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The First Coordination Polymers and Hydrogen Bonded Networks Containing Octahedral Nb_6 Clusters and Alkaline Earth Metal Complexes

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Three novel coordination polymers built of octahedral niobium cyanochloride clusters $[Nb_6Cl_{12}(CN)_6]$ and alkaline earth metal complexes have been prepared by reaction of aqueous solutions of $(Me_4N)_4Nb_6Cl_{18}$ and KCN with solutions of alkaline earth metal salts and 1,10-phenanthroline (*phen*) (1:2 molar ratio) in H_2O/EtOH. The structures of $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)(EtOH)_{1.6}$ (**1**), $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot 4H_2O$ (**2**), and $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (**3**) were determined by single-crystal X-ray diffraction. The three compounds were found to crystallize in the monoclinic system (space group *Pn*) with $a = 11.5499(6)$ Å, $b = 17.5305(8)$ Å, $c = 21.784(1)$ Å, $\beta = 100.877(1)°$ for **1**; triclinic system ($P\bar{1}$) with $a = 12.609(4)$ Å, $b = 13.262(4)$ Å, $c = 16.645(5)$ Å, $\alpha = 69.933(6)°$, $\beta = 68.607(6)°$, $\gamma = 63.522(5)°$ for **2**; and $a = 16.057(1)$ Å, $b = 16.063(1)$ Å, $c = 16.061(1)$ Å, $\alpha = 86.830(1)°$, $\beta = 64.380(1)°$, $\gamma = 67.803(1)°$ for **3**. Compounds **1** and **2** are built of cluster anions $[Nb_6Cl_{12}(CN)_6]^{4-}$ trans-coordinated by two Ca^{2+} complexes via CN ligands to form neutral macromolecular units $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]$ in **1** and $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]$ in **2**. Water of coordination and cyanide ligands form hydrogen bonded 3D and 2D frameworks for **1** and **2**, respectively. The structure of **3** consists of $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster anions and $[Ba(phen)_2(H_2O)]^{2+}$ complexes linked through bridging cyanide ligands to form a neutral three-dimensional framework in which each barium complex is bound to three neighboring Nb_6 clusters and each Nb_6 cluster is linked to six Ba complexes.

Introduction

The characteristic feature of compounds containing early transition metals in low oxidation states is the formation of metal clusters via metal−metal bonding.[1] These metal clusters can be subdivided into two classes: (a) late transition metal clusters which occur preferentially with π-acceptor organic ligands, such as carbonyl;[2] (b) early transition metal clusters which are typically formed with π-donor ligands (e.g. halogens, oxygen, chalcogens, or alkoxy groups).[1a,2] While discrete molecular cluster units are common for both classes, extended structures are formed almost exclusively from early transition metal clusters with π-donor ligands. These extended solids are synthesized primarily by solid-state chemistry techniques; however, a promising new route to cluster-containing frameworks by assembling cluster units from solutions has recently emerged. In reduced niobium and tantalum halides and oxides, the most common structural motif is the cluster unit $[(M_6L^i_{12})L^a_6]^{n-}$ (L = O, F, Cl, Br) which consists of a M_6 octahedron surrounded by 12 edge-bridging “inner” (L^i) and 6 apical “outer” (L^a) ligands. The solution chemistry of these clusters has primarily focused on excision of intact cluster units from solid-state materials prepared at high temperature, cation exchange,[3] and substitution of terminal ligand for phosphines,[4] thiocyanates,[5] azides,[6] cyanides,[7] oxygen donor ligands,[8] and N-donor ligands.[9] The use of these clusters as building blocks to form solids with extended frameworks remains largely unexplored.

