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Supramolecular arrays of the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ core-containing clusters mediated by transition metal ions

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Abstract

Vapor diffusion of diethyl ether into a methanol/dichloromethane (v/v, 1:1) solution of $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Cd}^{2+}$, Co^{2+} , Zn^{2+}) and the site-differentiated solvated cluster *trans*- $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2](\text{SbF}_6)_2$ afforded supramolecular arrays featuring the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ core-containing clusters mediated by the transition metal ions. The cluster complex with two 4,4'-dipyridyl moieties can be viewed as an expanded dipyridyl ligand, serving to coordinate the transition metal ions via a pair of $\text{N}_{\text{pyridyl}}\text{-M}$ dative bonds. All compounds have been characterized by microanalysis (CHN) and their solid-state structures have been established by single crystal X-ray diffraction. Two polymorphous forms (**1** and **2**) of the crystal of $\text{M} = \text{Cd}^{2+}$ have been obtained, one of which (**1**) exhibits a highly porous structure, whereas the other (**2**) displays a wavy one-dimensional arrangement. The latter form is isostructural with the complex with Co^{2+} (**3**). In the case of Zn^{2+} (**4**), the cluster complex ligand and the mediating Zn^{2+} are arranged in a zigzag fashion, with an average $\text{N}_{\text{pyridyl}}\text{-M-N}_{\text{pyridyl}}$ angle bond of 88° .

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1. Introduction

The goal of supramolecular chemistry – the “chemistry beyond molecules” – is to create novel structural and functional systems utilizing noncovalent interactions between prefabricated molecular and/or ionic building blocks [1]. Central to the success of the field has been the creative utilization and manipulation of intermolecular forces, among which hydrogen bonding (for selected reviews, see [2]) and metal–ligand interactions (for selected reviews, see [3]) are most prominent. Further development of this interdisciplinary research field hinges upon rational design and creative use of molecular building blocks with various built-in functional groups that dictate and direct noncovalent interactions in the subsequent supramolecular construction. The recent deliberate application of the “secondary building units” approach [4] is a manifestation of this design

philosophy, and many interesting results have been generated due to the utilization of such meticulously designed building blocks [5].

Metal-containing building blocks are of particular interest in supramolecular synthesis. The metal ions not only provide a structural scaffold for the attachment of various organic ligands (linking moieties in supramolecular synthesis), but also and more importantly, offer the possibility of realizing multifunctional (magnetic, electronic, optical, and catalytic) materials. To this end, transition metal ions, in conjunction with polydentate ligands, have been used to generate an impressive collection of one-, two-, and three-dimensional supramolecular systems [3]. A more recent but impressively fruitful approach has been the utilization of building blocks of expanded dimensions, with metal carboxylates [4,5] and metal-oxo clusters [6] being most prominent. With appropriately chosen spacer groups between these “enlarged” construction units, novel materials exhibiting useful properties have been realized [7].

An analogous yet probably more intriguing chemistry may be anticipated, in which metal–metal bonded

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clusters are utilized in a similar capacity. From a structural viewpoint, the availability of multiple metal sites in a cluster allows for stereochemically unique disposal of ligands in a supramolecular setting, a feature propitious to the creation of a range of targeted geometries. From the perspective of achieving certain useful functions, the inherent metal–metal and/or metal–ligand interactions are unique [8]. Such efforts are thus expected to offer many fascinating research problems with potentially important consequences. Indeed, the applications of metal–metal bonded dimeric clusters in supramolecular synthesis have recently been elaborated [9]. Porous solids [9,10] and liquid crystalline materials [11] have been realized by using these clusters as the fundamental building blocks.

Particularly impressive has been the recent success using the face-capped octahedral clusters containing the Re_6Q_8 (Q = S, Se, Te) core [12]. For example, Long [13], Fedorov [14], and others [15] have prepared cyano-bridged Re_6Q_8 cluster-metal framework solids, including cluster-expanded Prussian blue analogues by Long and coworkers. Our efforts along a similar line have been focused on the exploration of the utility of *site-differentiated* $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ cluster complexes [16,17] of the general formula $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PR}_3)_n\text{L}_{6-n}]^{2+}$ (R = C_2H_5 , $n = 4$ (*cis*- and *trans*-), 5; R = C_6H_5 ; $n = 4$, *cis*-; L = a pyridyl-based ligand) in stereospecific supramolecular synthesis. Unlike their well-known isomorphs of the earlier transition metal-halide/chalcogenides, the hexanuclear rhenium clusters are stable to aerobic handling and vigorous synthetic conditions, yet labile enough so that various cluster derivatives can be easily prepared via multiple step solution-phase syntheses [16,17]. The substitutionally inert phosphine ligands serve to protect the metal sites to which they are bound, while each of the pyridyl-based ligands, bearing an additional functionality, can participate in further *intermolecular* interactions in addition to its coordination with the Re(III) site(s). 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 supramolecular assembly [18]. Because of the cluster's large size, the assembly, whether molecular or polymeric, will be expanded relative to a mononuclear analog. This is of particular interest to the preparation of porous solids with extra large pores – an area that is being vigorously pursued in supramolecular chemistry. Furthermore, the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ clusters have interesting photophysical [17a,19] and electrochemical characteristics [12c,16c,17a] that may lend any bulk material unusual properties and possibly useful applications.

