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Article

New Compounds from Tellurocyanide Rhenium Cluster Anions and 3d-Transition Metal Cations Coordinated with Ethylenediamine

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The compounds $[Ni(en)_3]_2[Re_6Te_8(CN)_6] \cdot 10H_2O$ (**1**), $[Ni(NH_3)_4(en)]_2[Re_6Te_8(CN)_6] \cdot 2H_2O$ (**2**), $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2] \cdot 38H_2O$ (**3**), $[Co(NH_3)_2(en)_2]_2[\{Co(en)_2\}Re_6Te_8(CN)_6]Cl_2 \cdot H_2O$ (**4**), and $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}Re_6Te_8(CN)_6] \cdot 3H_2O$ (**5**) (en = ethylenediamine) have been synthesized and characterized. Compounds **1**, **4**, and **5** have been synthesized by the diffusion of an aqueous (for **1** and **5**) or an ammonia (for **4**) solution of $Cs_4[Re_6Te_8(CN)_6] \cdot 2H_2O$ into a glycerol solution of $NiCl_2 \cdot 6H_2O$ (for **1**), $CoCl_2 \cdot 6H_2O$ (for **4**), or $ZnCl_2$ (for **5**). Compounds **2** and **3** have been synthesized by the reaction of an aqueous solution of $Cs_4[Re_6Te_8(CN)_6] \cdot 2H_2O$ (for **2**) or $K_4[Re_4Te_4(CN)_{12}] \cdot 5H_2O$ (for **3**) with an ammonia solution of $Ni(en)_2Cl_2$. Compounds **1** and **2** are ionic whereas compounds **4** and **5** are one-dimensional polymers. Compound **3**, a two-dimensional polymer, possesses hexagonal shaped channels of approximate diameter 10–12 Å. Because the framework of compound **3** is robust, it is an attractive host for guest molecules of appropriate size and shape. The potential "guest" volume is about 37% of the unit cell volume.

Introduction

The construction of extended solids from preformed building blocks has attracted considerable attention.[1–3] From building blocks of different sizes with proper geometrical shapes and appropriate chemical, electronic, or magnetic characteristics it is possible to create compounds with predictable structures and tailored features. Many such compounds are of interest as host matrices in supramolecular chemistry and have potential as catalysts and as materials with special magnetic and optical properties. Solution-based methods may be used with these preformed building blocks to design extended solids. The use of building blocks with rigid geometries to prepare metal−organic frameworks is one of the most developed directions in such designs.[4,5]

Another large class of extended solids that are of interest as potentially porous materials are the polymeric compounds based on covalent cyano-bridged $M-C\equiv N-M'$ interactions. Progress on the design of such solids results from modifications of the Prussian Blue family.[6] In one such modification the linear coordination of *trans*-CN ligands from hexacyanometalates to three-coordinate cations, such as Me_3Sn^+ or Cp_3U^+, is utilized to provide elongation of the framework edges. A series of elegant examples with inclusion of large molecules has been reported.[7–9] Another modification, widely used in the past years,[10–17] employs "cluster expansion" of

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the cyano-bridged frameworks. The exchange of the metal atom M in the $[M(CN)_6]$ building block by a cluster core, for example M_6Q_8 or M_4Q_4 (Q = S, Se, or Te), affords various compounds with large cavities.[18-24] However, often these structures are close packed[24,25] or contain interpenetrating frameworks.[16,26] A possible way to stabilize a porous framework involves the inclusion of large organic cations.[17,27] Another approach, successfully used for mononuclear cyanides, is to coordinate chelating ligands to the transition metals to prevent the formation of close-packed structures.[28-34]

Here we have exploited this methodology with the use of ethylenediamine (en) as the chelating ligand. We describe the synthesis and characterization of five such complexes: $[Ni(en)_3]_2[Re_6Te_8(CN)_6]\cdot10H_2O$ (**1**), $[Ni(NH_3)_4(en)]_2[Re_6Te_8(CN)_6]\cdot2H_2O$ (**2**), $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot38H_2O$ (**3**), $[Co(NH_3)_2(en)_2]_2[\{Co(en)_2\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (**4**), and $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}Re_6Te_8(CN)_6]\cdot3H_2O$ (**5**). Compound **3** possesses a highly porous structure with large accessible channels.

