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Hydrogen-bonded supramolecular arrays of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing clusters

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Site-differentiated clusters of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nL_{6-n}](SbF_6)_2$ [L = nicotinamide: **1** ($n = 5$), **2** ($n = 4$, *trans*-), and **3** ($n = 4$, *cis*-)] have been made by ligand substitution reactions of the corresponding acetonitrile solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(MeCN)_{6-n}](SbF_6)_2$ ($n = 5$; $n = 4$, *cis*- and *trans*-) with nicotinamide. De-iodination of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nI_{6-n}]I_{n-4}$ [$n = 4$ (*cis*- and *trans*-), 5] with $AgSbF_6$ in the presence of 3,5-pyridinedicarboxylic acid (PDCA) produced a related series of cluster complexes $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nL_{6-n}](SbF_6)_2$ [L = PDCA: **4** ($n = 5$), **5** ($n = 4$, *trans*-), and **6** ($n = 4$, *cis*-)]. Retention of stereochemistry in each case was confirmed by ^1H and ^{31}P NMR and these new cluster derivatives were further characterized by satisfactory microanalyses (CHN). In addition, the solid-state structure of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(PDCA)_2](SbF_6)_2$ (**5**) was established crystallographically, which revealed zigzag arrays of clusters mediated by complementary hydrogen-bonding interactions involving only one of the acid groups per PDCA ligand; the second acid group extends into a small space between the chains and appears to be in close contact with a Se atom on a neighboring cluster, as well as a hydrogen atom of that cluster's triethylphosphine ligands. Each polymer chain is skewed with respect to its neighbors, forming a pronounced lamellar structure.

Introduction

Transition metal clusters have received much recent interest as structural and functional building blocks for supramolecular construction.[1] The significance of such efforts is double fold. On one hand, it is possible to develop aesthetically motivated supramolecular synthesis supported by expanded dimension and high symmetry of clusters. On the other hand, clusters frequently exhibit properties that are inherent to metal-metal bonded species, which allows for the creation of functional materials of practical importance.

In this vein our group[2] and others[3–6] have conclusively shown that the octahedral hexanuclear $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters are ideally suited to this capacity. The cluster core, shown in Fig. 1, can be viewed as an octahedron of rhenium atoms enclosed in a cube formed by substitutionally inert chalcogenide ligands. Terminal halides of the starting cluster $[Re_6(\mu_3\text{-}Q)_8X_6]^{4-}$ (X = Cl, Br, I; Q = S, Se), obtained initially from solid-state synthesis,[7] undergo facile ligand substitution reactions with triethylphosphine to yield site-differentiated complexes of the general formula $[Re_6(\mu_3\text{-}Q)_8(PEt_3)_nX_{6-n}]^{(n-4)+}$ (Q = S: n = 2–6, $X = Br^-$; Q = Se: n = 4–6, $X = I^-$).[8] Subsequent de-halogenation in coordinating media L, often a coordinating solvent, leads to corresponding derivatives of the general formula $[Re_6(\mu_3\text{-}Q)_8(PEt_3)_nL_{6-n}]^{2+}$ with unperturbed stereochemistry.[8a,9]

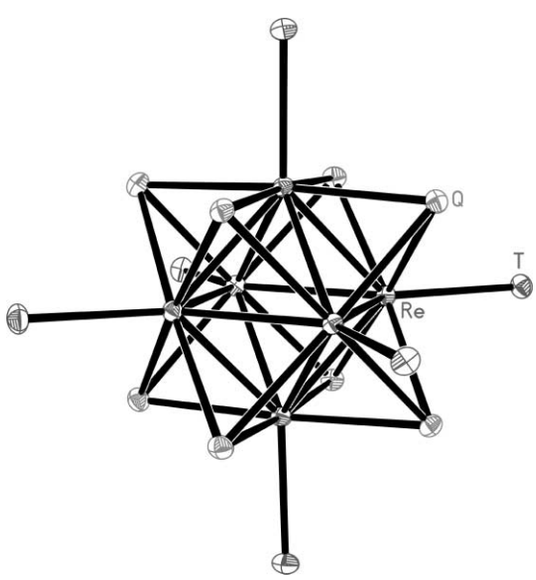

Fig. 1 The structure of the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ cluster core shown with terminal ligands T.

This readily modifiable stereochemistry makes the cluster a powerful geometric determinant of resulting supramolecular assemblies using these stereospecific clusters as building blocks. Indeed, we have successfully built a molecular Tinkertoy set consisting of site-differentiated cluster solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(CH_3CN)_{6-n}](SbF_6)_2$ ($n = 5$; $n = 4$, *cis*- and *trans*-)[8a,9] and pyridyl-based multitopic ligands, from which "clusters of clusters" featuring multiple cluster units linked by the multitopic ligands have been prepared. These entities include cluster-supported molecular squares,[2a] star-shaped tri- and tetra-clusters,[2b] and metallodendrimers of clusters.[2d] The interesting electrochemical[10] and photophysical[11,12] properties of the cluster building blocks may lead to useful applications of these multicluster arrays.