The synthetic utilities of such stereoisomers in supramolecular construction have been demonstrated. Multi-cluster arrays, including dumbbell-shaped diclusters

[16c], star-shaped tri- and tetraclusters [20a], cluster-supported molecular squares [20b], as well as dendrimers of clusters [20c], have been realized. The stereochemistry and molecular structure of these novel supramolecular assemblies, consisting of an appropriate number of cluster units interlinked by typically pyridyl-based multidentate bridging ligands, can be established by spectroscopic means. Single crystals of these materials are, however, frequently unavailable, making the correlation of the materials' properties with their structure difficult. The high charges, the concomitant presence of many easily disordered counterions, and the large void volume in the cases of porous assemblies are presumably responsible for this crystallization difficulty.

To address this challenge, we resorted to two genuine supramolecular approaches. In the first, a rhenium cluster complex is formed with at least one ligand L (isonicotinamide, for example) that bears functional group(s) capable of intermolecular hydrogen bonding. Supramolecular cluster arrays can then be produced by virtue of the intercluster hydrogen bonds. In the second, a ligand (4,4'-dipyridyl, for instance) possesses a free coordinating atom for secondary metal coordination (with respect to the primary ligand–Re interaction). Thus, multicluster arrays can be assembled via mediation by the single metal ions. This latter approach is in line with the well-established “complex-as-ligand” methodology [21], but using a much bulkier cluster motif in place of a single metal ion. Both 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.

Depending on the stereochemistry of the starting cluster complexes, various supramolecular structures may be envisioned. Indeed, various supramolecular arrays of metal clusters facilitated by intercluster hydrogen bonding have been realized, with the final structure dictated by the stereochemistry of the cluster components [22]. When the cluster complex is used as an expanded ligand for secondary metal coordination, one has to consider the additional complexity originating from the local coordination geometry of the metal ions and the cluster ligand–metal ion ratio. Indeed, using *cis*- $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2][\text{SbF}_6]_2$ as a cluster-expanded dipyridyl ligand to coordinate Cd^{2+} , a pseudo-one-dimensional chain of corner-sharing squares composed of the cluster ligands and corner-shared Cd^{2+} ion was obtained, while in the presence of excess Cd^{2+} , a one-dimensional zigzag chain, formulated as $\{[\text{Re}_6(\mu_3\text{-Se})_8(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2]\{\text{Cd}(\text{NO}_3)_3\}\}(\text{NO}_3)_3$ and featuring repeating units of $\{[\text{Re}_6(\mu_3\text{-Se})_8(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2][\text{Cd}(\text{NO}_3)_3]\}^-$ was isolated instead [23]. Nevertheless, the chains in both cases clearly reflect the geometric constraint imposed by the cluster ligands.

In this paper, we report the creation and structural determination of one of the simplest forms of such supramolecular assemblies, i.e., one-dimensional infinite chains, generated from a combination of *trans*-[Re₆(μ₃-Se)₈(PEt₃)₄(4,4'-dipyridyl)₂](SbF₆)₂ and a transition metal ion. Depending on the local coordination geometry of the transition metal ion, the chains may adopt, among other possible structures, a zigzag or a more linear arrangement.

2. Experimental

2.1. Preparation

The cluster complex, *trans*-[Re₆(μ₃-Se)₈(PEt₃)₄(4,4'-dipyridyl)₂](SbF₆)₂, was prepared according to a literature procedure [16c]. Other starting materials are of commercial origin and used as received. A sample of the cluster complex (30.0 mg, 10.0 μmol) was dissolved in 3 ml of dichloromethane to yield an orange–red solution. To this solution was added 3 ml of a saturated methanolic solution of M(NO₃)₂ (Aldrich, M = Cd, Co, Zn). The orange–yellow solution mixture thus obtained was stirred for 5 min, and overnight vapor diffusion with diethyl ether caused crystallization of the product in quantitative yields. If necessary, the product can be recrystallized from methanol and diethyl ether. The stoichiometry of the compounds was confirmed by microanalysis (Table 1), performed by Desert Analytics Laboratory, Tucson, Arizona.