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The ability of cyanide ligand to form stable complexes with transition metals is well established.[10] The cyanide ligand is able to act as bridging ligand binding two metal coordination centers. Cyanometalate anions have been extensively used as building blocks for coordination polymers due to their ability to form strong bonds with transition metal cations, leading to the formation of solids with diverse structural features and unique properties. The most representative examples are Prussian Blue and their analogues[11] and Hoffman clathrates.[12]

Face-capped octahedral metal chalcocyanides $[M_6Q_8(CN)_6]^{4-}$ (M = W, Re; Q = S, Se, Te) have been recently used as building blocks along with transition metal complexes to form a variety of extended cyano-bridged frameworks.[13−16] Recent studies on $[Nb_6Cl_{12}(CN)_6]^{4-}$ show that reactions of the Nb_6 clusters with simple transition metal ions lead to formation of solids with three-dimensional frameworks (3D), that can be considered as templated Prussian Blue analogues or double perovskite.[7e]

A relatively small number of group II coordination polymers have been reported in the literature compared to the well-studied transition metal complexes.[17] Investigations on the use of edge-bridged octahedral metal clusters and 1,10-phenanthroline (*phen*) alkaline earth metal complexes as building units of extended framework materials led to the preparation of three novel coordination polymers: $[Ca(phen)_2(H_2O)_3]_2\cdot[Nb_6Cl_{12}(CN)_6]$ (phen)$(EtOH)_{1.6}$ (**1**), $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot 4H_2O$ (**2**), and $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (**3**). The preparation, crystal structure, and IR spectra of these three compounds are reported.

Experimental Section

Materials and Synthesis. The cluster precursor $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ was prepared as described in the literature.[3b] Water was distilled and deionized with a Milli-Q filtering system. All other reagents were used as purchased without further purification.

Microanalyses for C, H, and N were performed by Atlantic Microlab, Inc. Infrared spectra were recorded as KBr pellets on a Mattson Infinity System FTIR spectrometer.

Synthesis of $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)(EtOH)_{1.6}$ (1) and $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot 4H_2O$ (2). A green precipitate formed immediately upon addition of 5 mL of an aqueous solution of $Ca(NO_3)_2$ (0.1 mmol, 0.0236 g) and a 7.5 mL solution of *phen* (0.2 mmol, 0.0396 g) in ethanol to 10 mL of an aqueous solution of $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ (0.05 mmol, 0.0718 g) and KCN (0.5 mmol, 0.0325 g). The precipitate was collected by centrifugation, washed with water (5 × 10 mL), and dried under vacuum. Single crystals suitable for X-ray analysis were grown by layering the solution of $Ca(NO_3)_2$ and *phen* in EtOH/H_2O over the aqueous solution of $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ and KCN in a narrow diameter Pyrex tube (i.d. 7 mm, 10 cm). After 3 days, a large number of dark green needlelike crystals of **1** (∼90%) and a small number of platelike crystals of **2** (∼5%) appeared at the interface between the two solutions. The crystals were separated manually under a microscope. Crystals of **1** and **2** were found to be air-stable as indicated by single-crystal XRD study. IR for **1** (KBr, cm^{-1}): $\nu(CN) = 2128$, $\nu(phen) = 731, 842, 1099, 1154, 1421$. IR for **2** (KBr, cm^{-1}): $\nu(CN) = 2126$, $\nu(phen) = 731, 840, 1139, 1420$.

Synthesis of $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (3). Addition of 1.5 mL of an aqueous solution of $BaCl_2\cdot 2H_2O$ (0.2 mmol, 0.0488 g) and 2 mL of an ethanolic solution of *phen* (0.4 mmol, 0.0792 g) to 10 mL of an aqueous solution of $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ (0.05 mmol, 0.0718 g) and KCN (0.5 mmol, 0.0325 g) resulted in the immediate formation of green precipitate. The precipitate was recovered by centrifugation, washed with water (5 × 10 mL), and dried under vacuum. Single crystals were grown by layering the solution of $BaCl_2\cdot 2H_2O$ and *phen* in EtOH/H_2O over the aqueous

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Table 1. Crystal Data and Structure Refinement Parameters for $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)(EtOH)_{1.6}$ **(1)**, $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot 4H_2O$ **(2)**, and $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ **(3)**

	1	**2**	**3**
formula weight	2291.76	2444.49	2170.51
temperature, K	296(2)	100(2)	193(2)
crystal system	monoclinic	triclinic	triclinic
space group	*Pn* (No. 7)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.5499(6)	12.609(4)	16.057(1)
b, Å	17.5305(8)	13.262(4)	16.063(1)
c, Å	21.784(1)	16.645(5)	16.061(1)
α, deg	90	69.933(6)	86.830(1)
β, deg	100.877(1)	68.607(6)	64.380(1)
γ, deg	90	63.522(5)	67.803(1)
V, Å^3	4331.5(4)	2264.7(12)	3429.4(4)
Z	2	1	2
d_{calc}, g/cm^3	1.757	1.792	2.102
$R_1{}^a$, $wR_2{}^b$	0.0441, 0.0845^c	0.0502, 0.0992^d	0.0450, 0.0777^e