Cluster arrays not directly supported by ligand–cluster dative bonding were also sought.[2e–g] If a ligand bound to the cluster bore additional functionality capable of secondary interactions such as hydrogen bonding or metal ion coordination, arrays of the clusters could be anticipated wherein individual cluster units are "glued together" by the secondary interactions. As compared with the aforementioned cluster-condensation approach,[2a,b,d,9] this self-assembly methodology offers the advantage of allowing the only "traditional" synthetic step to be the preparation of properly functionalized monocluster species that would be highly soluble and readily purified. The supramolecular intercluster linkage(s) would then be formed only upon concentration in the solid state, obviating the need for careful control of synthetic conditions and reagent stoichiometry. More importantly, hydrogen bonding and metal–ligand coordination are classic crystal engineering motifs,[13a] so the slow concentration and self-assembly of the monocluster units are likely to yield stable single crystals of predictable structure, a luxury not enjoyed by the aforementioned "clusters of clusters".[2a,b,d,9]

We have recently demonstrated the feasibility of this non-dative approach with the creation of three novel $[Re_6(\mu_3\text{-}Se)_8]^{2+}$

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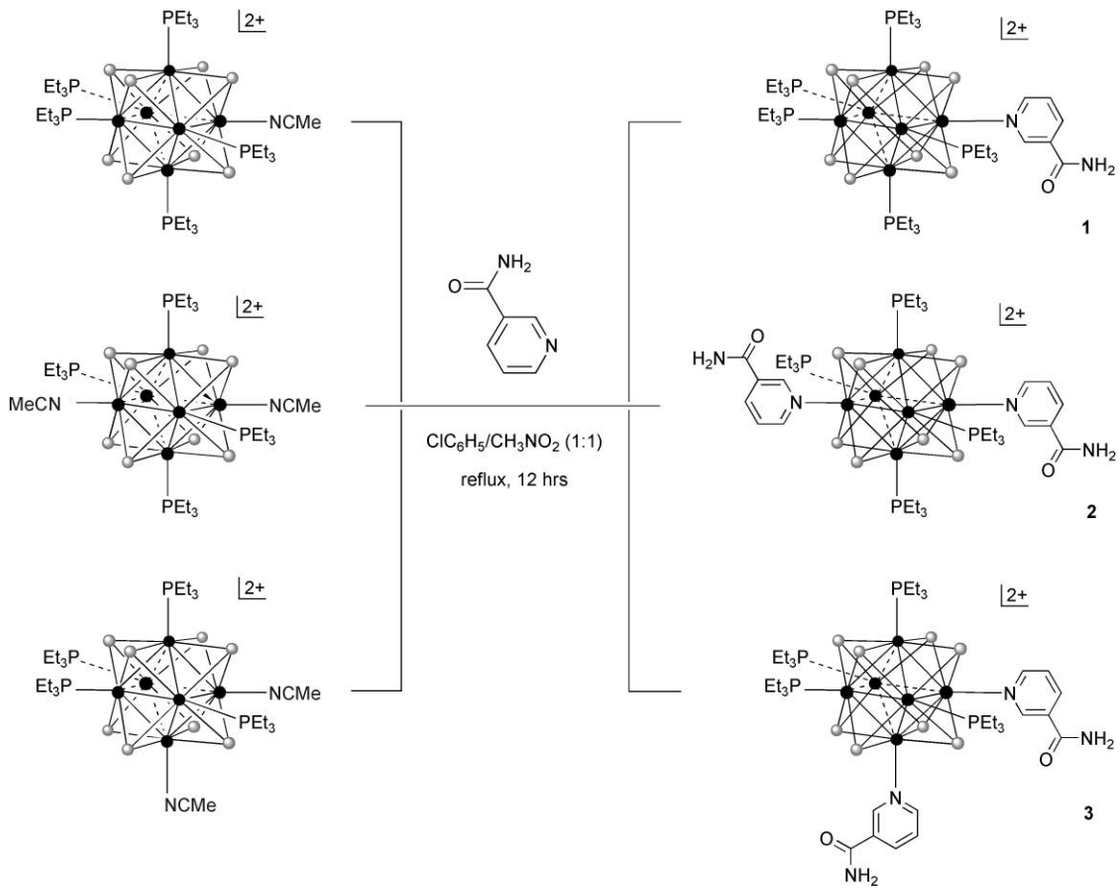


Scheme 1

cluster complexes featuring isonicotinamide ligand(s).[2e] In the solid state, these complexes organize themselves into arrays *via* paired hydrogen bonding involving the amide groups of neighboring clusters. The cluster stereochemistry 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.

