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Octahedral Metal Clusters $[Nb_6Cl_{12}(CN)_6]^{4-}$ as Molecular Building Blocks: From Supramolecular Assemblies to Coordination Polymers

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This microreview is dedicated to the memory of Ekatherina Anokhina

Keywords: Metal clusters / Self-assembly / Supramolecular Chemistry / Coordination polymers

There are considerable advantages for using metal clusters as building units of supramolecular materials because of their unique structural, chemical, and physical properties, all of which fall in between normal valence compounds and the metals. In this microreview, we describe the synthetic methodology and structural properties of recent findings in the use of octahedral niobium hexacyanochloride anions as building units of assemblies of different size, charge, and dimensionality. We focus on the use of a metal-directed approach to prepare cluster-based supramolecular assemblies and coordination polymers with one-, two-, and three-dimensional frameworks. The materials described herein are all built from diamagnetic cyanochloride cluster anions $[Nb_6Cl_{12}(CN)_6]^{4-}$ and coordinatively unsaturated metal complexes such as $[Mn(salen)]^+$ and their derivatives. The overall structures are largely determined by the number of coordination sites available for linkage to the cluster unit and coordination preferences of the metal complexes.

1. Introduction

Supramolecular chemistry "chemistry beyond the molecule" focuses on the rational design and preparation of supramolecular structures through self-assembly processes in which building units are linked through noncovalent forces such as hydrogen bonding, coordination bonds, electrostatic and charge-transfer attractions, and aromatic π-π stacking interactions.[1,2] It is fundamentally related to the field of crystal engineering which focuses on the organization of molecular or ionic building units into functional crystalline materials with desired structures and properties.[3]

Abdou Lachgar graduated from the University of Nantes, France in 1982 and obtained his Ph.D. degree in materials science and solid state chemistry from the Institute of Materials Jean Rouxel in Nantes in 1987. He joined the group of John Corbett at Iowa State University (1988–1990) to pursue his postdoctoral studies and investigated the chemistry of reduced zirconium and scandium iodides. In 1990, he joined the University of Washington in Seattle, as a research fellow with James Mayer. He concentrated on the synthesis of extended solids from molecular precursors by using electrochemical processes. In 1991, he joined the Department of Chemistry at Wake Forest University as an Assistant Professor. He was promoted to Associate Professor in 1996 and then to Professor in 2002. His teaching and research interests are in the area of materials chemistry with a focus on the use of the molecular building block approach for the rational preparation of hybrid inorganic–organic materials. He was awarded visiting faculty fellowships from the Japanese Government in 1997 and 1998, and he was a visiting Professor at the Institute of Materials Jean Rouxel in 2003 and the institute Gallile in Paris in 2006.

Huajun Zhou obtained his B.S in chemistry from Beijing University (China) in 1999. After conducting research on Li-ion batteries as a research scientist for two years at BYD Co. Ltd (China), he joined Professor Lachgar's group at Wake Forest University in 2002. His current research focuses on strategies used in crystal engineering for the preparation of supramolecular materials built from octahedral cyanochloride clusters and metal ions/metal complexes as building units and the correlation of their structures with their observed properties.

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Progress in supramolecular chemistry has led to the use of more complex molecular building units to prepare materials with novel structures and properties. Inspired by the success of using hexacyanometalate anions $[M(CN)_6]^{n-}$ as building units to construct functional solids with diverse structures,[4] several groups are actively exploring the use of their expanded analogues, such as octahedral transition metal clusters, as building units to investigate the effect of the metal–metal bonds on their physicochemical properties. Octahedral transition metal clusters based on an M_6 octahedron in which six metal atoms are linked to each other through metal–metal bonds and μ_2 or μ_3 ligands to give a M_6L_{12} or M_6L_8 cluster core (Figure 1) have received considerable interest since the discovery of the Chevrel phases which consist of 3D frameworks based on the 6–8 type clusters.[5] Different synthetic methodologies have been developed to excise these clusters from their solid-state precursors through solution chemistry routes.[6] The cluster core $[M_6L_{12}]^{n+}$ or $[M_6L_8]^{n+}$ has an atom- or ion-like behavior. It is larger in size compared with mononuclear metal complexes, has versatile electronic structures, multiple coordination sites, and potential catalytic properties that make them promising candidates as building units of supramolecular structures.[7] Face-capped octahedral cluster units $[W_6S_8(CN)_6]^{6-}$ and $[Re_6Q_8(CN)_6]^{n-}$ (Q = S, Se and Te) have been used as building units of supramolecular structures, some of which show functional properties such as catalysis and molecular sieves.[8]