2.2. X-ray crystallography

Structures were determined for the five compounds reported herein. For simplicity, in this and following sections, the cationic clusters will be referred to by their compound numbers. X-ray quality parallelepiped-shaped crystals of **1–4** were obtained from respective aqueous solutions at room temperature. Data were collected with Mo Kα radiation (λ = 0.71073 Å) using a Bruker SMART CCD-based diffractometer at 170 K. Cell parameters were obtained using SMART software [24] and refined using SAINT [25] on all observed re-

flections. Empirical absorption corrections were applied using the program SADABS [26] for compounds **1–3** and **4**. The structures were solved using SHELXS in the Bruker SHELXTL (Version 5.0) software package [27]. Refinements were performed using SHELXL and illustrations were made using XP. Solution was achieved utilizing direct methods followed by Fourier synthesis. For compounds **1–5**, hydrogen atoms were added to the appropriate atoms of the main residue. Where possible, hydrogen atoms were included for free solvent molecules. The hydrogen atoms were constrained to ride upon their bound atom in geometrically idealized positions and given thermal parameters of 1.2 or 1.5 U_{iso} of the bound atom. Most of the compounds exhibited some degree of disorder. Disordered dichloromethane and methanol molecules were generally treated by identifying one set of sites for the constituent atoms, constraining their internuclear distances to “standard” covalent bond lengths, and splitting the first site into two or more partially occupied sites. The positions of the solvent sites were then allowed to refine freely. Disorder in the main residues was typically librational disorder of the ethyl groups of the phosphine ligands and/or the nitrate/nitrate ligands and counterions. The main residue disorder was treated in a manner analogous to the solvent disorder; splitting the offending moieties and altering their occupancies always resulted in a much-improved model. Disordered groups were refined with isotropic thermal parameters. Comments on specific refinement models used, together with other details of the structural determinations, are deposited as Supporting Information.

Details of the data collection parameters, crystallographic data, and final agreement factors are collected in Table 2. Selected bond lengths and angles are given in Table 3.

3. Results and discussion

3.1. Synthesis

Coordination polymers consisting of hexanuclear rhenium–chalcogenide clusters and single transition metal ions were sought in this work. Using *trans*-[Re₆

Table 1
Molecular formula and microanalytical data for compounds **1–4**

{Cd(NO ₃) ₃ [Re ₆ (μ ₃ -Se) ₈ (PEt ₃) ₄ (4,4'-dipyridyl) ₂]}(SbF ₆) (1) C ₄₄ H ₇₆ N ₇ F ₆ O ₉ P ₄ Re ₆ Se ₈ SbCd (porous)	<i>Anal.</i> C, 17.06; H, 2.38; N, 3.33 <i>Calc.</i> C, 17.23; H, 2.50; N, 3.19
{Cd(NO ₃) ₃ [Re ₆ (μ ₃ -Se) ₈ (PEt ₃) ₄ (4,4'-dipyridyl) ₂]}(SbF ₆) (2) C ₄₄ H ₇₆ N ₇ F ₆ O ₉ P ₄ Re ₆ Se ₈ SbCd (wavy)	<i>Anal.</i> C, 17.54; H, 2.50; N, 3.13 <i>Calc.</i> C, 17.23; H, 2.50; N, 3.19
{Co(NO ₃) ₃ [Re ₆ (μ ₃ -Se) ₈ (PEt ₃) ₄ (4,4'-dipyridyl) ₂]}(SbF ₆) ₂ CH ₃ OH (3) C ₄₆ H ₈₄ N ₇ F ₆ O ₁₁ P ₄ Re ₆ Se ₈ SbCo (wavy)	<i>Anal.</i> C, 18.08; H, 2.68; N, 3.10 <i>Calc.</i> C, 17.89; H, 2.74; N, 3.17
{Zn(NO ₃) ₃ [Re ₆ (μ ₃ -Se) ₈ (PEt ₃) ₄ (4,4'-dipyridyl) ₂]}(SbF ₆) (4) C ₄₄ H ₇₆ N ₇ F ₆ O ₉ P ₄ Re ₆ Se ₈ SbZn (zigzag)	<i>Anal.</i> C, 17.64; H, 2.54; N, 3.27 <i>Calc.</i> C, 17.50; H, 2.54; N, 3.24