Experimental Section

Materials and Synthesis. $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ and $K_4[Re_4Te_4(CN)_{12}]\cdot5H_2O$ were synthesized as described previously.[35,36] All other reagents were used as purchased.

All the syntheses described below were quantitative, based on Re. Microanalyses for C, H, and N were performed by Oneida

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Research Services, Whitesboro, NY. Infrared spectra were collected on a Bio-Rad Digilab FTS-60 FTIR as KBr pellets. X-ray powder diffraction data were collected on a Philips APD 1700 instrument. Thermal stability was determined on a Sinku-Riko T7000 instrument. The density measurements were made in bromoform/toluene mixtures.

$[Ni(en)_3]_2[Re_6Te_8(CN)_6]\cdot10H_2O$ (1). In a narrow-diameter tube a solution of 1.0 mg (0.35 μmol) of $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ in 0.5 mL of water was allowed to diffuse into a solution of 3.5 mg of $NiCl_2\cdot6H_2O$ (0.015 mmol) (Aldrich) in 0.5 mL of glycerol (Fisher, 99.9%) to which 0.09 mL (1.35 mmol) en (Aldrich, 99.5+%) had been added. After 1 week dark red-brown crystals were obtained. Anal. Calcd for $C_{18}H_{48}N_{18}Ni_2Re_6Te_8\cdot10H_2O$: C, 7.32; H, 2.32; N, 8.54. Found: C, 7.45; H, 2.11; N, 8.59. IR (cm^{-1}): 2081 s, 2119 w (ν_{CN}).

$[Ni(NH_3)_4(en)]_2[Re_6Te_8(CN)_6]\cdot2H_2O$ (2). A solution of 0.025 g (0.1 mmol) of $Ni(en)_2Cl_2$ in 5 mL of aqueous ammonia (Fisher, 30%) was added to a solution of 0.02 g (0.007 mmol) of $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ in 5 mL of water. After 3 days dark red-brown crystals formed. Anal. Calcd for $C_{10}H_{40}N_{18}Ni_2Re_6Te_8\cdot2H_2O$: C, 4.44; H, 1.64; N, 9.32. Found: C, 4.45; H, 1.49; N, 9.33. IR (cm^{-1}): 2088 s (ν_{CN}).

$[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot38H_2O$ (3). This compound was synthesized as for **2** with the substitution of 0.02 g (0.011 mmol) of $K_4[Re_4Te_4(CN)_{12}]\cdot5H_2O$ for $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$. The resultant dark red-brown crystals were filtered off and dried on filter paper. Examination of these crystals with an EDX-equipped Hitachi S-3500 SEM gave the ratio Re:Ni:Te of 2:1:2. IR (cm^{-1}): 2134 s, 2165 m (ν_{CN}). ρ_{obs} = 2.92 g/cm^3 vs ρ_{calc} = 2.94 g/cm^3 for freshly filtered crystals. ρ_{obs} = 2.62 g/cm^3 for crystals left in air for a few days.

$[Co(NH_3)_2(en)_2]_2[\{Co(en)_2\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (4). This compound was prepared in a manner similar to that of **1** with the substitution of 3.5 mg (0.015 mmol) of $CoCl_2\cdot6H_2O$ (Aldrich, 98%) for $NiCl_2\cdot6H_2O$ and aqueous ammonia for water to afford dark red-brown crystals. Anal. Calcd for $C_{18}H_{60}Cl_2Co_3N_{22}Re_6Te_8\cdot H_2O$: C, 7.23; H, 2.09; N, 10.31. Found: C, 7.31; H, 2.13; N, 10.24. IR (cm^{-1}): 2087 s, 2107 w (ν_{CN}).

$[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}Re_6Te_8(CN)_6]\cdot3H_2O$ (5). This compound was prepared in a manner similar to that of **1** with the substitution of 3.5 mg (0.026 mmol) of $ZnCl_2$ (Aldrich, 98%) for $NiCl_2\cdot6H_2O$ to afford dark red-brown crystals. Anal. Calcd for $C_{14}H_{32}N_{14}Re_6Te_8Zn_2\cdot4H_2O$: C, 6.14; H, 1.47; N, 7.16. Found: C, 6.17; H, 1.49; N, 7.09. IR (cm^{-1}): 2091 s (ν_{CN}).

Crystallography. Single-crystal X-ray diffraction data were collected at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.[37] Graphite-monochromatized Mo Kα radiation (λ = 0.71073 A) was used. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure times were 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT,[37] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[38] The program SADABS[37] was then employed to make incident beam and decay corrections.