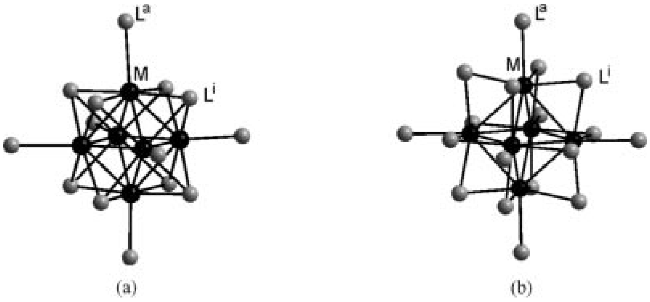


Figure 1. (a) The structure of the cluster $[(M_6L_8{}^i)L_6{}^a]$ common for M = Mo, W, Re; L = halides, S, Se, Te. (b) The structure of the cluster $[(M_6L_{12}{}^i)L_6{}^a]$ common for M = Nb, Ta; L = Cl, Br, O; and M = Zr; L = halides.

The use of edge-capped octahedral niobium halide clusters as building units remains largely unexplored compared with the extensive work that has been reported on octahedral face-capped rhenium and tungsten clusters. These two cluster types differ from each other not only in terms of the coordination mode of inner ligands, but also by the number of valence electrons available for metal–metal bonding (VEC). The use of the cyanochloride cluster $[Nb_6Cl_{12}(CN)_6]^{n-}$ as building units should, in principle, lead to the formation of supramolecular materials with new structures and properties. This microreview describes our recent results in the use of $[Nb_6Cl_{12}(CN)_6]^{4-}$ and metal complexes as building units of supramolecular structures by using the cyanide ditopic coordination ability and the coordination requirement of the metal complexes.

2. Synthetic Strategy

The cluster anion $[Nb_6Cl_{12}(CN)_6]^{4-}$ can be considered as an expanded analogue of $[Fe(CN)_6]^{4-}$ in which Fe^{2+} is replaced by an $[Nb_6Cl_{12}]^{2+}$ cluster core. As in the case of $[Fe(CN)_6]^{4-}$, the cyanochloride cluster reacts with virtually all hydrated $[M(H_2O)_6]^{2+}$ ions to afford compounds that are expanded analogues of the iron-based Prussian-blue.[9] Their crystal structure is based on edge-bridged $[Nb_6Cl_{12}]^{2+}$ clusters and M^{2+} ions bridged by cyanide ligands to form a cubic face centered anionic framework $[MNb_6Cl_{12}(CN)_6]^{2-}$ in which all tetrahedral sites are occupied by the cations $[Me_4N]^+$, which act as charge compensating templates.

After investigating the interaction between the cyanochloride cluster and simple metal ions, we focused on the use of the "directional-bonding" approach first cited by Stang and coworkers and systematized by coordination chemists to prepare supramolecular species.[10,11] The fundamental principle of this approach is the use of coordinatively unsaturated metal complexes as building units. These complexes have specific coordination sites available for ligands from other building units located at appropriate angles to "direct" the formation of desired supramolecular structures. For instance, *cis*-$[Ni(bpy)_2(\mu_{1,3}\text{-}N_3)](PF_6)$[12] and *trans*-$[Ni(N\text{-}Eten)_2(\mu_{1,3}\text{-}N_3)](PF_6)$[13] have been used to prepare 1D coordination polymers with different structural features because of different angles between the two coordination sites available for the incoming azide ligand. Similar strategies have been developed for metal clusters where site-differentiated clusters $[Re_6Se_8(PEt_3)_n(MeCN)_{6-n}]^{2+}$ have been used as building units of supramolecular assemblies.[14]

The reactivity between coordinatively unsaturated metal complexes and $[Nb_6Cl_{12}(CN)_6]^{4-}$ equipped with six cyanide ligands was studied. Two types of metal complexes have been investigated: 1) complexes with tetradentate salen-type ligands (*L1*–*L3*) (Figure 2) chosen for their potential catalytic properties,[15] and 2) complexes coordinated by one or two chelating diamine ligands (phen and en) that block two or four coordination sites, respectively. This leaves different numbers of coordination sites available depending on the nature of the metal ions. The structures of the compounds obtained can be, to a certain extent, predicted from the coordination requirements of the metal complexes. However, the competition between different geometries with similar stoichiometries does not allow complete predictability without considering the effect of solvent, counterions, and stability of the complexes.[16] This review intends to highlight some basic structures to illustrate the use of the concept of "metal complex directed assembly" to build supramolecular structures with versatile geometrical and topological features. Investigations into the combination of metal complexes such as $[Mn(salen)]^+$ with Re_6 clusters resulted in the synthesis of extended framework materials, whereas the use of metal porphyrins with Re_6 clusters led to discrete supramolecular units that have shown excellent catalytic activity toward the epoxidation of olefins.[17,8d]