Table 2
Crystallographic data and final refinement parameters for compounds 1–4*

	1	2	3	4*
Empirical formula	C ₄₆ H ₈₀ CdC ₁₄ F ₆ N ₇ O ₁₁ P ₄ Re ₆ SbSe ₈	C ₄₈ H ₉₂ CdF ₆ N ₇ O ₁₅ P ₄ Re ₆ SbSe ₈	C ₄₈ H ₇₆ CoF ₆ N ₇ O ₁₄ P ₄ Re ₆ SbSe ₈	C _{47.50} H ₇₆ N ₈ O _{15.5} P ₄ Re ₆ Se ₈ Zn
Formula weight	3269.88	3228.20	3142.60	2945.29
Crystal size (mm)	0.20 × 0.10 × 0.02	0.30 × 0.20 × 0.10	0.25 × 0.10 × .05	0.35 × 0.20 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	C2/c	P2(1)/n	P2(1)/n	Pbcn
Unit cell dimensions	a = 35.413(12) Å b = 18.054(4) Å c = 15.455(6) Å β = 100.817(6)°	a = 16.955(3) Å b = 11.857(2) Å c = 21.055(4) Å β = 104.99(3)°	a = 16.7533(16) Å b = 11.8072(12) Å c = 20.935(2) Å β = 104.710(2)°	a = 23.924(5) Å b = 25.868(5) Å c = 29.116(6) Å
Volume (Å ³)	9706(5)	4088.6(14)	4005.5(7)	18 019(6)
Z	4	2	2	8
Density calculated (Mg/m ³)	2.238	2.622	2.606	2.171
Absorption coefficient (mm ⁻¹)	11.169	13.132	13.344	11.643
F(000)	5984	2968	2878	10 824
2θ range for data (°)	1.77–26.51	1.79–25.77	1.40–26.42	1.16–23.30
Limiting indices	−44 ≤ h ≤ 44 −22 ≤ k ≤ 22 −19 ≤ l ≤ 19	−20 ≤ h ≤ 20 −14 ≤ k ≤ 14 −25 ≤ l ≤ 25	−20 ≤ h ≤ 15 −12 ≤ k ≤ 14 −24 ≤ l ≤ 25	−26 ≤ h ≤ 26 −28 ≤ k ≤ 25 −32 ≤ l ≤ 30
Reflections utilized	58 016	39 923	21 315	75 059
Independent reflections	10 027 [R(int) = 0.1258]	7776 [R(int) = 0.0543]	7948 [R(int) = 0.1733]	12 978 [R(int) = 0.1577]
Completeness at max. 2θ (%)	99.6	99.0	96.4	99.7
Transmission, max./min.	1.0/0.649239	1.0/0.498305	1.0/0.582873	1.0 and 0.464517
Data/restraint/parameter	10,027/129/464	7776/2/410	7948/20/407	12,978/436/714
GOF on F ²	1.083	1.116	0.927	1.121
R indices [I > 2σ(I)]	R1 = 0.0618 wR2 = 0.152	R1 = 0.0356 wR2 = 0.0758	R1 = 0.0629 wR2 = 0.1489	R1 = 0.0766 wR2 = 0.1963
R indices (all data)	R1 = 0.1395 wR2 = 0.1998	R1 = 0.0656 wR2 = 0.0935	R1 = 0.1193 wR2 = 0.1874	R1 = 0.2141 wR2 = 0.3158
Largest difference peak/hole (e Å ⁻³)	0.946 and −0.873	2.239 and −1.835	3.744 and −4.161	2.410 and −2.435

Table 3
Selected bond lengths (Å) and angles (°) for compounds 1–4*

	1	2	3	4*
Re–Re	2.622(1)	2.638(8)	2.634(1)	2.633(2)
Re–Se	2.508(2)	2.520(1)	2.519(2)	2.518(4)
Re–P	2.475(6)	2.479(8)	2.480(5)	2.47(1)
Re–N _{pyridyl}	2.168(2)	2.220(8)	2.23(1)	2.21(3)
N _{pyridyl} –M ²⁺	2.267(2)	2.346(9)	2.14(2)	2.13(3)
M ²⁺ –O(η ₁)	2.386(9)	2.263(9)	2.00(1)	2.13(4)
M ²⁺ –O(η ₂)	2.435(5)	2.45(1)	2.19(2)	2.28(3)
N _{pyr} –M ²⁺ –N _{pyr}	178(1)	159.5(5)	169(1)	88(1)

(μ₃-Se)₈(PEt₃)₄(4,4'-dipyridyl)₂[(SbF₆)₂] – a stereospecific complex of the face-capped octahedral rhenium cluster – as a cluster-expanded dipyrindyl ligand for secondary coordination with Cd²⁺, polymeric cluster arrays mediated by the metal ions were obtained. The synthesis was straightforward and the product yield is quantitative. In stark contrast to the starting cluster complex, these highly crystalline compounds are insoluble in dichloromethane, which can be easily rationalized in terms of their structural rigidity. It is worth noting that water addition to a heterogeneous mixture of the coordination polymer in dichloromethane led to the dissolution of the crystalline solids, presumably due to the disruption of its polymeric structure. The starting

cluster complex was subsequently reclaimed in pure form by extraction using this solvent system. The coordination polymers are, as expected, readily soluble in alcoholic solvents as well as other polar organic solvents (MeCN, DMF, and DMSO, for example), but the extended structure is presumably disrupted in these highly polar solvents; otherwise the rigid polymeric arrays should exhibit limited solubility. Adding support to this de-polymerization argument are the identical ¹H and ³¹P NMR spectra of such complexes when dissolved in CD₃CN with that of *trans*-[Re₆(μ₃-Se)₈(PEt₃)₄(4,4'-dipyridyl)₂](SbF₆)₂, the starting monocluster. Upon ether vapor diffusion to these solutions, the hybrid polymers can be re-generated, as judged by cell parameter deter-

mination of the single crystals. Indeed, this dissolution and recrystallization process provides a convenient means of purifying the products. The stoichiometry of all the compounds reported herein was confirmed by satisfactory elemental analysis (CHN). Please note that the elemental analysis of compound **4**, as for compounds **1–3**, is in excellent agreement with charge balancing by three nitrato ligands and one SbF_6^- counteranion, but the crystallographic work revealed four nitrato ligands. This could be due to an anion exchange during work-up. The single crystal is thus designated as **4***.