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Table 1. Crystal Data and Structure Refinements for **1−5**

	1	2	3	4	5
chem formula	$C_{18}H_{68}N_{18}Ni_2O_{10}$-$Re_6Te_8$	$C_{10}H_{44}N_{18}Ni_2O_2$-$Re_6Te_8$	$C_{20}H_{73}N_{21}Ni_2O_{19}$-$Re_4Te_4$	$C_{18}H_{62}Cl_2Co_3N_{22}O$-$Re_6Te_8$	$C_{14}H_{40}N_{14}O_4$-$Re_6Te_8Zn_2$
fw	2952.32	2704.05	2284.54	2988.59	2737.34
space group	*Pnnm*	*P2₁/n*	*P3̄*	*Cmmm*	*P2₁/n*
a (Å)	20.6680(15)	10.3607(7)	30.996(4)	14.4302(11)	10.7689(6)
b (Å)	15.2680(11)	10.6377(7)		15.9821(12)	16.5594(9)
c (Å)	18.4691(13)	21.2875(14)	9.312(2)	12.3157(10)	24.3631(14)
β (deg)		97.170(1)			92.070(1)
V (Å³)	5828.1(7)	2327.8(3)	7748(2)	2840.3(4)	4341.8(4)
Z	4	2	6	2	4
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	153	153	153	153	153
ρ_{calc} (g/cm³)	3.365	3.858	2.938	3.494	4.188
μ (cm⁻¹)	170.17	212.71	123.5	177.43	230.50
$R(F)^a$	0.0443^c	0.0335	0.0568^c	0.0388	0.0330
$R_w(F^2)^b$	0.1061	0.0805	0.1641	0.0973	0.0811

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. ^{c} Before SQUEEZE $R(F) = 0.063$ for **1** and 0.076 for **3**.

All structures were solved by means of the direct methods program SHELXS of the SHELXTL[38] suite of programs and were refined by full-matrix least-squares techniques with the use of the program SHELXL.[38]

Because there was the possibility that these compounds might be porous solids, the SQUEEZE option[39] of the PLATON suite of programs[40] was used to assess any remaining voids in the five refined structures. No voids were found in compounds **2**, **4**, or **5**.

During the refinement of the structure of **1** it was obvious that there were waters of solvation but the positions of the O atoms of the solvent were not well-defined. SQUEEZE found voids of 716 Å³ at ($^1/_2$, 0, 0) and (0, $^1/_2$, 0) for a total of 1432 Å³, which corresponds to 25% of the cell volume. SQUEEZE removed 405 e⁻, corresponding to 40 H₂O/cell or 10 H₂O/formula unit.

The structure of compound **3** presented special problems, because it contains large channels. The refinement proceeded cleanly to define the positions of the atoms in the cluster anion and in one and one-half [Ni(en)₂]²⁺ cations as well as three H₂O molecules in the asymmetric unit. The positions of two or three additional O atoms from solvent molecules could be discerned, but they did not refine well; these additional O atoms were therefore omitted. SQUEEZE then found a 1188 Å³ void at (0, 0, 0) corresponding to 15% of the cell volume and symmetry related 532 Å³ voids at ($^1/_3$, $^2/_3$, 0.345) and ($^2/_3$, $^1/_3$, 0.655), each corresponding to 7% of the cell volume. From these voids SQUEEZE removed 561 e⁻, 384 e⁻, and 384 e⁻, respectively. The total electron count of 1329 e⁻ must not only comprise water molecules but also cations whose total charge in the unit cell is 6+. Given the EDX analyses, the density measurements, and the chemical route to compound **3** we assume that this positive charge results from three Ni²⁺ species per unit cell. The refined cations are *trans*-Ni(en)₂ species with their fifth and sixth positions about the Ni centers being N atoms from the CN groups of the clusters. We therefore believe that the most likely cations buried in the channels are [Ni(NH₃)₂(en)₂]²⁺ species. If we subtract the electrons contributed by three such species, there remain 981 e⁻ in the cell. Given the approximate nature of these calculations and the order of the space group, we take these to correspond to 96 H₂O/unit cell or 16 H₂O/asymmetric (Re₄) unit. With the three defined H₂O molecules this leads to 19 H₂O molecules per Re₄ unit.

More experimental details are given in Table 1 and in the Supporting Information.