The aim of present work is to further the synthetic utility of this hydrogen bonding-supported approach to other supramolecular cluster arrays. Specifically, we explore what effect, if any, modifying the hydrogen bonding donor–acceptor (DA) pairs and arranging them in symmetrically significant directions might have on the overall structure. To this end, two series of cluster derivatives have been prepared. The first features nicotinamide, the *meta*-substituted amide, as the purpose-specific ligand. The complexes with such ligands might engender the adoption of polar or helical arrangements in the solid state. The second series of complexes are those with at least one PDCA ligand whose two pairs of hydrogen bonding DA groups are placed at 120° from each other on the pyridyl ring. The carboxylic acid-based DA groups are subject to a variety of different hydrogen bonding modes. The combined effect of the increased number of DA units per molecule and the fixed relative arrangement of the DA units is to provide additional structure-directing power, in additional to the influence of the cluster stereochemistry, over the final self-assembled architecture. The resultant hydrogen-bonded arrays should therefore 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.

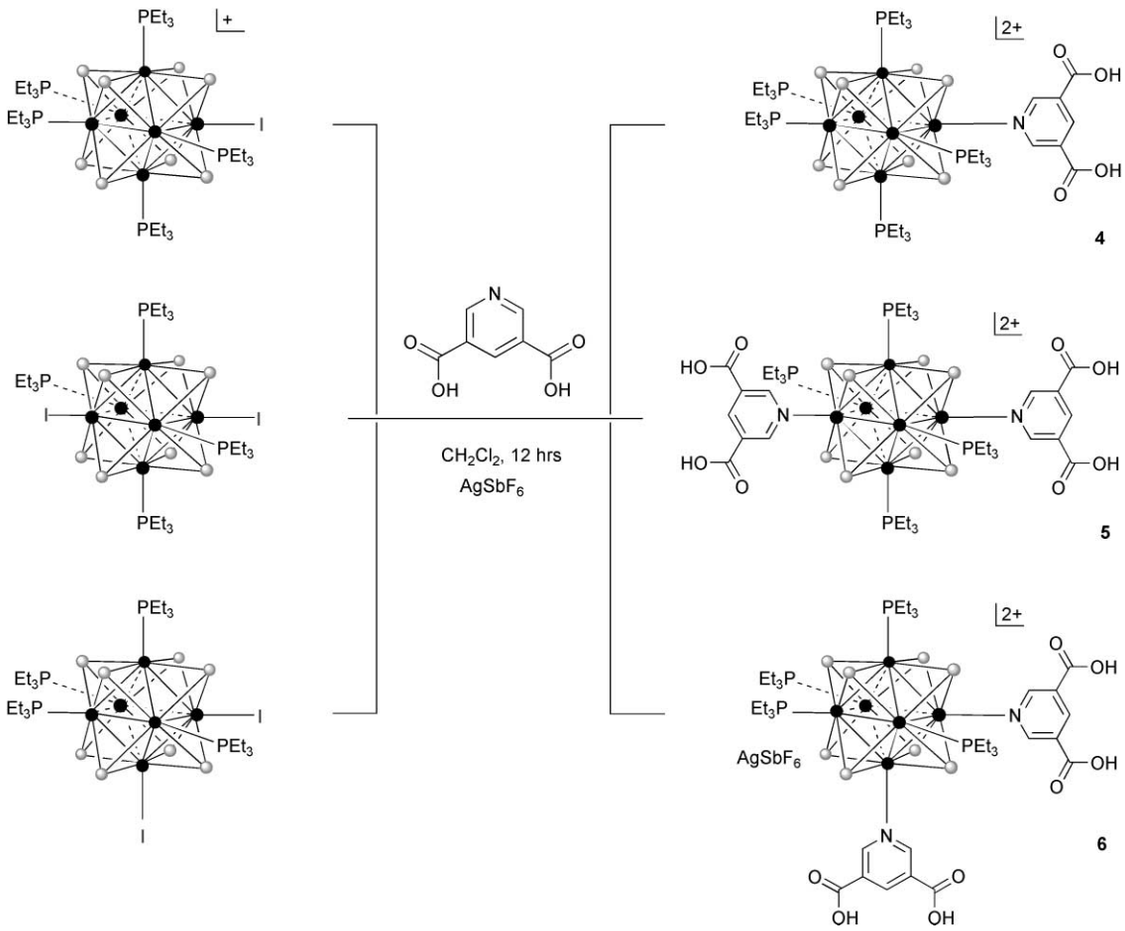
Results and discussion

Synthesis and characterization of cluster complexes

In this work, we sought the synthesis, structural characterization, and supramolecular organization of site-differentiated cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n\text{-}L_{6-n}](SbF_6)_2$ [L = nicotinamide: **1** (n = 5), **2** (n = 4, *trans*-), **3** (n = 4, *cis*-); L = PDCA: **4** (n = 5), **5** (n = 4, *trans*-), **6** (n = 4, *cis*-)].