3.2. Structure description

Compound **1** was the first complex synthesized in the series. The ORTEP representation of its asymmetric unit is shown in Fig. 1. Many of its structural features are shared with the rest of the molecules, with one surprising exception. Compound **1** is a linear polymer with a repeat unit consisting of a single *trans*- $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2]$ unit bound to a Cd^{2+} ion via the open nitrogen of a single 4,4'-dipyridyl ligand. The cadmium (and all M^{2+} species in the series) is bound to a second pyridyl nitrogen from the next repeat unit. The dimensions of the metal clusters are unremarkably similar to those for literature precedents and the $\text{N}_{\text{pyridyl}}\text{-M}^{2+}$ distances fall into the normal ranges (Table 3). For compounds **1–3**, the $\text{N}_{\text{pyridyl}}\text{-M}^{2+}\text{-N}_{\text{pyridyl}}$ coordination mode is *trans*. Charge is balanced in **1** by a single SbF_6^- counterion located near the cluster and three nitrato ligands bound to the cadmium ion. All nitrato species were disordered; one

monodentate site was disordered about a twofold axis and the two remaining nitrato sites were half bidentate and half monodentate. 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 Cd^{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 compounds **2** and **3**. The curvature results in the polymers forming sinusoidal chains of modest amplitude. The chains in compounds **1–3** form lamellar structures in the solid state with each layer composed of parallel polymer chains. Compound **1** is unique however, in the manner in which the chains interact within a given layer. Each adjacent chain is oriented with the cluster units and the Cd^{2+} units exactly parallel and in close contact. In this way the peaks and troughs of the neighboring sinusoidal chains meet and are held together by hydrophobic and hydrophilic interactions at the cluster and cadmium positions, respectively. The result of this unique packing mode is a large opening between sets of chains. When viewed down the *c*-axis, this opening is clearly a large channel that runs parallel to the *c*-direction (Fig. 2). A PLATON check [28] revealed the volume of this channel to be 848 \AA^3 . This channel is likely filled with diffuse solvent that could not be accurately located. Concerns regarding inaccurate cell determination or twinning that might give rise to an erroneous structure with such a large void volume were duly investigated and were found to be unwarranted.

Compound **2** is chemically identical to **1**, but does not feature the large pores found in **1**. Instead, the chains

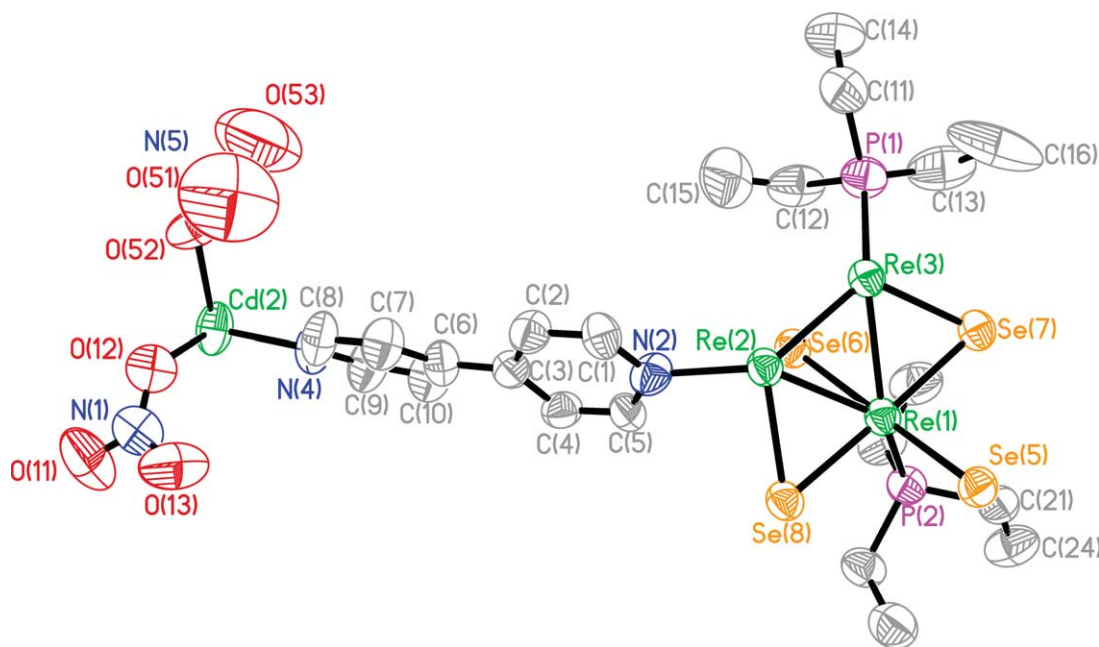


Fig. 1. An ORTEP representation of the asymmetric unit of the porous polymorph of the Cd^{2+} chain (**1**). Hydrogens, solvent, and uncoordinated counterions are omitted for clarity. The projection is along the *c*-axis.