Results

Syntheses. Previously,[41] we demonstrated that highly viscous glycerol solutions are effective in slowing the crystallization process. This technique was utilized here to synthesize and crystallize [Ni(en)₃]₂[Re₆Te₈(CN)₆]·10H₂O (**1**), [Co(NH₃)₂(en)₂]₂[{Co(en)₂}Re₆Te₈(CN)₆]Cl₂·H₂O (**4**), and [{Zn(H₂O)(en)₂}{Zn(en)₂}Re₆Te₈(CN)₆]·3H₂O (**5**) from the reactions of aqueous solutions (or aqueous ammonia solutions for **4**) of Cs₄[Re₆Te₈(CN)₆]·2H₂O with glycerol solutions of NiCl₂·6H₂O, CoCl₂·6H₂O, and ZnCl₂, respectively, containing an excess of en. [Ni(NH₃)₄(en)]₂[Re₆Te₈-(CN)₆]·2H₂O (**2**) and [Ni(NH₃)₂(en)₂][{Ni(en)₂}₃{Re₄Te₄-(CN)₁₂}₂]·38H₂O (**3**) have been synthesized by the reaction of aqueous solutions of Cs₄[Re₆Te₈(CN)₆]·2H₂O and K₄[Re₄-Te₄(CN)₁₂]·5H₂O, respectively, with ammonia solutions of Ni(en)₂Cl₂. All these syntheses are facile and provide quantitative yields.

Structures. All compounds **1−5** have been characterized by single-crystal X-ray diffraction methods. If we ignore hydrogen bonding then compounds **1** and **2** are simple salts, compound **3** is a complex salt possessing two-dimensional polymeric anions and large channels, compound **4** is a salt with one-dimensional polymeric anions, and compound **5** is a neutral polymer.

The [Re₆Te₈(CN)₈]⁴⁻ anion in the structures of **1**, **2**, **4**, and **5** is similar to that found in Cs₄[Re₆Te₈(CN)₆]·2H₂O and related compounds.[11,28,29,35,41,42] It contains an octahedral Re₆ cluster inscribed in a cube of μ_3-Te ligands; each Re atom in addition is ligated by a CN group. The Re−Re distances range from 2.6727(7) to 2.6979(7) Å in **1**, from 2.6735(5) to 2.6812(4) Å in **2**, and from 2.6723(3) to 2.7014(4) Å in **5**, and they are 2.6813(5) and 2.6868(7) Å in **4**. The Re−Te distances range from 2.6758(7) to 2.7217(6) Å in **1**, from 2.6888(6) to 2.7027(6) Å in **2**, from 2.6915(6) to 2.7039(7) Å in **4** , and from 2.6877(5) to 2.7145(5) Å in **5**. The Re−C

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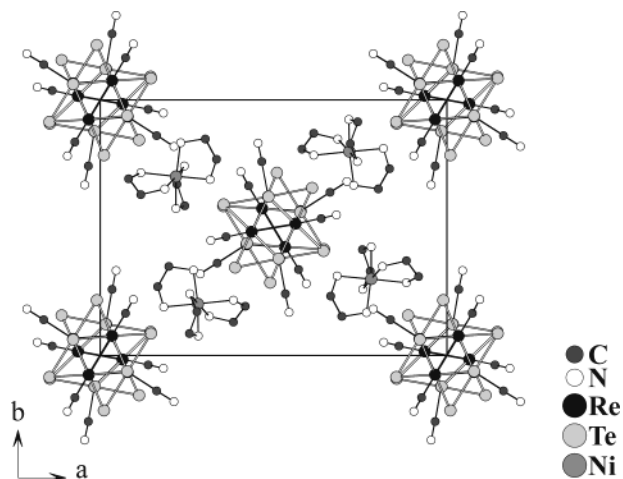
Figure 1. View down [001] of the crystal packing in [Ni(en)$_3$]$_2$[Re$_6$Te$_8$-(CN)$_6$]·10H$_2$O (**1**). H$_2$O molecules and H atoms on the en ligands have been omitted for clarity.

distances range from 2.08(2) to 2.11(2) Å in **1**, from 2.095(8) to 2.106(9) Å in **2**, from 2.07(1) to 2.10(1) Å in **4**, and from 2.093(6) to 2.117(7) Å in **5**. The C−N distances range from 1.14(2) to 1.20(2) Å in **1**, from 1.14(1) to 1.15(1) Å in **2**, from 1.14(1) to 1.15(2) Å in **4**, and from 1.138(9) to 1.158(10) Å in **5**.

