenium apices *trans* to each other, the expected hydrogen bonding should yield a one-dimensional chain of clusters in the solid state. Complex **2** was accordingly prepared. The synthesis was accomplished in the same manner as **1**, with the only difference of using *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ as the starting cluster. As in the case of **1**, formation of **2** is marked by the displacement of MeCN with isonicotinamide, as confirmed by ^{1}H NMR studies. In the ^{1}H spectrum, the *ortho* and *meta* proton multiplets are centered about 9.30 and 7.55 ppm, respectively, clearly shifted from those of the free ligand. The amide protons in **2** appear as two magnetically nonequivalent signals at $\delta = 6.42$ and 7.00 ppm, respectively. A single peak at -16.7 ppm in the ^{31}P spectrum suggests one symmetric phosphine environment and retention of the *trans* stereochemistry upon reaction. In comparison, the ^{31}P resonance of the starting dinitrile complex appears at -17.9 ppm.[13a]

Compound **3** was prepared with the hope of achieving a discrete square-shaped tetracluster array with hydrogen-bonded isonicotinamide ligands serving to link neighboring clusters. Upon assembly in the solid state, however, only one-dimensional zigzag polymeric chains of clusters mediated by hydrogen bonding have been obtained (see later). This is in fact not surprising considering nature's abhorrence toward void space, which has been manifested by the formation of numerous polymeric supramolecular structures whose presumably more desired supramolecular isomorphs[24] are the porous structures. Displacement of the nitrile ligands was indicated by the disappearance of the ^{1}H signal of the originally bound nitrile molecules. Accompanying are the ^{1}H signals of the newly implemented isonicotinamide ligands. The ^{31}P spectrum confirms the preservation of the cluster stereochemistry, with two peaks of equal intensity at -17.5 and -20.4 ppm, respectively; the corresponding values of *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ appear at -15.6 and -19.0 ppm, respectively.

Molecular and Supramolecular Structures of the Cluster Complexes. Structures were determined for the three compounds reported in Table 1. The metrical parameters describing the cluster core and its terminal bonding are summarized in Table 2 and are unremarkably similar to the corresponding values reported for similar compounds.[11,13,14,17−23] Only distinct features pertinent to inter-

(24) Zaworotko, M. J. *Chem. Commun.* **2001**, 1.

cluster hydrogen bonding and the resulting supramolecular organization are discussed.

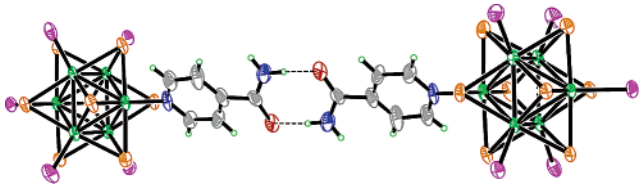

Figure 2. Thermal ellipsoid diagram of the hydrogen-bonded dimer of **1**. Thermal ellipsoids rendered at the 50% probability level. Phosphine ethyl groups, non-hydrogen-bonding hydrogen atoms, and counterions are excluded for clarity. Color scheme: C (gray), N (blue), P (purple), Re (green), O (red), and Se (yellow).

Table 2. Interatomic Distances (Å) and Angles (deg) for Cluster Complexes **1**−**3**

	range	mean
Re−Re	2.617(1)−2.645(1)	2.636(7)
Re−Se	2.508(1)−2.529(1)	2.517(13)
Re−P	2.470(4)−2.486(2)	2.478(8)
Re−N	2.186(6)−2.213(4)	2.204(7)
Re−N−C	117.4(5)−121.6(3)	120.0(1)