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]]^{1/2}$. ^{c} $w^{-1} = \sigma^2F_o^2 + (0.0555P)^2 + 0.88P$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. ^{d} $w^{-1} = \sigma^2F_o^2 + (0.0324P)^2 + 4.15P$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. ^{e} $w^{-1} = \sigma^2F_o^2 + (0.0305P)^2$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

solution of $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ and KCN in a narrow diameter tube (i.d. 7 mm, 10 cm). After 1 week, a small amount of dark green air-stable rhombus crystals of **3** formed at the interface of the two solutions. IR (KBr, cm^{-1}): ν(CN) = 2122, 2131, ν(phen) = 732, 843, 1138, 1420.

Single-Crystal X-ray Diffraction. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer equipped with monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Cell refinement and data reduction were carried out with the use of the program SAINT,[18] and the program SADABS[18] was employed for absorption correction. All structures were solved by means of direct methods and were refined by full-matrix least-squares techniques with the use of the SHELXTL[19] suite of programs.

The structure of **1** was solved and refined in the monoclinic system, space group *Pn* as a racemic twin and checked for additional symmetry elements with the program PLATON.[20] The structures of **2** and **3** were solved and refined in the triclinic system, space group $P\bar{1}$. Additional crystal data and refinement parameters are given in Table 1 and in Supporting Information.

Results and Discussion

Synthesis. Compound **2** was obtained as a minor byproduct (~5%) of compound **1** when layering EtOH/H_2O solution containing $Ca(NO_3)_2$ and *phen* in a 1:2 ratio over an aqueous solution containing the cluster precursor $[(CH_3)_4N]_4[Nb_6Cl_{18}]$ and KCN. Direct addition of EtOH/H_2O solution containing $Ca(NO_3)_2$ and *phen* in a 1:2 ratio to the aqueous cluster solution led to the formation of green powder whose X-ray powder diffraction pattern matched that calculated on the basis of the crystal structure of compound **1**. The identity of the powder was also verified by elemental analysis. In the case of Sr, layering a EtOH/H_2O solution of Sr−*phen* in a 1:2 ratio over an aqueous solution containing the clusters led to the formation of dark green needlelike crystals, which were investigated by single-crystal X-ray diffraction and were found to be isostructural with compound **1** with cell parameters $a = 11.545(2)$ Å, $b = 17.860(3)$ Å, $c = 22.006(4)$ Å, $\beta = 100.162(3)°$, $V = 4466(2)$ Å^3. The barium compound **3** was obtained in low yield (~10%) by layering a EtOH/H_2O solution of Ba−*phen* in a 1:2 ratio over an aqueous solution containing clusters. No attempts were made to optimize the yield.

Crystal Structures. The crystal structures of **1**, **2**, and **3** all contain the $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster anion as a building unit. The cluster is similar to that found in related compounds.[7b,e] The cyanochloride cluster is built of an octahedral Nb_6 core in which twelve inner ligands bridge the edges of the octahedron, and six CN ligands coordinate to Nb in apical positions. The intracluster Nb−Nb distances range from 2.9138(8) to 2.9370(10) Å, and the Nb−Cl distances range from 2.441(2) to 2.477(2) Å, confirming the presence of 16 valence electrons per cluster (VEC = 16). The Nb−C distances range from 2.264(3) to 2.293(6) Å, and C−N distances range from 1.129(8) to 1.155(6) Å. The Nb−C−N angles range from 174.0(5)° to 179.0(5)° in **1**, from 174.2(3)° to 178.1(3)° in **2**, and from 169.7(6)° to 177.4(7)° in **3**.

Structure of $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)(EtOH)_{1.6}$ (1). In compound **1**, each cluster is connected to two crystallographically independent calcium complexes via two CN ligands in trans configuration to form neutral trimeric macromolecular species $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]$ (Figure 1a). The unit cell contains two trimeric units that are crystallographically related by *n* glide plane. The units link to each other to form a hydrogen bonded 3D framework (Figure 1b).