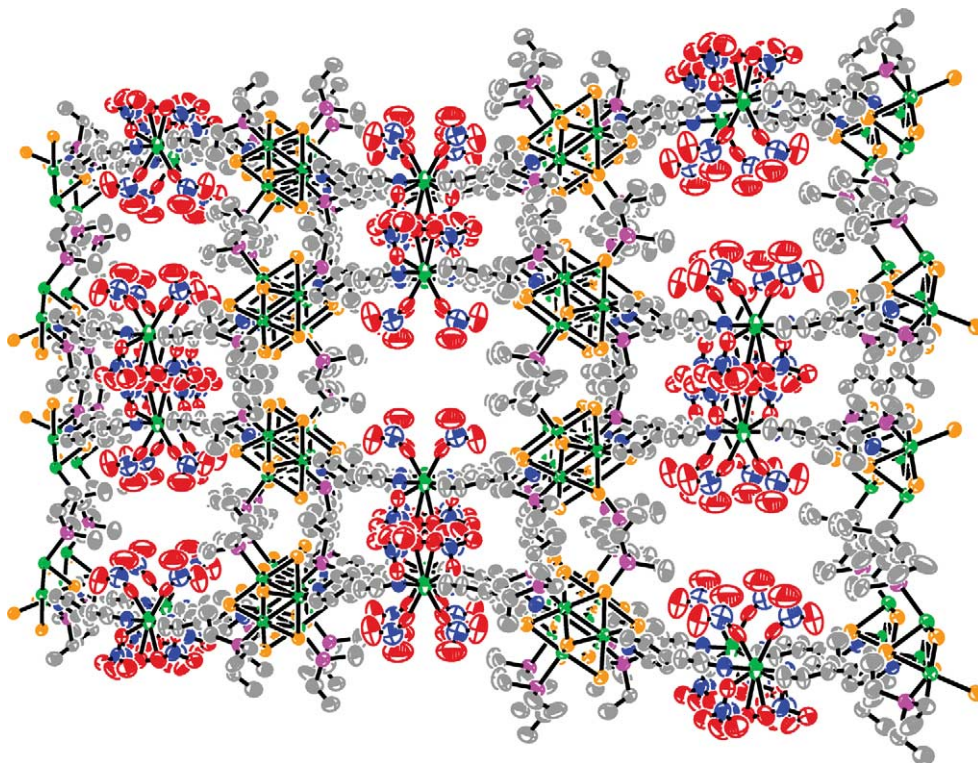


Fig. 2. A packing diagram of **1**, with hydrogens, solvent, and uncoordinated counterions omitted for clarity. The projection is along the *c*-axis.

within a given layer pack in a more dense fashion. Adjacent chains have the cluster and cadmium units shifted slightly with respect to one another (Fig. 3). The sinusoidal shape of the chains observed in **1** persists, but alternating layers have opposing “phases” which serve to make the overall packing scheme denser. The nitrate disorder was not observed in **2**, with the Cd^{2+} coordination sphere (excluding pyridyl) completed by one η_2 - and two η_1 -nitrate ligands. Compound **3** is the Co^{2+} analog of **2**, and is isomorphous and isostructural, differing only by the number of solvent molecules that could be located. Solvent disorder may have contributed

to the large residual peaks and holes in the crystallographic determination.

Compound **4***, the final complex in the series, uses Zn^{2+} as the secondary metal ion and is chemically very similar to compounds **1–3**, except that the structure does not contain any SbF_6^- counterions, instead charge balance is achieved entirely with nitrate/nitrato groups. Structurally however, it is quite distinct. The repeat unit is essentially the same as **1–3** except that the $\text{N}_{\text{pyridyl}}-\text{Zn}^{2+}-\text{N}_{\text{pyridyl}}$ coordination mode is *cis* – with respect to the zinc ion, with an average $\text{N}_{\text{pyridyl}}-\text{Zn}^{2+}-\text{N}_{\text{pyridyl}}$ angle of 88° . The effect of this coordination mode is to pro-

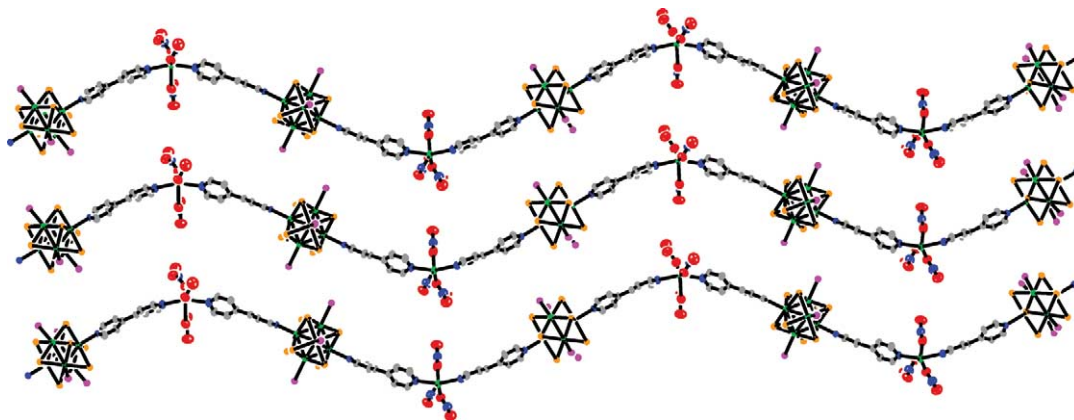


Fig. 3. One layer of the nonporous polymorph of the Cd^{2+} chain structure (**2**) shown with ethyl groups, hydrogen atoms, unbound counterions, and solvent omitted for clarity.