$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(isonicotinamide)](SbF_6)_2$ (1). This monoisonicotinamide complex is derived from the penta(triethylphosphine)-substituted cluster unit $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5]^{2+}$. As shown in Figure 2, the isonicotinamide ligand is bound to the non-phosphine-protected Re site via the pyridyl nitrogen. The amide portion of the ligand is twisted with respect to the pyridyl plane, but the deviation is within normal limits relative to that observed for the free ligand.[25] Each cluster engages in self-complementary amide−amide hydrogen bonding to a cluster in a neighboring cell, generating a hydrogen-bonded dimer. Parameters manifesting hydrogen-bonding interactions are collected in Table 3. The dimers' packing arrangement yields pseudochains being formed along a body diagonal, with each neighboring dimer translated $^1/_4$ of a repeating unit along the pseudo-chain axis. Small voids are found at the ends of dimer units along a given chain in which librationally disordered solvent (CH_2Cl_2) and SbF_6^- counterions reside (Figure 3). Interestingly, the pseudochain of **1** packs into a checkerboard-like pattern, resulting in small channels running parallel to the pseudochain axis (Supporting Information). Located in these channels are additional counterions, some portions of which appear to be in close contact with the pendant hydrogen of the amide group, suggesting the existence of a weak hydrogen bond to fluorine. However, the disorder of both the SbF_6^- moiety and the amide unit prohibits direct calculation of the hydrogen bond. Similar observations have also been made in the structures of **2** and **3**, as described.

Table 3. Selected Metrical Parameters Indicating Hydrogen-Bonding Interactions

complex	*d*(NH···O) (Å)	*d*(N···O) (Å)	∠NHO (deg)
1	2.23−2.26	3.05(4)-3.07(4)	149.4−158.4
2	2.03	2.908(6)	172.9
3	1.95−1.98	2.82(2)-2.86(2)	167.3−177.1

***trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(isonicotinamide)_2](SbF_6)_2$ (2).** This compound is the *trans*-bis(isonicotinamide) derivative of the *trans* isomer of the tetra(triethylphosphine)-substituted cluster unit $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4]^{2+}$. The two symmetry-related isonicotinamide ligands are bound to the Re centers via the pyridyl nitrogen. The amide groups undergo conventional N−H···O hydrogen bonding (Table 3) with the ligand of a neighboring cluster complex, generating infinite chains featuring the cluster units and the pairwise cluster-linking hydrogen bonds (Figure 4). The amide portion of the ligands is twisted by 38.3(6)° out of the pyridyl ring plane. This canting of the amide moieties is likely the result of a weak hydrogen-bonding interaction with a fluorine atom of one of the SbF_6^- counterions that occupy the spaces above and below the amide nitrogen. The fluorine hydrogen bonding is to the pendant hydrogen atom of the amide and does not disrupt the N−H···O scheme.

A packing mode of the linear polymer chains of **2**, similar to the one for **1**, is observed (Supporting Information). When