The structure of [Re$_4$Te$_4$(CN)$_{12}$]$^{4-}$ anion in compound **3** is also similar to that in the starting material and in other related compounds.[14,28,32,36,43] It contains a Re$_4$Te$_4$ cubane-like cluster core formed from a nearly regular Re$_4$ tetrahedron. The Re−Re and Re−(μ_3-Te) distances range from 2.8428(7) to 2.8732(7) Å and from 2.6086(9) to 2.6455(9) Å, respectively. Each Re atom is further ligated by three terminal cyano ligands; Re−C distances range from 2.06(1) to 2.14(1) Å; C−N distances range from 1.12(2) to 1.20(2) Å.

The crystal packing of [Ni(en)$_3$]$_2$[Re$_6$Te$_8$(CN)$_6$]·10H$_2$O (**1**) is shown in Figure 1. There are two crystallographically distinct anions, each with 2/m symmetry. The water molecules were difficult to define in a conventional refinement, and their contributions to the electron density were removed with SQUEEZE. The cations and anions in this salt are presumably connected through a hydrogen bonding scheme that involves these water molecules that occupy voids corresponding to 25% of the unit cell volume.

The crystal packing of [Ni(NH$_3$)$_4$(en)]$_2$[Re$_6$Te$_8$(CN)$_6$]·2H$_2$O (**2**) is shown in Figure 2. The anion in this structure possesses a crystallographic center of symmetry. The cations and cluster anions are packed in a body-centered motif. An extensive system of weak hydrogen bonds joins the ions to one another and to the water molecules of crystallization. The shortest interactions of a given type include N−H···N hydrogen bonds between NH$_3$ and CN groups (3.104 Å), N−H···N hydrogen bonds between NH$_2$ and CN groups (3.044 Å), N−H···O bonds between NH$_3$ groups and H$_2$O molecules (2.999 Å), and O−H···N bonds between H$_2$O molecules and CN groups (3.131 Å).
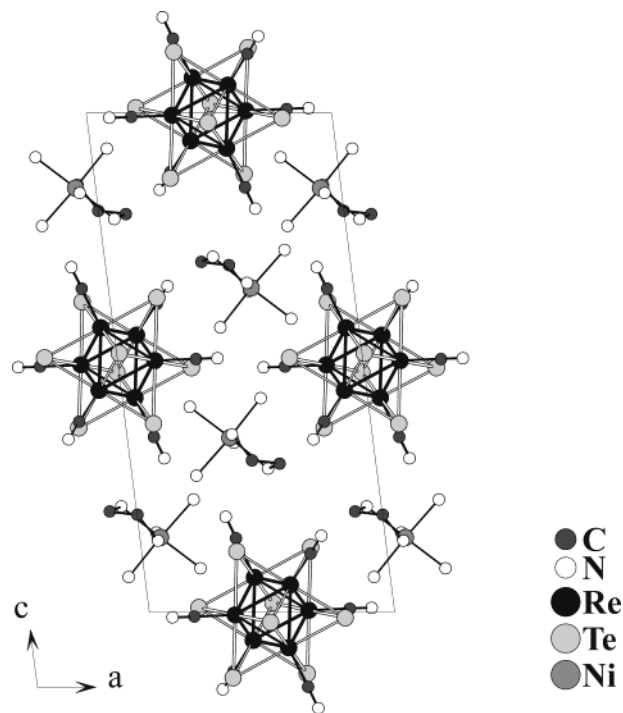
(43) Mironov, Y. V.; Oeckler, O.; Simon, A.; Fedorov, V. E. *Eur. J. Inorg. Chem.* **2001**, 2751−2753.