duce pseudo-linear zigzag polymer chains, rather than the sinusoidal polymers of **1–3** (Fig. 4). Indeed, one might consider the zigzag motif of 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 four 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 (Fig. 5). This packing mode results in the formation of small channels that pass through the crystal in the *b*-direction between neighboring Zn^{2+} sites. These channels are filled with solvent molecules and one badly disordered nitrate ligand that required extensive constraints, which is probably responsible for the large residual peaks and holes. The Zn^{2+} coordination sphere

consisted of the two *cis*-4,4'-dipyridyl ligands, two η_2 - and one η_1 -nitrate ligands. The fourth nitrate was located in the interstices close to the cluster.

4. Summary and outlook

The synthesis and structural characterization of several hybrid coordination polymers featuring the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ core-containing cluster complexes mediated by transition metal ions have been reported. The rigid geometry of the site-differentiated clusters limits the number of possible supramolecular architectures, and in each of the examples presented here, the geometry of the cluster is faithfully expressed in the solid state by the cluster complex ligand– M^{2+} interaction at specific cluster apices. The self-assembly process is nevertheless dependent as well on the coordination geometry of the secondary metal ions, which eventually dictates the overall architectures of the resulting polymers. In this context, the combined effect of the cluster

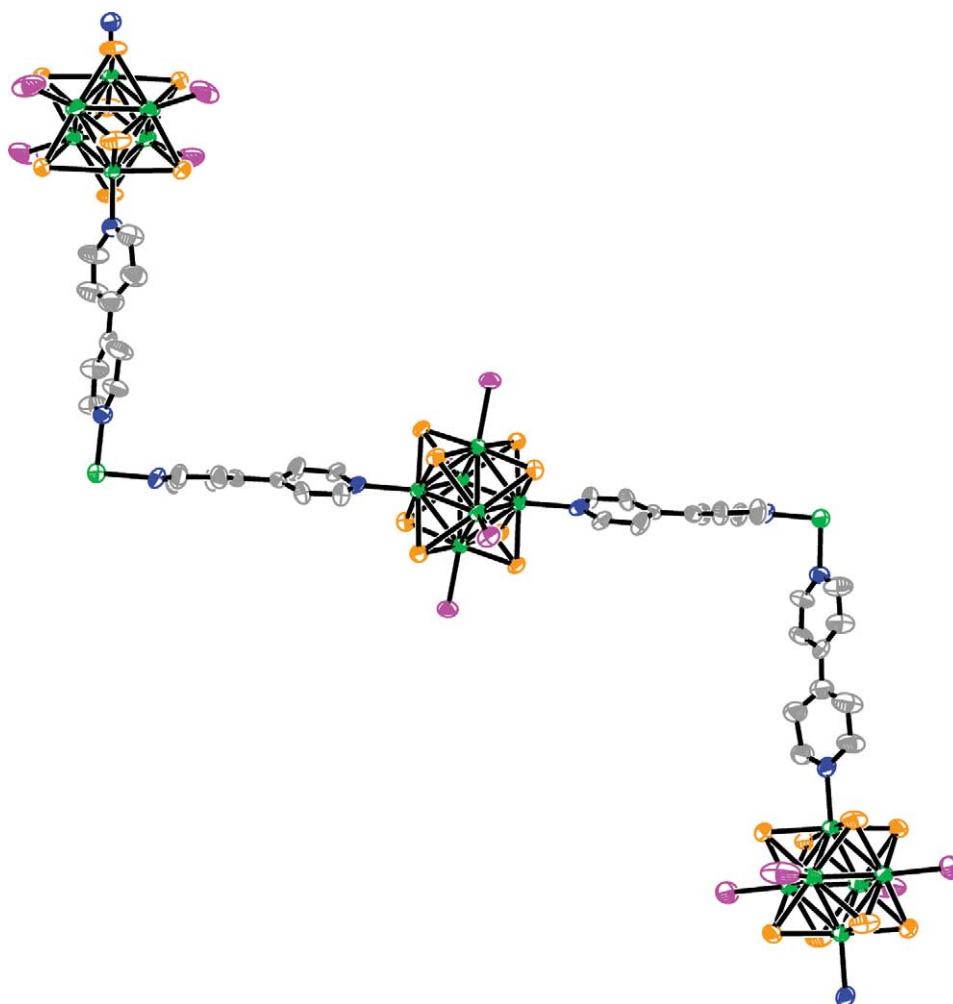


Fig. 4. A single chain of the Zn^{2+} -mediated cluster assembly (**4**). Ethyl groups, protons, counterions, and solvent omitted for clarity.