The calcium atoms (Ca1 and Ca2) are eight-coordinated, and their coordination environment may be described as distorted square-antiprism composed of four N from two *phen* ligands, one N from a bridging CN ligand, and three oxygen atoms from water molecules. The Ca−N distances involving the two *phen* ligands (2.576(5)−2.647(4) Å for Ca1, 2.555(5)−2.596(5) Å for Ca2) are longer than those involving the cyano ligands (2.545(4) Å for Ca1, 2.525(4) Å for Ca2). The dihedral angles between the two *phen* ligands are 116.2° for Ca1 and 114.3° for Ca2. The average Ca−O (H_2O) bond lengths, 2.462(4) Å for Ca1, and from 2.440(4) Å for Ca2, are comparable with other eight-coordinated calcium complexes.[21−24] The Ca−N−C bond angles are 172.3(5)° and 173.7(5)°. The Ca−N−C−Nb torsion angles are 34.7° and 27.2°, giving the trimeric units bent arrangement.[25,26]

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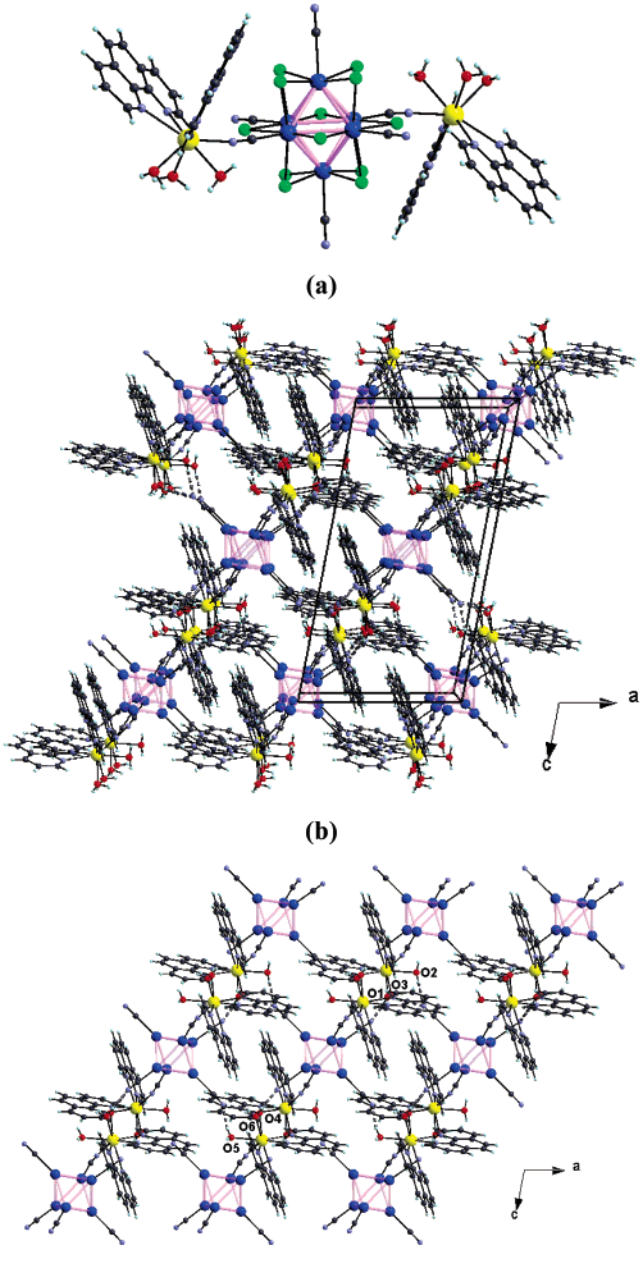

(a)

(b)

(c)

Figure 1. (a) A trimeric unit in **1** formed of $[Nb_6Cl_{12}(CN)_6]$ clusters connected by two "trans" cyanide ligands to two $[Ca(phen)_2(H_2O)_3]$. (b) A projection of the 3D structure of $[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)\text{-}(EtOH)_{1.6}$ **1** along the [010] crystallographic direction. (c) Trimeric units are connected through hydrogen bonds between coordinated water molecules and CN ligands to form layers parallel to the *ac* plane. (Nb, large, dark blue spheres; Cl, green spheres; Ca, yellow spheres; C, black spheres; N, medium size, medium blue spheres; O, red spheres; H, small, light blue spheres.)