The first series of clusters, **1**–**3**, were prepared *via* the reaction of the corresponding acetonitrile solvates[8a,9] $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(MeCN)_{6-n}](SbF_6)_2$ with excess nicotinamide in a mixture of chlorobenzene–nitromethane (1 : 1) under reflux for 12 h (Scheme 1). Each of the three complexes was obtained in good yields after straightforward work-up procedures.

Several lines of spectroscopic evidence support the formation of the desired products. For example, upon the formation of **1**, the ^{1}H NMR resonance of the coordinated nitrile of the starting solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ disappears, indicating the displacement of the bonded solvent molecule. This is corroborated by the emergence of two signals at 9.38 and 9.79 ppm (Fig. 2(a)), attributable to the protons α- to the cluster-coordination pyridyl N atom; these two resonances are significantly downfield-shifted from the free nicotinamide signals at 8.76 and 9.02 ppm, respectively. The β-H and γ-H signals, appearing at 7.40 and 8.24 ppm, respectively, remain essentially unchanged as compared with free nicotinamide (7.42 and 8.17 ppm, respectively). The ^{1}H NMR also reveals two magnetically nonequivalent amide protons, shown as broad singlets at 6.36 and 6.96 ppm, respectively. The ^{31}P NMR spectrum of **1** is uncomplicated, showing two resonance peaks at −21.2 and −25.0 ppm, respectively, in a relative ratio of 4 : 1 characteristic of a pentaphosphine-substituted species (Fig. 2(b)). The corresponding signals of the starting nitrile solvate appear at −23.8 and −27.6 ppm, respectively.



Scheme 2

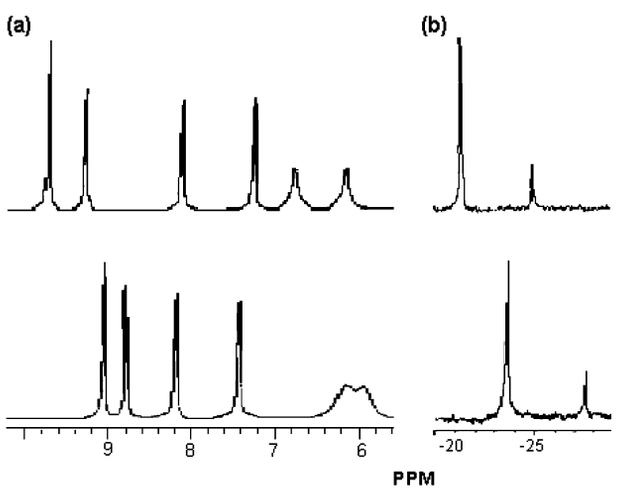


Fig. 2 (a) ^{1}H NMR spectra of **1** (top) and free nicotinamide. The ethyl region (PEt_3) is not shown for clarity. (b) ^{31}P NMR spectra of **1** (top) and $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)](SbF_6)_2$.

Equally successful was the preparation of both *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(nicotinamide)_2](SbF_6)_2$ (**2**) and *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(nicotinamide)_2](SbF_6)_2$ (**3**) starting from their respective nitrile solvates. As in the case of **1**, formation of **2** and **3** is marked by the disappearance of ^{1}H signal of the originally bound nitrile molecules. Accompanying are the ^{1}H signals of the newly implemented nicotinamide ligands. The ^{31}P spectra, showing one and two resonances of equal intensity for **2** and **3**, respectively, confirm the preservation of the cluster stereochemistry in both cases.

All three clusters are readily soluble in common polar organic solvents, such as dichloromethane, acetone, and acetonitrile to afford orange-red solutions. Unfortunately, despite providing single crystals, all of the samples were too delicate to survive the duration of the diffraction experiment. This is likely the result of inefficient packing enforced by the nicotinamide ligand; further complicated by the inclusion of large amounts of volatile solvent necessary to fill the resultant void volume. In contrast, the straight extension of the amide moiety of closely related isonicotinamide appears to yield sufficiently stable packing modes *via* collinear (with respect to the ligand cluster bond vector) hydrogen bonding, allowing complete crystallographic analysis.[2e]

The second series of complexes (**4**–**6**) were prepared according to Scheme 2. Owing to the poor solubility of the free PDCA in ordinary organic solvents, the ligand exchange was carried out by executing de-halogenation of the iodo-complexes[8a] $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nI_{6-n}]I_{n-4}$ [n = 5, 4 (*cis*- and *trans*-)] using $AgSbF_6$ in the presence of excess PDCA in dichloromethane. All three new clusters were obtained in reasonable yields after a similar work-up procedure to the one used for isolating clusters **1**–**3**.