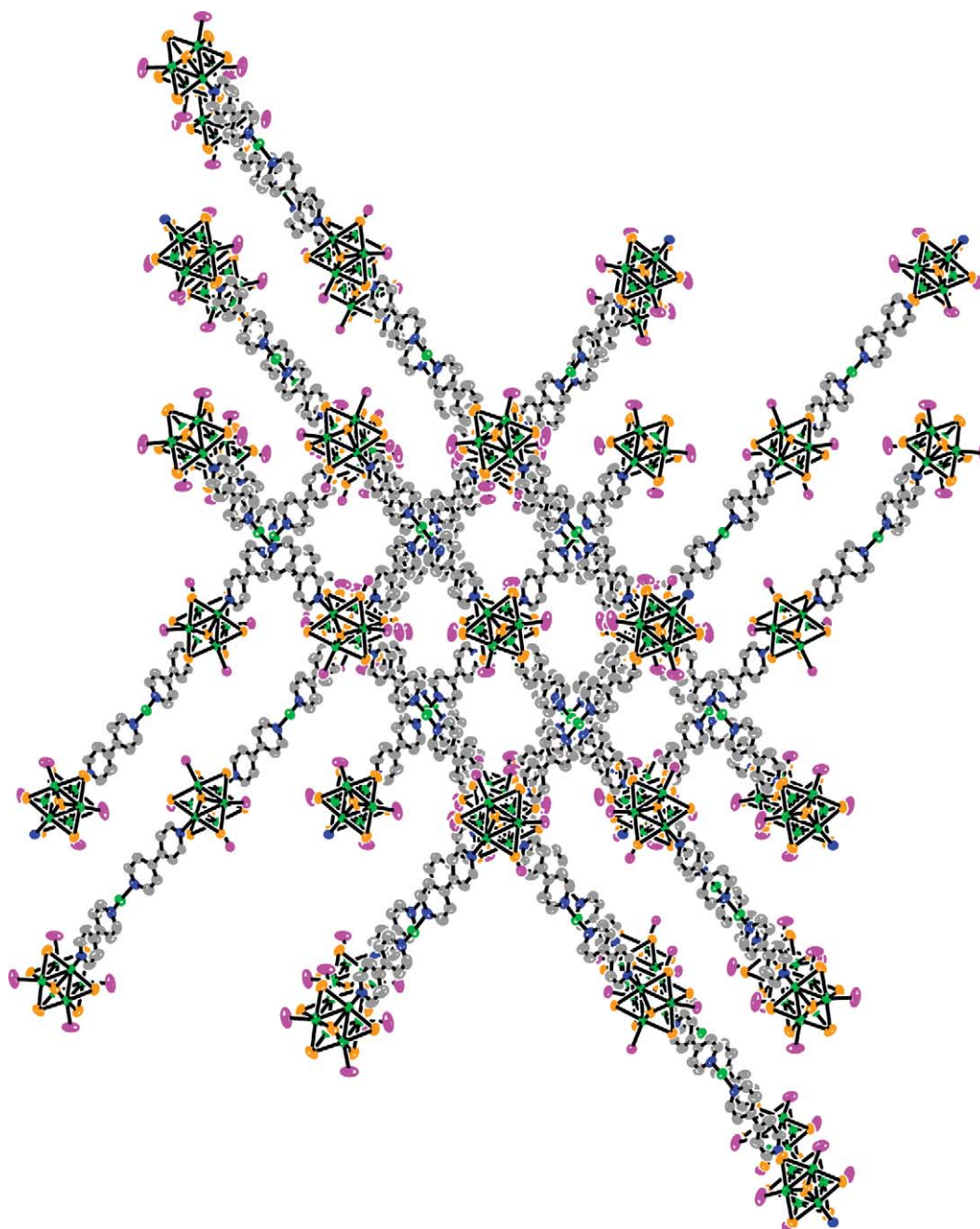


Fig. 5. A packing diagram of the Zn^{2+} structure viewed down the b -axis. Ethyl groups, hydrogens, and counterions omitted for clarity.

core's geometric directing power and the reasonable predictability of the metal–ligand interaction points to the possibility of generating truly “molecularly engineered” materials with the proper combinations of cluster isomers and transition metal ions. Tantalizing examples include two- or three-dimensional frameworks possessing extra-large pores; such materials may find exciting applications in separation science, catalysis, and sensor technology. Our efforts in this direction are underway.

5. Supplementary material

Additional material comprising of atomic coordinates, anisotropic thermal parameters, a full list of bond lengths and angles for complexes **1–4*** have been deposited with the Cambridge Crystallographic Data Center in CIF format as supplementary publications no. CCDC 183418–183421. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-

1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:
http://www.ccdc.cam.ac.uk).

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