Two adjacent trimeric units are connected through hydrogen bonds between water molecule ligands of calcium (O1−O6) and cyanide ligands of the cluster to form layers parallel to the *ac* plane (Figure 1c). Hydrogen bond lengths and angles range from 2.779(1) to 3.038(1) Å and from 165.17(1)° to 179.44(1)°. Adjacent layers are linked via another set of hydrogen bonds resulting in the formation of a 3D framework with channels along the *a* axis where free *phen* and ethanol molecules are located. No $\pi-\pi$ interactions were found between the *phen* ligands, which stack at an average distance of 11.550(1) Å.

Structure of $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot 4H_2O$ (2). In compound **2**, each cluster is connected to two crystallographically related $Ca(phen)_2(H_2O)_2$ complexes via two CN ligands in trans configuration to form neutral trimeric units $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]$ (Figure 2a) that link to each other via extensive hydrogen bonds to form a 2D network (Figure 2b).

The trimeric units are connected by strong hydrogen bonds between coordinated H_2O and cyanide ligands with O1···N2 (2.794(5) Å, 172°) and O2···N2 (2.918(4) Å, 147°) to form double helical chains along the *b* axis (Figure 2c). Further hydrogen bonds between coordinated and free water molecules O1···O3 (2.703(4) Å, 178°) and between cyanide ligands and free water N1···O3 (2.804(5) Å, 175°) connect the doubles helices to form layers that stack parallel to the *ab* plane (Figure 2d). Free *phen* molecules are located between the layers.

The Ca atom is coordinated by two chelating *phen* ligands, two water molecules, and one cyanide ligand from the cluster to form a highly distorted monocapped trigonal prism coordination environment.[26−28] The Ca−N distances involving the two chelating *phen* ligands (2.535(3)−2.555(3) Å) are longer than those involving the cyano group (2.434(3) Å). The dihedral angle between the two *phen* ligands is 66.1°. The Ca−O (H_2O) bond lengths (2.340(2)−2.368(3) Å) are shorter than those in **1**, but comparable with other seven coordinated calcium complexes.[26−29] The Ca−N−C angle is 148.1(3)°, and the Ca−N−C−Nb torsion angle is 13.5°, giving the trimeric units a slightly bent arrangement.

Two compounds containing Ca−*phen* complexes and $[Fe(CN)]^{3-}$, with 3D hydrogen bonded frameworks, have been reported.[26,31] In $[Ca(phen)_2(H_2O)_2Fe(CN)_6Ca(phen)_2(H_2O)(NO_3)]\cdot H_2O$, the trimeric units $[Ca(phen)_2(H_2O)_2Fe(CN)_6Ca(phen)_2(H_2O)(NO_3)]$ are connected by hydrogen bonds through free water molecules to form a 3D framework, while in $[Ca_2(phen)_4(H_2O)_6Fe(CN)_6][\{Ca(phen)_2(H_2O)_2Fe(CN)_6\}_2]\cdot(phen)_3\cdot(phenH)\cdot 14H_2O\cdot CH_3OH$, the trimeric units $[Ca_2(phen)_4(H_2O)_6Fe(CN)_6]$ and tetrameric units $[\{Ca(phen)_2(H_2O)_2Fe(CN)_6\}_2]$ are connected through hydrogen bonds together with free water molecules to form a 3D framework.

Structure of $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (3). Compound **3** has a neutral 3D framework built of $[Nb_6Cl_{12}(CN)_6]^{4-}$ clusters and $[Ba(phen)_2(H_2O)]^{2+}$ metal complexes connected by all six CN ligands (Figure 3a). Each Nb_6 cluster is surrounded by three Ba1 and three Ba2 arranged in a *mer* configuration, and each $[Ba(phen)_2(H_2O)]^{2+}$ complex is linked to three different clusters. Ba1 connects the clusters along the *c* axis while Ba2 connects the clusters along the *b* axis to form ladderlike chains (Figure 3b).