Spectroscopic analyses of **4**–**6** confirm the molecular structure of the series. The ^{31}P spectra of all the compounds are consistent with retention of cluster stereochemistry during the ligand metathesis reaction, as might be expected on basis of our previous observations of related clusters. The characteristic resonances of cluster **4** in 4 : 1 ratio appear at −24.3 and −28.7 ppm, respectively. A single peak at −19.3 ppm is observed for cluster **5**, while twin ^{31}P signals, at −20.5 and −23.6 ppm, are shown in the case of **6**. As no nitrile signal is present to track the conversion of the iodo-complexes into the target compounds, only the ^{1}H NMR signals of the PDCA ligand are useful spectroscopic handles for confirming the cluster ligation. For **4**, these appear as a singlet at 9.97 ppm of the two equivalent α-pyridyl protons, significantly down-field shifted

Table 1 Interatomic distances (Å) and angles (°) for **5**

	Range	Mean
Re–Re	2.632(1)–2.641(1)	2.636
Re–Se	2.510(1)–2.520(1)	2.515
Re–P	2.474(4) and 2.476(2)	2.475
Re–N	2.211(6)	
Re–N–C	118.6(5) and 123.8(6)	121.2

from 9.30 ppm of free PDCA. Interestingly, the γ-proton resonance at 8.80 ppm is essentially unaffected by the cluster coordination. Similar chemical shifts were observed for **5** and **6** with negligible shifts in each case.

In contrast to free PDCA, clusters **4**–**6** are readily soluble in dichloromethane, acetonitrile, and other common polar organic solvents. Vapor diffusion of diethyl ether to the resulting orange–red solutions produced analytically pure crystalline samples in all cases. However, with the sole exception of **5**, structural determination by X-ray diffraction proved to be difficult, due largely to the extremely rapid de-solvation of the short-lived single crystals.

Structural determination

X-Ray crystallographic analysis was carried out on single crystals of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(PDCA)_2](SbF_6)_2$ (**5**). Details of data collection and refinement experiment are summarized in the Experimental section (see below). The metrical parameters describing the cluster core and its terminal bonding are summarized in Table 1 and are unremarkably similar to the corresponding values reported for similar compounds.[2–10] Only distinct features pertinent to intercluster hydrogen bonding (Table 2) and the resulting supramolecular organization are discussed below.

As shown in Fig. 3, cluster **5** is the *trans*-bis(3,5-pyridinedicarboxylic acid) complex of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4]^{2+}$. The centroid of the cluster sits on an inversion center. The unique non-phosphine ligand is bound to a Re center (Re3) *via* the pyridyl nitrogen atom (N1). Applying the inversion operator reveals that the PDCA ligands, including the carboxylic acid moieties, are virtually coplanar with the plane of four Re atoms (Re2, 2a, 3 and 3a) that includes the two to which they are bound. The inversion related carboxylic acid groups [O71(H71a)–C7–O72, O71a(H71aa)–C7a–O72a] undergo complementary hydrogen bonding with the neighboring sets. As the ligands are *trans*-coordinated to Re sites, and only one of the two sets per ligand

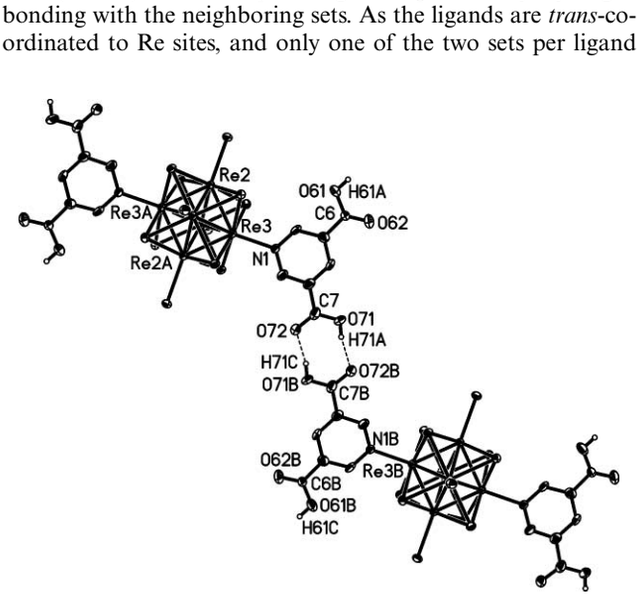


Fig. 3 An ellipsoid (rendered at 50% probability) plot of two units of the cationic cluster **5** interacting *via* hydrogen bonding. Counterions (SbF_6^-), ethyl groups of the triethylphosphine ligands, and the ring hydrogen atoms of the nicotinamide ligands have been omitted for clarity.