Figure 2. View down [010] of the crystal packing in [Ni(NH$_3$)$_4$(en)]$_2$-[Re$_6$Te$_8$(CN)$_6$]·2H$_2$O (**2**). H$_2$O molecules and H atoms on the ammonia and en ligands have been omitted for clarity.
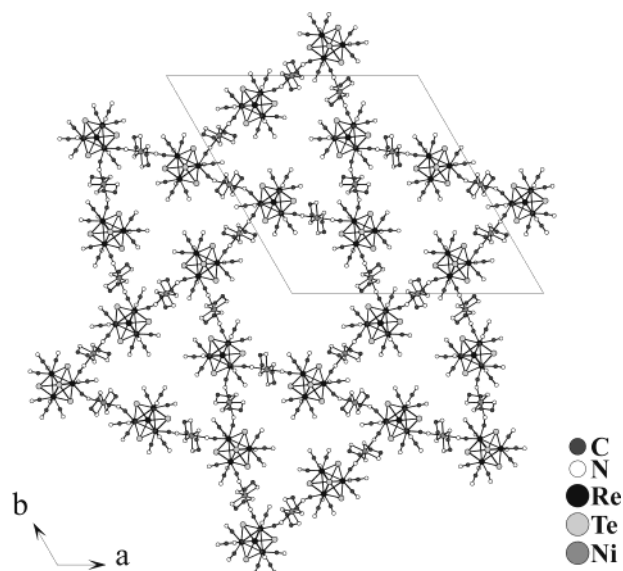
Figure 3. View down [001] of the crystal packing of the [{Ni(en)$_2$}$_3$-{Re$_4$Te$_4$(CN)$_{12}$}$_2$]$^{2-}$ polymeric anion of [Ni(NH$_3$)$_2$(en)$_2$][{Ni(en)$_2$}$_3${Re$_4$-Te$_4$(CN)$_{12}$}$_2$]·38H$_2$O (**3**). H atoms on the en ligands are not shown.

The crystal packing in [Ni(NH$_3$)$_2$(en)$_2$][{Ni(en)$_2$}$_3${Re$_4$Te$_4$-(CN)$_{12}$}$_2$]·38H$_2$O (**3**) is shown in Figure 3. Only the anion is shown. The large hexagonal channel at the origin and the smaller triangular channels are evident. In these channels the disordered cations and the water molecules reside. Their contributions to the electron density were removed with SQUEEZE. The polymeric anion features Ni(en)$_2$ groups connected in a trans fashion by Ni−N(CN) bonds to the Re$_4$ clusters. There are two crystallographically independent Ni(en)$_2$ groups, one with imposed $\bar{1}$ symmetry. The Ni−N(C) bond lengths range from 2.04(1) to 2.09 Å, and

Figure 4. View of the crystal packing in [Co(NH₃)₂(en)₂]₂[{Co(en)₂}-Re₆Te₈(CN)₆]Cl₂·H₂O (**4**). Cl⁻ anions, H₂O molecules, and H atoms on the en and NH₃ ligands have been omitted for clarity.

the Ni−N−C bond angles are 158.4(11)°, 168.2(9)°, and 168.8(10)°.

Part of the structure of [Co(NH₃)₂(en)₂]₂[{Co(en)₂}Re₆-Te₈(CN)₆]Cl₂·H₂O (**4**) is shown in Figure 4. This structure features a Co center both in the cation and in an infinite one-dimensional anionic chain. Chloride anions complete the charge balance. The cation of symmetry *mmm* comprises a six-coordinate Co center with *trans*-NH₃ ligands (Co−N = 2.207(8) Å) and two en ligands (Co−N = 2.147(6)). In the one-dimensional infinite anionic chain Re₆Te₈(CN)₆ groups of symmetry *mmm* are linked in a linear fashion by Co(en)₂ groups of symmetry 2/*m*. The Co−NC distance is 2.11(1) Å whereas the Co−N(en) distance is 2.20(1) Å. These chains extend along the [100] direction to form layers in the (011) plane. The [Co(NH₃)₂(en)₂]²⁺ cations, Cl⁻ anions, and water molecules of crystallization are located between the chains. An extensive system of weak hydrogen bonds exists.