The environments around the crystallographically independent Ba1 and Ba2 atoms are similar; each barium atom

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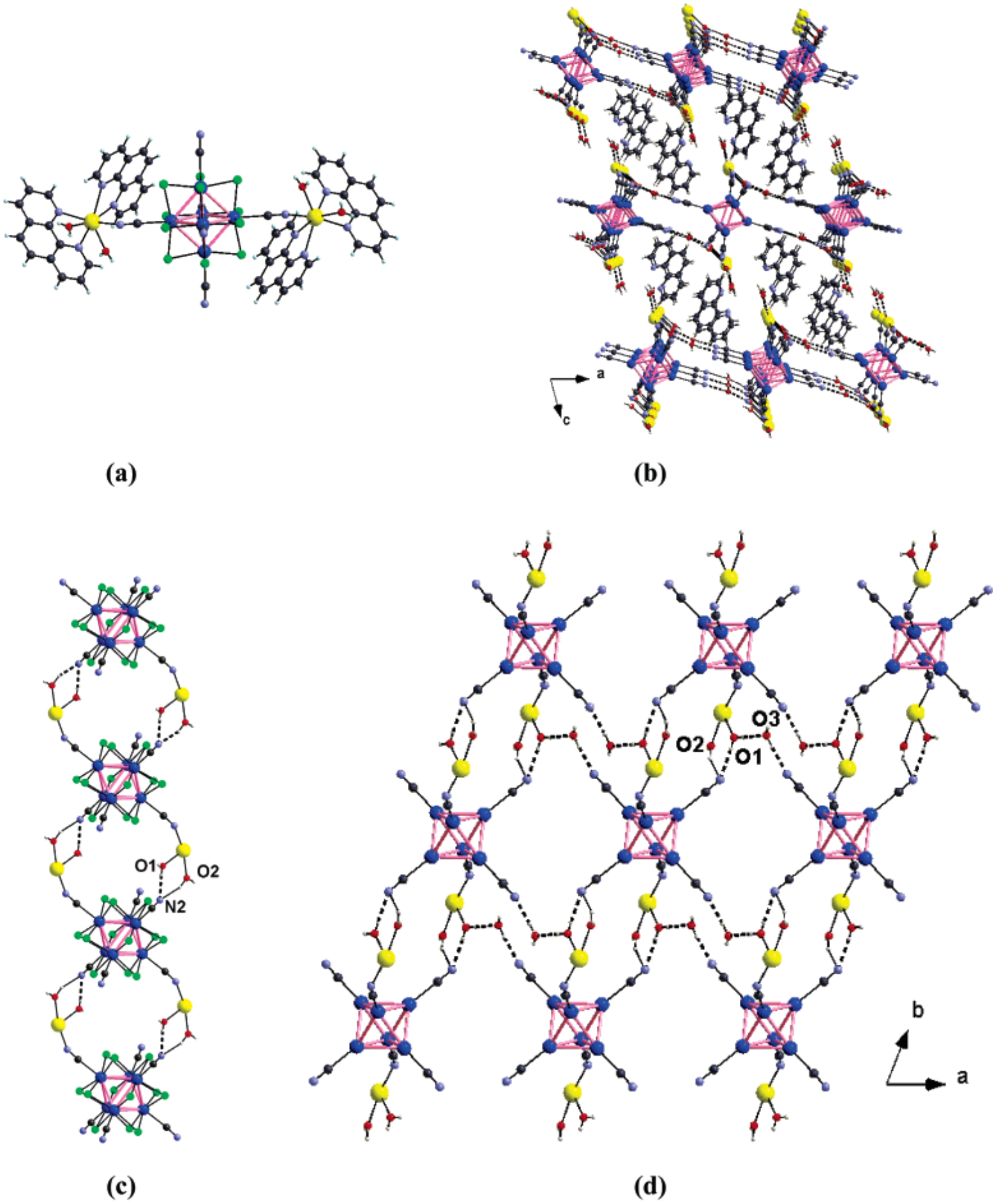
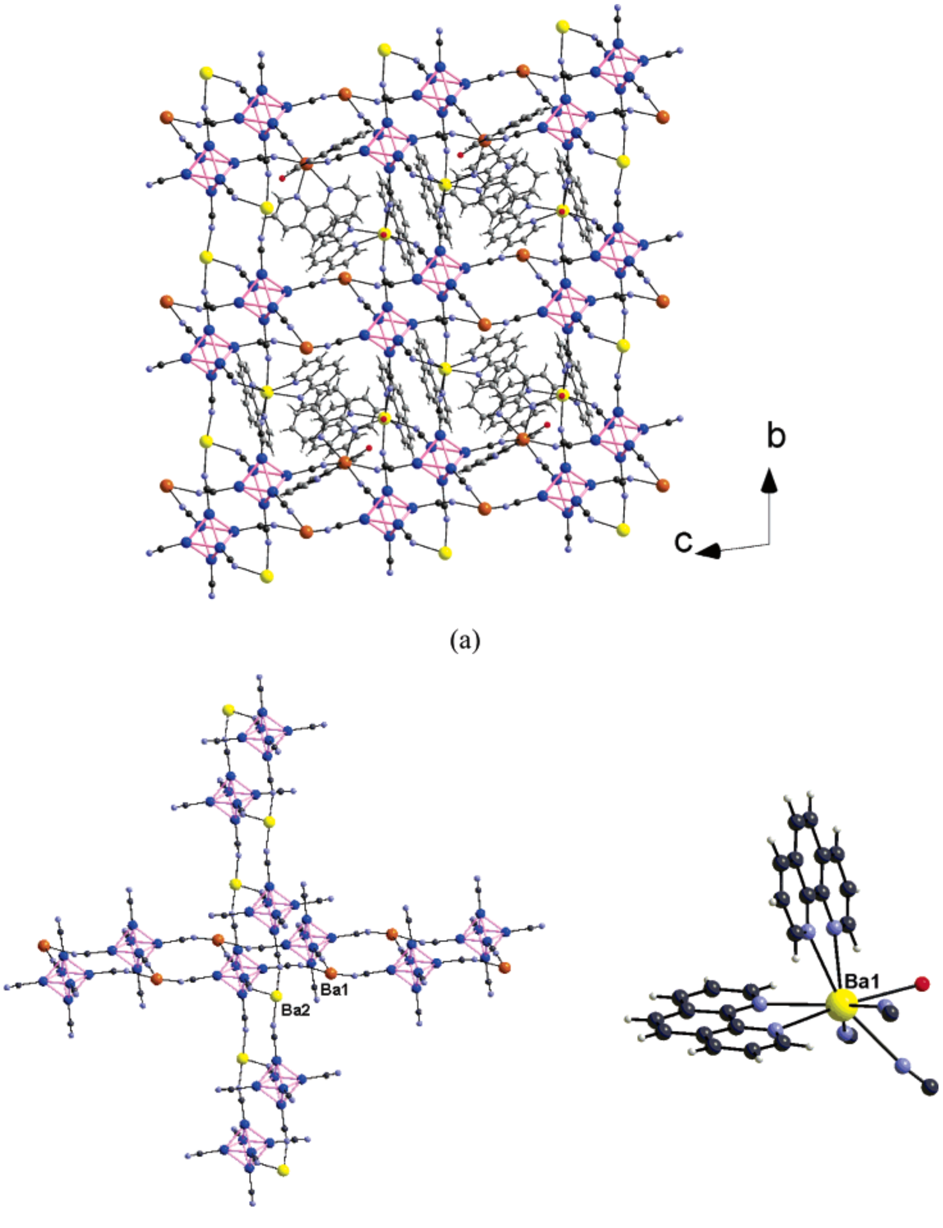