Table 2 Selected metrical parameters indicating hydrogen-bonding interactions in **5**

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
O71–H71a ··· O72	0.84 Å	1.807 Å	2.635 Å	168.27°

engages 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, which extend parallel to the *a*–*b* cell face (Fig. 4). Each chain is skewed with respect to its neighbors by approximately 0.25 translational units in the *a* and *c* directions, forming a pronounced lamellar structure (Fig. 4). The layers of chains span the *a*–*b* dimension, and are stacked along *c*. Disordered SbF_6^- counterions occupy the space between the layers. Interestingly, the second acid group on each ligand [O61(H61a)–C6–O62] does not participate in any hydrogen bonding. Instead, it extends into a small space between the chains and appears to be in close contact with a Se atom on a neighboring cluster, as well as a hydrogen atom of that cluster's triethylphosphine ligands. When viewed along the *c* axis, small channels are revealed (Fig. 5). The channels are filled with the ethyl groups of the site-protecting phosphine ligands and severely disordered solvent molecules, for which an adequate model could not be found. Application of the SQUEEZE module in the PLATON suite of programs[14] reveals the presence of 67 electrons in the void space. This number corresponds approximately to the non-hydrogen electron count of 1.5 diethyl ether and 1.5 acetonitrile molecules per unit cell.

The fact that the second acid group does not engage in the complementary hydrogen-bonding mode of its companion is somewhat surprising, as this is considered a strong hydrogen-bonding interaction. A key tenet of crystal engineering is that strong hydrogen bonding-capable groups will optimize their interactions to the greatest extent that geometry sterics will allow.[13] However, given the expanded dimension of the cluster scaffold, such an optimization in the present case would likely lead to the formation of hexagonal voids that are analogous to, but significantly larger than, the melamine/cyanuric acid rosettes prepared by Whitesides *et al.*[15] These voids would likely overwhelm the thermodynamic stability provided by maximizing the number of hydrogen bonds. Consequently, the chains are slipped slightly from the positions necessary to create the hexagonal voids, leaving one acid group free and an overall denser structure. A very similar hydrogen-bonding scheme is observed in a mononuclear *trans*-$Pd(PDCA)_2Cl_2$ analog recently reported by Puddephatt and co-workers.[16] Although the hydrogen bonding in their case is mediated by methanol molecules, the zigzag chain motif is observed, as well as the chain skewing. The free carboxylic acid group in their work is stabilized by weak hydrogen bonding to the chloride ligands of neighboring complexes, quite analogous to the close contacts observed in our own example.

In summary, six new cluster derivatives of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core have been prepared and characterized. These complexes are designed to feature at least one ligand that is capable of hydrogen bonding interactions. The purpose of this work at the outset was to demonstrate the synergy between cluster geometry and ligand influence on overall aggregate architecture with the hope of producing cluster arrays different from those with straightforward isonicotinamide ligand. The increased complexity in molecular structure unfortunately also translates to complications in crystallization. With the nicotinamide ligand, no stable crystals could be obtained, possibly the result of the additional kink in the ligand prohibiting an efficient packing mode. Similar results are observed with the 3,5-pyridinedicarboxylic acid ligand, wherein the vagaries of the hydrogen-bonding motif may further complicate the picture. Nevertheless, a single structure was obtained in the 3,5-

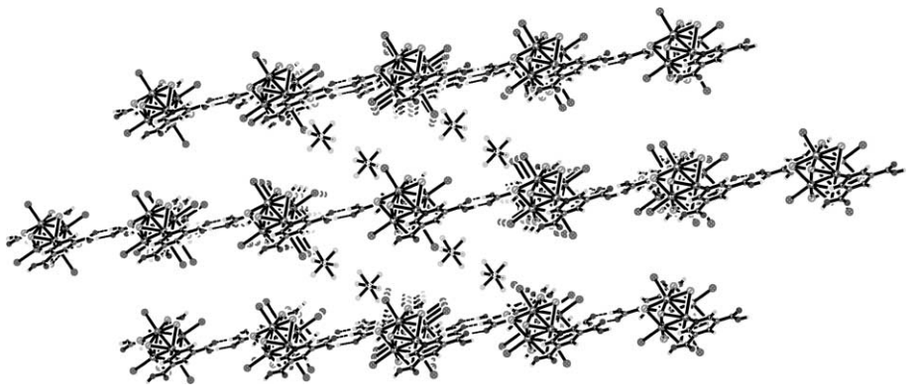


Fig. 4 The lamellar structure formed by zigzag hydrogen-bonded cluster polymers of **5**. Some SbF_6^- counterions are shown to occupy the space between the layers of the hydrogen bonded clusters. Ethyl groups of the triethylphosphine ligands and the ring hydrogen atoms of the nicotinamide ligands have been omitted for clarity.