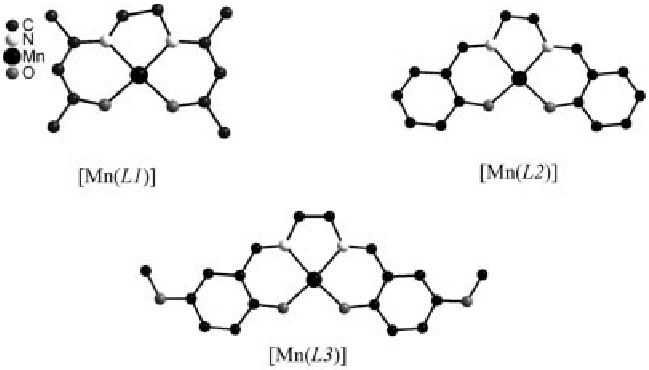


Figure 2. Molecular structures of Mn^{III} complexes with tetradentate salen-type ligands used in the present study. $L1^{2-}$ = bis(acetylacetonato)ethylenediamine; $L2^{2-}$ = bis(salicylidene)ethylenediaminato; $L3^{2-}$ = bis(5-methoxysalicylidene)ethylenediaminato.

3. Synthesis of the $[Nb_6Cl_{12}(CN)_6]^{4-}$ Building Unit

The clusters are prepared following a three-step procedure. Firstly, solid-state precursors containing the chloride cluster $[Nb_6Cl_{12}]^{2+}$ are prepared from reactions between Nb metal, $NbCl_5$, and chloride salts that provide the cations as needed. The reactants are sealed in silica containers under vacuum and heated at 700–900 °C.[18] The second step involves dissolving the solid state precursor in a common polar solvent to excise the chloride cluster. In the third step, substitution of all outer chloride ligands by cyanides is performed. $Li_2Nb_6Cl_{16}$ was used as the solid-state precursor because of its ease of preparation, high yield, and ease of solubility in different solvents. The complete procedure is described by the chemical equations given in steps 1–3.

Scheme 1 shows the use of $Li_2Nb_6Cl_{16}$ as the solid state precursor for the preparation of $[Nb_6Cl_{12}(CN)_6]^{4-}$. $Li_2Nb_6Cl_{16}$ features a 2D framework in which each $[Nb_6Cl_{18}]^{4-}$ cluster is connected to four neighboring clusters by sharing four outer chloride ligands. $[Me_4N]_3[Nb_6Cl_{18}]$ (**1**), which contains the 15-electron cluster $[Nb_6Cl_{18}]^{3-}$, was obtained by dissolving $Li_2Nb_6Cl_{16}$ in EtOH and adding excess Me_4NCl.[9] The reaction time was substantially reduced to 30 min when these two steps were performed at 60 °C. Addition of excess KCN to a solution of **1** in $MeCN/H_2O$ followed by recrystallization from MeOH/ether results in the formation of $[Me_4N]_4[Nb_6Cl_{12}(CN)_6]$ (**2**).[19] The compounds were characterized by single-crystal XRD. The average Nb–Nb [2.983(5) Å], Nb–Cl^i [2.441(6) Å], and Nb–Cl^a [2.53(1) Å] bond lengths in **1** are close to those reported for compounds containing the 15-electron cluster $[Nb_6Cl_{18}]^{3-}$.[20] The average bond lengths of Nb–Nb [2.927(4) Å] and Nb–Cl^i [2.464(7) Å] in **2** are the same as those observed in $Li_2Nb_6Cl_{16}$ [Nb–Nb: 2.919(6) Å; Nb–Cl^i: 2.46(2) Å], which contains the 16-electron cluster $[Nb_6Cl_{18}]^{4-}$. The bond lengths Nb–C [2.282(1) Å] and C≡N [1.131(6) Å] are close to those observed in other compounds containing $[Nb_6Cl_{12}(CN)_6]^{4-}$.[21,22] The stretching frequency for the C≡N group appears at 2126 cm^{-1} in the IR spectrum, which is higher than that observed in $K_4[Fe(CN)_6]$ (2044 cm^{-1}) but close to that found in $K_3[Cr(CN)_6]$ (2129 cm^{-1}).[23] The Nb–C≡N linkages are almost linear [∠ Nb–C≡N = 178.3(6)°].