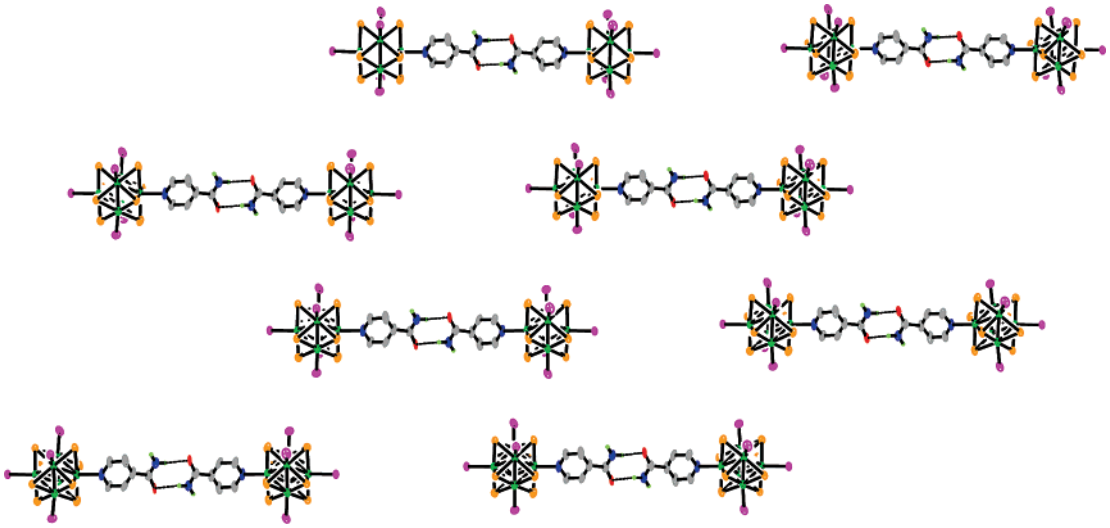

Figure 3. Packing diagram of **1** showing one layer of the pseudo-chain structure. Voids shown, each formed by four dimer units, two in the same chains and one above and one below the space between those two dimers in the same chain, are occupied by disordered solvent molecules. Thermal ellipsoids rendered at the 50% probability level. Phosphine ethyl groups, non-hydrogen-bonding hydrogen atoms, solvent, and counterions are excluded for clarity. Color scheme: C (gray), N (blue), P (purple), Re (green), O (red), and Se (yellow).

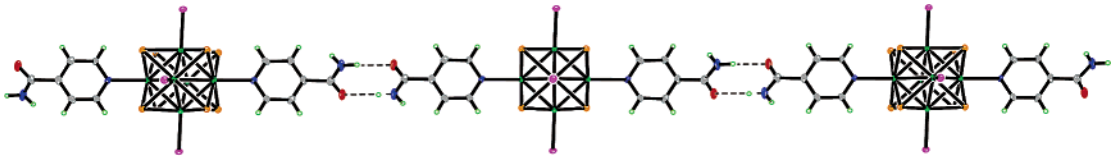

Figure 4. Thermal ellipsoid diagram of the hydrogen-bonded polymer of **2**. Thermal ellipsoids rendered at the 50% probability level. Phosphine ethyl groups and counterions are excluded for clarity. Color scheme: C (gray), N (blue), P (purple), Re (green), O (red), and Se (yellow).