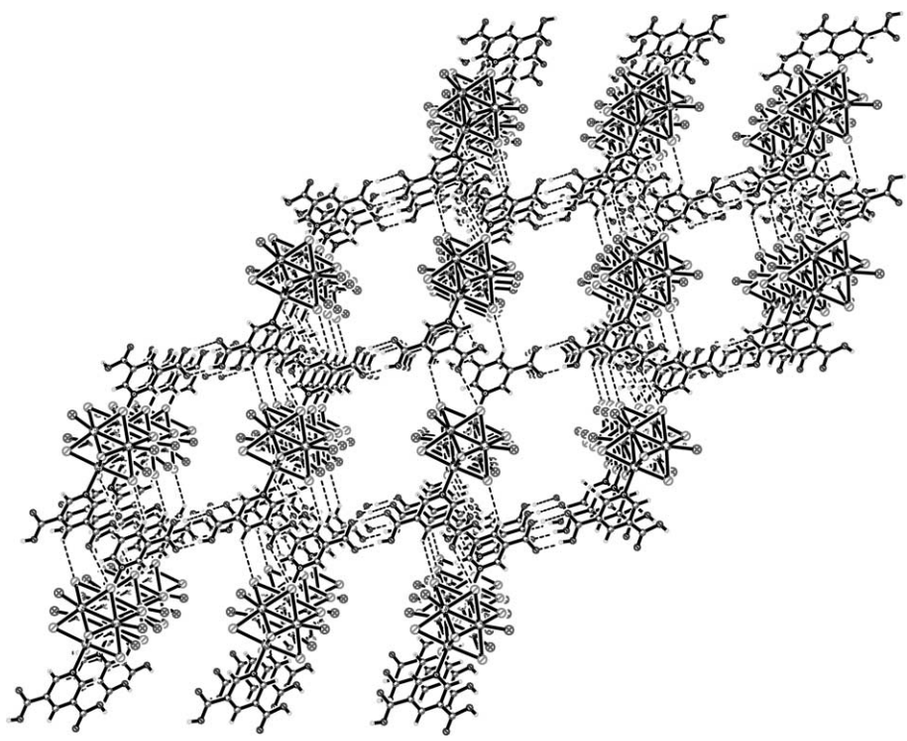


Fig. 5 Packing of the zigzag polymer chains of **5** displaying channel structures along the *c* axis. Counterions (SbF_6^-) and ethyl groups of the triethylphosphine ligands have been omitted for clarity.

pyridinedicarboxylic acid series, which exhibits an interesting zigzag chain structure that is primarily a function of the ligands' DA unit orientation, rather than the strict linear polymer expected from the *trans*-displacement of the ligands. Future work will be focused on utilizing functional organic moieties, including chiral ligands, so that even more sophisticated structural or functional properties can be expressed in the form of supramolecular assemblies.

Experimental

General

Nicotinamide, 3,5-pyridinedicarboxylic acid and $AgSbF_6$ were purchased from Aldrich and used as received. Cluster starting materials, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_nI_{6-n}]I_{n-4}$ [$n = 4$ (*cis*- and *trans*-), 5][8a] and $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_n(CH_3CN)_{6-n}](SbF_6)_2$ [n = 4 (*cis*- and *trans*-), 5][8a,9] were prepared according to published procedures. ^1H and ^{31}P NMR spectra were recorded on a Bruker AM 300 spectrometer in CD_3CN (s, singlet; d, doublet; m, multiplet; q, quintet; dd, doublet of doublet). Chemical shifts of ^{31}P spectra were referenced to 85% H_3PO_4 (δ = 0.0 ppm, with negative values meaning upfield). Microanalyses (CHN) were performed by Desert Analytics Laboratory, Tucson, AZ, USA.

X-Ray crystallographic study

Data were collected at 170(2) K using a Bruker SMART 1000 CCD-based area detector diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structure was solved with direct methods followed by Fourier synthesis using Bruker's SHELXTL (v. 5.1) software package.[17] 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. Crystal data for **5**: $C_{38}H_{70}F_{12}N_2O_8P_4Re_6Sb_2Se_8$, M = 3027.22, triclinic, space group $P\bar{1}$, a = 12.509(1), b = 12.517(1), c = 12.564(1) Å, α = 105.420(2), β = 94.520(2), γ = 90.674(2)°, V = 1889.4(3) Å^3, Z = 1, D_c = 2.661 g cm^{-3}, μ = 14.277 mm^{-1}. Full-matrix least squares refinement on F^2 (22860 reflections measured, 8717 independent, R_{int} = 0.0436) converged to $R1 = 0.0714$, $wR2 = 0.1035$ for all data.

CCDC reference number 216175.

See http://www.rsc.org/suppdata/dt/b3/b309004c/ for crystallographic data in CIF or other electronic format.