$[Et_4N]_4[Nb_6Cl_{12}(CN)_6]$ was prepared through a cation metathesis reaction in which an aqueous solution of Et_4NBr was added to an aqueous solution of **2**.

$$[Me_4N]_4[Nb_6Cl_{12}(CN)_6]\ (aq.) + 4Et_4NBr\ (aq.) \rightarrow [Et_4N]_4[Nb_6Cl_{12}(CN)_6]\ (s) + 4Me_4NBr\ (aq.)$$

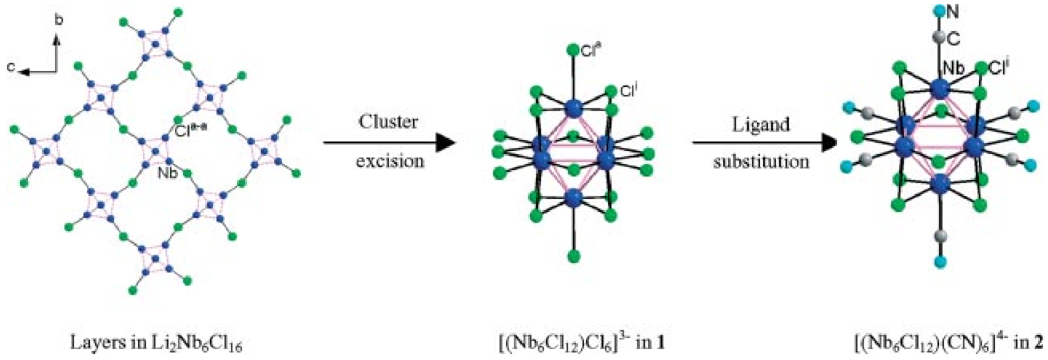
4. Supramolecular Assemblies and Their Hydrogen-Bonded Frameworks

Supramolecular assemblies in which the cluster is coordinated by a different number of metal complexes have been isolated and investigated. For a clearer description, we con-

$$\text{Step 1: } 10LiCl + 14NbCl_5 + 16Nb \xrightarrow[\text{sealed tube}]{700^{\circ}C} 5Li_2Nb_6Cl_{16}$$

$$\text{Step 2: } Li_2Nb_6Cl_{16} \xrightarrow{EtOH,\ 60^{\circ}C} 2LiCl + [Nb_6Cl_{14}(EtOH)_4] \xrightarrow[EtOH,\ 60^{\circ}C]{\overset{\text{excess}}{Me_4NCl}} [Me_4N]_3[Nb_6Cl_{18}]$$

$$\text{Step 3: } [Me_4N]_3[Nb_6Cl_{18}] + 7CN^- + Me_4N^+ \xrightarrow{MeCN,\ H_2O} [Me_4N]_4[Nb_6Cl_{12}(CN)_6] + \tfrac{1}{2}(CN)_2 + 6Cl^-$$



Scheme 1.

sider each cluster as an entity and follow the nomenclature that is widely used for assemblies built from hexacyanometalates and metal complexes.[24,25] For example, supramolecular assemblies with two metal complexes attached to one cluster will be referred to as heterotrimers.

In compounds **3**, **4**, and **6**, each cluster is coordinated by one, two, or four manganese complexes to give di-, tri-, and pentamers. Each cluster in **5** is coordinated by two $[Ca(phen)_2(H_2O)_3]^{2+}$ to give neutral trimeric units, whereas **7** is built from a combination of cationic heptamers and anionic trimers. In all these compounds, the supramolecular assemblies are held together through significant hydrogen bonding to form one-, two-, and three-dimensional frameworks.