In [{Zn(H₂O)(en)₂}{Zn(en)₂}Re₆Te₈(CN)₆]·3H₂O (**5**) the six-coordinate Zn center is bound in two different ways to the Re₆Te₈(CN)₆ group to form a neutral extended structure. A Zn(H₂O)(en)₂ group is bound to an N(−C−Re) site of a Re₆Te₈(CN)₆ cluster. To two N(−C−Re) sites cis to that site (e.g., on the same Re₃ triangular face) are bound Zn(en)₂ groups that bridge to adjoining Re₆Te₈(CN)₆ groups to form the extended structure (Figure 5). The water molecules engage in an extended hydrogen bonding network with the N, NH₂, and OH₂ portions of the metal cluster. In the Zn-(H₂O)(en)₂N(−C−Re) portion of the structure the Zn−N-(−C−Re) distance is 2.339(6) Å and trans to it the Zn−OH₂ distance is 2.134(6) Å; the Zn−N(en) distances range from 2.108(6) to 2.175(6) Å. The Zn−N−C angle is 137.0(5)°. The Zn(en)₂ bridges involve Zn−N(−C−Re) distances of 2.191(6) and 2.242(5) Å and Zn−N(en) distances ranging from 2.125(6) to 2.152(8) Å. The Zn−N−C angles of 146.1(5)° and 151.1(5)° result in zigzag chains.
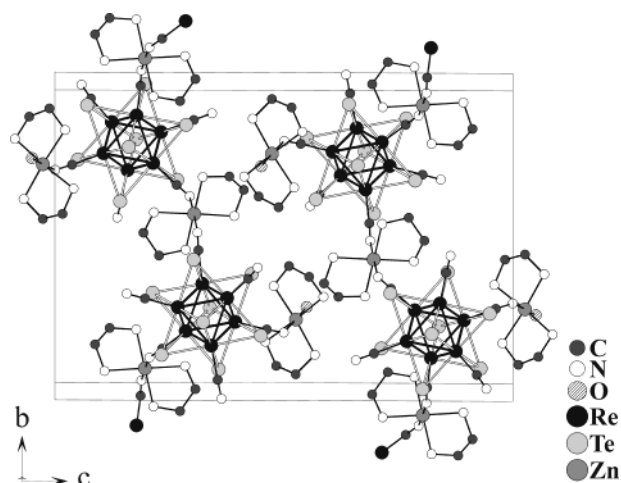
Figure 5. View down [100] of the crystal packing in [{Zn(H₂O)(en)₂}-{Zn(en)₂}Re₆Te₈(CN)₆]·3H₂O (**5**) The H₂O molecules of crystallization and the H atoms on the en and H₂O ligands have been omitted for clarity.

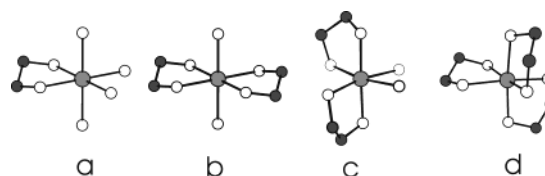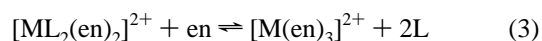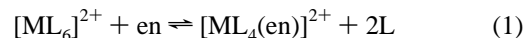**Figure 6.** Possible forms of [ML$_{6-2x}$(en)$_x$]²⁺.

Discussion

The interaction of a six-coordinate M²⁺ transition-metal cation with en in aqueous or aqueous ammonia solution leads to the formation of species with different M/en ratios. Examples are shown in the equilibria in eqs 1−3, where L = H₂O, NH₃. Some possible arrangements of these cationic

$$[ML_6]^{2+} + en \rightleftharpoons [ML_4(en)]^{2+} + 2L \qquad (1)$$

$$[ML_4(en)]^{2+} + en \rightleftharpoons [ML_2(en)_2]^{2+} + 2L \qquad (2)$$

$$[ML_2(en)_2]^{2+} + en \rightleftharpoons [M(en)_3]^{2+} + 2L \qquad (3)$$

species are shown in Figure 6. In the present instance these cations, which may be present in solution simultaneously, can interact with the cluster anions [Re₄Te₄(CN)₁₂]⁴⁻ or [Re₆Te₈(CN)₆]⁴⁻ to form new species. What species form depends on concentrations and stability constants; what compounds crystallize from solution depends on those factors and on solubility. [Ni(en)₃]₂[Re₆Te₈(CN)₆]·10H₂O (**1**) is obtained in the presence of a large excess of en. This appears to favor the formation of the completely coordinated metal cation [M(en)₃]²⁺ (Figure 6d) and the resultant salt. When the starting material is Ni(en)₂Cl₂, the ionic compound [Ni-(NH₃)₄(en)]₂[Re₆Te₈(CN)₆]·2H₂O (**2**) is obtained. This salt contains the cationic species shown in Figure 6a. However, when the starting material is Cu(en)₂Cl₂, then the compound [{Cu(en)₂}₂Re₆Te₈(CN)₆]·5H₂O is obtained.[28] In this compound the starting Cu(en)₂ moiety remains unchanged and is coordinated to *trans*-CN ligands of a Re₆Te₈(CN)₆ cluster. This difference in behavior between Ni(en)₂Cl₂ and Cu(en)₂-Cl₂ may be attributed to the increased stability toward NH₃