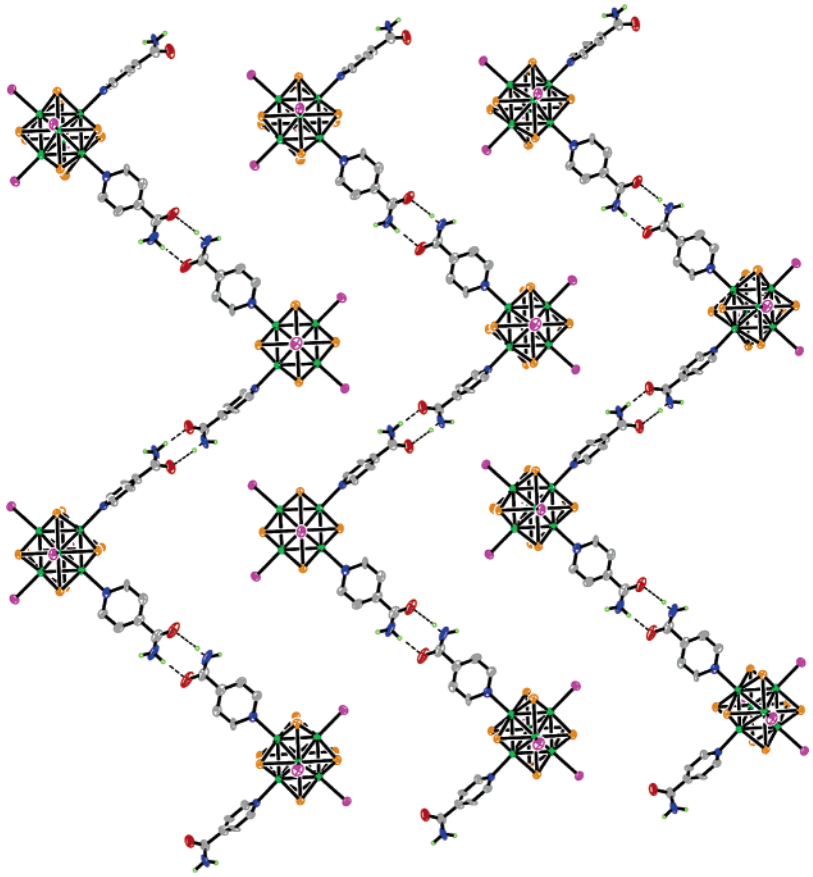

Figure 5. Single layer displaying three individual hydrogen-bonded chains of **3**. Thermal ellipsoids rendered at the 50% probability level. Phosphine ethyl groups, non-hydrogen-bonding hydrogen atoms, solvent, and counterions are excluded for clarity. Color scheme: C (gray), N (blue), P (purple), Re (green), O (red), and Se (yellow).

viewed down the chain axis, the polymers form a pseudohexagonal array with individual polymer chains extending along a body diagonal. However, the formation of an additional hydrogen bond in **2** due to the second isonicotinamide ligand prohibits the formation of the intrachain voids as observed for **1**. Thus, all solvent and counterions contained in such voids are forced, in the present case, into the interchain channels. As a result, a more open and less dense framework of **2** is generated.

***cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2](SbF_6)_2$ (3).** This compound is the *cis*-bis(isonicotinamide) derivative of the *cis* isomer of the tetra(triethylphosphine)-substituted cluster unit $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4]^{2+}$. The two *cis* disposed isonicotinamide ligands are bound to the Re centers via the pyridyl nitrogen, and the amide−amide hydrogen bonding (Table 3) leads to infinite chains of clusters (Figure 5) as observed for **2**. Similar to those of **1** and **2**, the chains of **3** extend along a body diagonal. However, due to *cis* displacement of the isonicotinamide ligands, the hydrogen-bonded chains have a zigzag topology. This zigzag shape results in the chains fitting together to form sheets of chains. The lamellae are apparently stabilized by hydrophobic interdigitation of the phosphine groups between layers. Disordered solvent molecules and counterions are found in the interlayer spaces. Like **2** (and possibly **1**), **3** undergoes with one of the fluorine atoms of the counterion a secondary hydrogen-bonding interaction that does not interrupt the primary homotopic amide−amide linkage.

Summary and Outlooks

Judiciously designed $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster complexes can be used as novel building blocks for hybrid inorganic/organic supramolecular assemblies. The cluster core's relative inertness prohibits stereochemical scrambling, ensuring a fixed geometry for a given isomer. In effect, the cluster complex is a rigid building block with defined geometry that limits the structural possibilities of a multicluster array upon assembly. In particular, we have shown in this work that

(25) Toriumi, Y.; Kasuya, A.; Itai, A. *J. Org. Chem.* **1990**, *55*, 259.

the use of secondary hydrogen-bonding interactions is a viable means of generating crystalline, cluster-supported supramolecular arrays. In each of the examples presented here, the geometry of the cluster is faithfully expressed in the solid state by the hydrogen-bonded isonicotinamide moiety placed at specific metal apices. The combined effect of the cluster's geometric directing power and the predictability of the formation of complementary hydrogen bonds points to the possibility of generating other novel metal-cluster-supported supramolecular architectures and possibly molecularly engineered materials. For example, multicluster arrays that are topologically different from the examples herein described may be achieved by making use of angled hydrogen-bonding motifs, such as those derived from nicotinamide or nicotinic acid. Probably more tantalizing is the prospect of creating cluster-supported porous solids with enlarged pore size for guest sensing and separation. This goal may be fulfilled by employing cluster building blocks possessing three or more ligands that are capable of hydrogen bonding. Research along both lines is underway.

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Supporting Information Available: X-ray crystallographic data in CIF format for the three structures reported in Table 1 and packing diagrams of **1** and **2**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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