4.1 Anionic Heterodimers

Reactions between methanolic solutions of **2** and [Mn(*L1*)]Cl afforded $[Me_4N][Mn(L1)(MeOH)_2]_2\{[Mn(L1)(MeOH)][Nb_6Cl_{12}(CN)_6]\}$ (**3**).[26] In **3**, each cluster is coordinated by one $[Mn(L1)(MeOH)]^+$ through a Nb–C≡N–Mn linkage to give anionic heterodimers $\{[Mn(L1)(MeOH)][Nb_6Cl_{12}(CN)_6]\}^{3-}$ (Figure 3a). Only one of the six CN ligands is bridging, whereas the other five are involved in extensive hydrogen bonding. The bond length of the bridging C≡N ligand [1.150(7) Å] is significantly longer than those for nonbridging CN ligands [1.133(7) Å]. IR spectra show a broad unsymmetrical absorption band at 2134 cm^{-1}, which corresponds to the CN bond stretching frequency. The Mn–C≡N linkage is significantly bent [∠Mn–N≡C = 150.3(4)°] because of the electronic structure of the metal complex. The heterodimers are connected to each other through strong hydrogen bonds between the CN^- ligand and the coordinated MeOH molecule. The dimers are further connected to each other by two solvated metal complexes $[Mn(L1)(MeOH)_2]^+$ through hydrogen bonding between the CN^- ligand and the coordinated MeOH to afford hybrid tubular-like chains (Figure 3b). The manganese adopts distorted octahedral coordination environments (MnN_3O_3 in the dimer and MnN_2O_4 in the cations). The chains lie on top of each other when viewed along the crystallographic *a* axis to form layers within which the chains are parallel to each other and separated by solvent molecules and cations. The layers are related to each other by an inversion center. Analogous dimers built from hexacyanometalates and Mn^{III} Schiff-base complexes were found in $[Et_4N]_2\{[Mn(saldmen)(H_2O)][Fe(CN)_6]\}$ (**I**).[27]

The anionic charge of the heterodimer is balanced by two solvated Mn complex cations, which leads to an $Mn:Nb_6$ ratio of 3:1; however, **3** also formed even when the starting ratio $Mn:Nb_6$ was increased to 6:1. Interestingly, direct mixing of the two solutions followed by vigorous stirring led to slow formation of the Prussian-blue analogue $[Me_4N]_2[MnNb_6Cl_{12}(CN)_6]$[9] probably because of slow decomposition of the manganese complex in methanol followed by further hydrolysis to afford Mn^{2+} ions.[28]

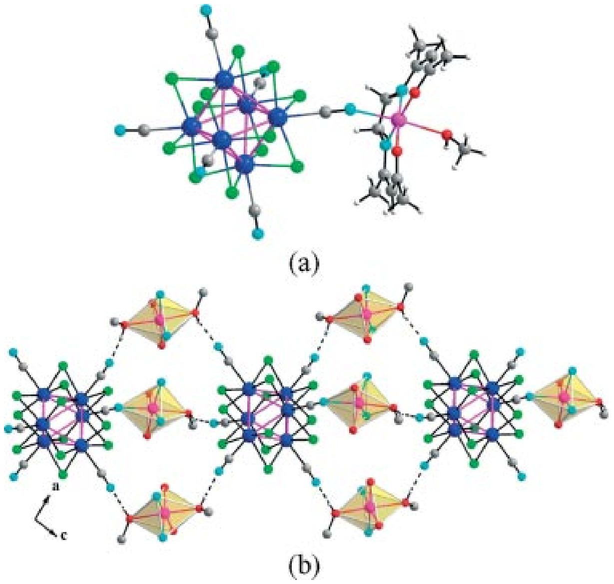


Figure 3. (a) The anionic heterodimeric unit $\{[Mn(L1)(MeOH)][Nb_6Cl_{12}(CN)_6]\}^{3-}$. (b) The anionic tubular-like chain built through extensive hydrogen bonding. *L1* ligands except N_2O_2 atoms, and all hydrogen atoms except those involved in hydrogen bonding are omitted for clarity. Hydrogen bonding is represented as dashed lines. The Mn complexes are shown as $\{MnN_3O_3\}$ and $\{MnN_2O_4\}$ octahedra.