substitution for en of the $[Cu(en)_2]^{2+}$ cation compared with the $[Ni(en)_2]^{2+}$ cation: the second stepwise stability constants are about 4×10^{19} and 6.3×10^{13}, respectively, for Cu and Ni.[44] The difference in behavior may also involve the coordination preferences of Cu^{2+} vs Ni^{2+}. The compound $[Co(NH_3)_2(en)_2]_2[\{Co(en)_2\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (**4**) possesses the cationic species shown in Figure 6b.

We sought to prevent the formation of close-packed structures through the use of chelating ligands, in this instance en. This has been realized in $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot38H_2O$ (**3**). Its structure is also built from $Ni(en)_2$ moieties, but, as opposed to the other compounds in this series, it has a two-dimensional framework. The two-dimensional $\{\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2\}^{2-}$ layers pack on top of one another in such a fashion as to form two types of large accessible channels located along the c axis. One centered at $(0, 0, 0)$ comprises large hexagonal-shaped channels of approximate diameter $10-12$ Å; two others at $(^1/_3, ^2/_3, 0.345)$ and $(^2/_3, ^1/_3, 0.655)$ comprise smaller triangular channels. Each hexagonal channel is surrounded by six triangular channels. The channels are filled by $[Ni(NH_3)_2(en)_2]^{2+}$ cations and water molecules of crystallization.

From calculations with the use of SQUEEZE on the framework atoms $[\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]$ of compound **3** the volume of the large cavity is 1590 Å³ and the volume of each of the two smaller ones is 640 Å³. The total potential solvent volume per unit cell is 2870 Å³, corresponding to about 37% of unit cell volume. Compound **3** presents the first example of a porous structure derived from the tetrahedral Re_4Q_4 cluster core. Although none were found in the present study, there are also porous structures involving the octahedral Re_6Q_8 cluster core. In the frameworks of the compounds $Ga_4[Re_6Se_8(CN)_6]_3\cdot38H_2O$,[11] $Fe_4[Re_6Te_8(CN)_6]_3\cdot27H_2O$,[11] and $Na_2Zn_3[Re_6Se_8(CN)_6]_2\cdot24H_2O$[3,21] the void volumes are 1579, 1275, and 1340 Å³, respectively.

Molecules of en coordinated to Ni atoms make the framework in $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot38H_2O$ (**3**) robust and prevent its collapse after dehydration. Indeed powder diffraction studies of samples left in air for weeks at room temperature and after heating to 120 °C (a temperature at which the material is completely dehydrated, according to thermal analysis) indicate that the original crystal structure remains essentially unchanged.

Compound **3** loses water very easily in air. Thermal and chemical analyses, including measurements of the densities of single crystals (Anal. Calcd for $C_{20}H_{47}N_{21}Ni_2O_6Re_4Te_4$: C, 11.7; H, 2.3; N, 14.3; $\rho_c = 2.637$ g/cm³. Calcd for $C_{20}H_{41}N_{21}Ni_2O_3Re_4Te_4$: C, 12.0; H, 2.1; N, 14.7; $\rho_c = 2.567$ g/cm³. Found: C, 11.9; H, 1.6; N, 13.3; $\rho_o = 2.62$ g/cm³), tend to support the retention of six H_2O per Re_4 unit rather than three H_2O per Re_4 unit. The latter formulation was deduced from the X-ray diffraction analysis that found among residual peaks in the difference electron density synthesis the O atoms of three H_2O molecules that could be readily refined. In any event, the observed density of 2.92 g/cm³ for freshly filtered crystals is in excellent agreement with that of 2.938 g/cm³ calculated for composition with 19 H_2O.

The walls of the large channels of the framework of $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot38H_2O$ (**3**) are decorated by twelve N atoms from terminal CN ligands of the $Re_4Te_4(CN)_{12}$ cluster in every sheet (Figure 3). This feature makes that robust framework an attractive matrix for inclusion of molecules or ions of corresponding size and shape based on "host−guest" principles. The N atoms directed into the channel are able to form with guest molecules both covalent bonds with any N-acceptor atoms such as transition metals and hydrogen bonds with H-containing molecules such as alcohols.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC040046J

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