Figure 2. (a) A trimeric unit in **2** formed of $[Nb_6Cl_{12}(CN)_6]$ clusters connected to two $[Ca(phen)_2(H_2O)_2]$ by cyanide ligands in trans configuration. (b) View of the trimeric units packing in $[Ca(phen)_2(H_2O)_2]_2[Nb_6Cl_{12}(CN)_6]\cdot(phen)_2\cdot4H_2O$ **(2)** down [010]. (c) The trimeric units in **2** are connected through hydrogen bonds between coordinated water molecules and CN ligands to form double helix chains along the *b* axis. (d) The double helix chains are connected through hydrogen bonds O1···O3 and N1···O3 to form layers parallel to the *ab* plane. (Nb, large, dark blue spheres; Cl, green spheres; Ca, yellow spheres; C, black spheres; N, medium size, medium blue spheres; O, red spheres; H, small, light blue spheres.)

is chelated by two *phen* ligands, three N from cyanide ligands, and one water molecule. Thus, each Ba center is eight-coordinated and has distorted square-antiprism coordination environment. The Ba−N distances involving the chelating *phen* ligands (2.861(6)−2.918(6) Å for Ba1, 2.864(6)−2.905(6) Å for Ba2) are longer than those involving the cyano ligands (2.816(6)−2.861(6) Å for Ba1, 2.798(6)−2.805(6) Å for Ba2). The dihedral angles between the two *phen* ligands are 76.6° for Ba1 and 111.9° for Ba2. The Ba−O(H_2O) distances (2.857(5) and 2.978(6) Å) are comparable to those in similar complexes.[25,30] The Ba−N−C angles vary through a wide range (130.5(6)° to 172.7(6)°) due to the ladder structure.

In contrast to **3** the structure of $[Ba_2(phen)_4(H_2O)_6Fe(CN)_6]\cdot Cl\cdot(phen)_2\cdot3H_2O$,[25] which is based on $[Fe(CN)_6]^{3-}$ and barium *phen* complexes, is characterized by a 1D framework in which $[Fe(CN)_6]^{3-}$ mononuclear complexes are linked by two $[Ba_2(phen)_2(H_2O)_6]$ dimers in trans positions to form cationic polymeric zigzag chains.

Structural Comparison between 1, 2, and 3. Both compounds **1** and **2** are cluster-based supramolecular assemblies that form 3D **(1)** and 2D **(2)** hydrogen bonded frameworks. In both compounds, the trimeric units are composed of the same $[(Nb_6Cl_{12})(CN)_6]^{4-}$ octahedral clusters connected to two calcium complexes via two CN ligands in trans configuration. The coordination environments of calcium in **1** and **2** differ only in the number of coordinated water molecules. In both compounds the calcium atoms are coordinated by two chelating *phen* ligands and one CN ligand; however, each Ca is coordinated to three water



(a)

(b)

(c)

Figure 3. (a) Perspective view of the three-dimensional framework of **3** with chelating *phen*. (b) The clusters are connected by Ba1 along the *c* axis and Ba2 along the *b* axis to form ladderlike chains based on $-Nb_6-C{\equiv}N-Ba-N{\equiv}C-Nb_6-$ linkages. Chlorine atoms and water molecules are omitted for clarity. (Nb, large, dark blue spheres; Cl, green spheres; Ba1, orange spheres; Ba2, yellow spheres; C, black spheres; N, medium size, medium blue spheres; O, red spheres; H, small, light blue spheres.) (c) Coordination environment of Ba1 in compound **3**. Barium is coordinated by four N from two *phen* ligands, three N from cyanide ligands that link to the cluster units, and one water molecule.

molecules in **1**, while in **2** the calciums are coordinated by two water molecules only. The difference in the number of water molecules around calcium and the overall symmetry (monoclinic (Pn) in **1** and triclinic ($P\bar{1}$) in **2**) dictate the dimensionality of the overall hydrogen bonded framework. In contrast, **3** has 3D coordination framework based on $-Nb_6-C{\equiv}N-Ba-N{\equiv}C-Nb_6-$ linkages. In all three compounds, the alkaline earth metal to *phen* ratio is 1:2, however, in **3** barium has three free sites available to coordinate with three CN from clusters, while in **1** and **2**, calcium has only one free site available to coordinate to the cyanide ligands from the clusters.

Conclusions

Three compounds based on octahedral edge-bridged $[Nb_6Cl_{12}(CN)_6]^{4-}$ clusters and alkaline metal complexes have been prepared and characterized. In the case of Ca and Sr, the structures consist of macromolecular species in which the cluster is trans coordinated by two metal complexes to form trimeric units that hydrogen bond to each other leading to the formation of 3D and 2D frameworks. Reaction of the Ba$-$phen complex with $[Nb_6Cl_{12}(CN)_6]^{4-}$ forms a 3D coordination polymer built of ladderlike chains through $-Nb_6-C{\equiv}N-Ba-N{\equiv}C-Nb_6-$ linkages.

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Supporting Information Available: IR spectra for compounds **1**, **2**, and **3**, powder X-ray diffraction pattern of **1**, and X-ray crystallographic files in CIF format of the three compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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