Synthetic procedures

$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(nicotinamide)](SbF_6)_2$ (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 (1 : 1 v/v) was added nicotinamide (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%). ^{1}H NMR: δ 0.99–1.17 (m, $5CH_3$), 2.07–2.30 (m, $5CH_2$), 6.36 (br s, amide 1H), 6.96 (br s, amide 1H), 7.40 (dd, pyridyl 1H), 8.24 (d, pyridyl 1H), 9.38 (d, pyridyl 1H), 9.79 (s, pyridyl 1H). ^{31}P NMR: δ −21.2 ($4PEt_3$), −25.0 ($1PEt_3$). Anal. Calc. for $C_{36}H_{81}N_2F_{12}OP_5Re_6Se_8Sb_2$: C, 14.68; H, 2.92; N, 1.06. Found: C, 14.82; H, 2.72; N, 1.13%.

Trans-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(nicotinamide)_2](SbF_6)_2$ (2). Prepared following the preceding procedure but with the use of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CH_3CN)_2](SbF_6)_2$ instead of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)](SbF_6)_2$ (yield: 75%). ^{1}H NMR: δ 1.15 (q, CH_3), 2.32 (q, CH_2), 6.32 (br s, amide 1H), 6.96 (br s, amide 1H), 7.38 (dd, pyridyl 1H), 8.22 (d, pyridyl 1H), 9.24 (d, pyridyl 1H), 9.69 (s, pyridyl 1H). ^{31}P NMR: δ −20.1. Anal. Calc. 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, 14.42; H, 2.59; N, 1.94%.

Cis-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(nicotinamide)_2](SbF_6)_2$ (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%). ^{1}H NMR: δ 1.08–1.23 (m, CH_3), 2.23 (q, CH_2), 2.35 (q, CH_2), 6.37 (br s, amide 1H), 6.97 (br s, amide 1H), 7.42 (dd, pyridyl 1H), 8.27 (d, pyridyl 1H), 9.51 (d, pyridyl 1H), 9.83 (s, pyridyl 1H). ^{31}P NMR: δ −17.6, −20.5. Anal. Calc. 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, 14.79; H, 2.25; N, 2.06%.

$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(3,5\text{-pyridinedicarboxylic acid})](SbF_6)_2$ (4). To a mixture of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5I]I$ (26 mg, 9.0 μmol) and 3,5-pyridyldicarboxylic acid (150 mg, 898 μmol) in 5 mL of dichloromethane was added 150 mg of $AgSbF_6$. The mixture was stirred at room temperature in the absence of light for 12 h. The resulting mixture was then exposed to light with stirring for 2 h before the solvent was removed under vacuum. About 20 mL of dichloromethane was added to the residue, and the resulting mixture was filtered through a plug of Celite. The orange–red filtrate was collected, and the product was obtained as an orange–yellow solid upon removal of the solvent (20.5 mg, yield: 79%). ^{1}H NMR: δ 1.01–1.17 (m, $5CH_3$), 2.07–2.19 (q, $1CH_2$), 2.21–2.35 (q, $4CH_2$), 8.80 (s, pyridyl 1H), 9.97 (s, pyridyl 2H). ^{31}P NMR: δ −24.3 ($4PEt_3$), −28.7 ($1PEt_3$). Anal. Calc. for $C_{37}H_{80}N_1F_{12}O_4P_5Re_6Se_8Sb_2$: C, 14.93; H, 2.69; N, 0.47. Found: C, 15.27; H, 2.89; N, 0.65%.

Trans-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(3,5\text{-pyridinedicarboxylic acid})_2](SbF_6)_2$ (5). Prepared following the preceding procedure but with the use of *trans*-$Re_6(\mu_3\text{-}Se)_8(PEt_3)_4I_2$ instead of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5I]I$ (yield: 75%). ^{1}H NMR: δ 1.15 (q, CH_3), 2.32 (q, CH_2), 8.70 (s, pyridyl 1H), 9.76 (s, pyridyl 2H). ^{31}P NMR: δ −19.3. Anal. Calc. for $C_{38}H_{70}N_2F_{12}O_8P_4Re_6Se_8Sb_2$: C, 15.08; H, 2.31; N, 0.92. Found: C, 15.32; H, 2.48; N, 1.21%.

Cis-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(3,5\text{-pyridinedicarboxylic acid})_2](SbF_6)_2$ (6). Prepared in a manner similar to **4** except that *cis*-$Re_6(\mu_3\text{-}Se)_8(PEt_3)_4I_2$ was used in place of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5I]I$ (yield: 75%). ^{1}H NMR: δ 1.05–1.25 (m, CH_3), 2.24 (q, CH_2), 2.36 (q, CH_2), 8.81 (s, pyridyl 1H), 10.02 (s, pyridyl 2H). ^{31}P NMR: δ −20.5, −23.6. Anal. Calc. for $C_{38}H_{70}N_2F_{12}O_8P_4Re_6Se_8Sb_2$: C, 15.08; H, 2.31; N, 0.92. Found: C, 15.26; H, 2.07; N, 1.18%.

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