4.2 Anionic Heterotrimers

Reactions between $[Et_4N]_4[Nb_6Cl_{12}(CN)_6]$ and $[Mn(L2)](ClO_4)\cdot 2H_2O$ in methanol led to precipitation of $[Et_4N]_2\{[Mn(L2)(MeOH)]_2[Nb_6Cl_{12}(CN)_6]\}$ (**4**).[19] In **4**, each cluster is *trans*-coordinated by two $[Mn(L2)(MeOH)]^+$ complexes to afford anionic heterotrimers $\{[Mn(L2)(MeOH)]_2[Nb_6Cl_{12}(CN)_6]\}^{2-}$ (Figure 4a). The cluster core $[Nb_6Cl_{12}]^{2+}$ in **4** is similar to that found in **3** in terms of its bond lengths and angles. Of the six CN ligands, two link the cluster to Mn complexes, and four have their N atom involved in hydrogen bonding. The bond lengths of the bridging C≡N ligand [1.143(5) Å] are not significantly different from those found for the nonbridging ones [1.146(5) Å]. Only one band at 2131 cm^{-1} in the IR spectrum was observed for the C≡N stretching frequency. The bond angle Mn–C≡N [157.2(3)°] is slightly larger than that in **3** because of the differences between the salen-type ligands. The heterotrimers are connected to each other through hydrogen bonds between coordinated MeOH molecules and CN^- ligands to afford chains along the crystallographic *a* axis (Figure 4b). The chains run parallel to each other and are separated by solvent molecules and ammonium ions.

Analogous trimeric units built from $[M(CN)_6]^{3-}$ (M = Fe, Cr) *trans*-coordinated by two Mn Schiff-base (SB) complexes have been previously reported.[29–31] For instance, in $K\{[Mn(5\text{-}Br\text{-}salen)(H_2O)]_2[Fe(CN)_6]\}\cdot 2H_2O$ (**II**) each $[Fe(CN)_6]^{3-}$ anion is coordinated by two solvated Mn complexes to afford the units $\{[Mn(5\text{-}Br\text{-}salen)(H_2O)]_2[Fe(CN)_6]\}^-$.

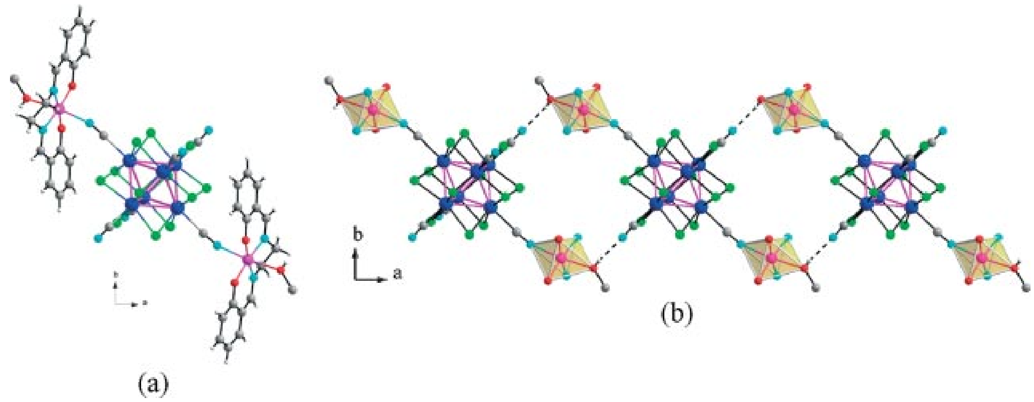


Figure 4. (a) The anionic heterotrimeric unit $\{[Mn(L2)(MeOH)]_2[Nb_6Cl_{12}(CN)_6]\}^{2-}$ in which each cluster is coordinated by two $[Mn(L2)(MeOH)]^+$ complexes in a *trans* fashion. (b) The anionic chain along the *a* axis in which the heterotrimeric units are connected to each other through hydrogen bonds. All hydrogen atoms except those involved in hydrogen bonding are omitted.

4.3 Neutral Heterotrimers

$\{[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\}$ (**5**) was obtained by mixing a solution of $Ca(NO_3)_2$ and phen (mol ratio = 1:2) in H_2O/EtOH with an aqueous solution of $[Me_4N]_4[Nb_6Cl_{18}]$ and KCN.[32] In **5**, each cluster is *trans*-coordinated by two $[Ca(phen)_2(H_2O)_3]^{2+}$ complexes through Nb–C≡N–Ca linkages to form neutral trimeric units $\{[Ca(phen)_2(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\}$ (Figure 5a). Each Ca ion is coordinated by four N atoms from two phen ligands, one N atom from the cyanide ligand, and three O atoms from water molecules to give an overall eight coordination environment (distorted square antiprism) that is common for calcium.[33–35] For the cyanide ligands coordinated to Ca ions, the C≡N bond length is 1.149(9) Å, whereas for nonbridging cyanide ligands the bond lengths range from 1.11(1) to 1.15(1) Å. Only one absorption band at

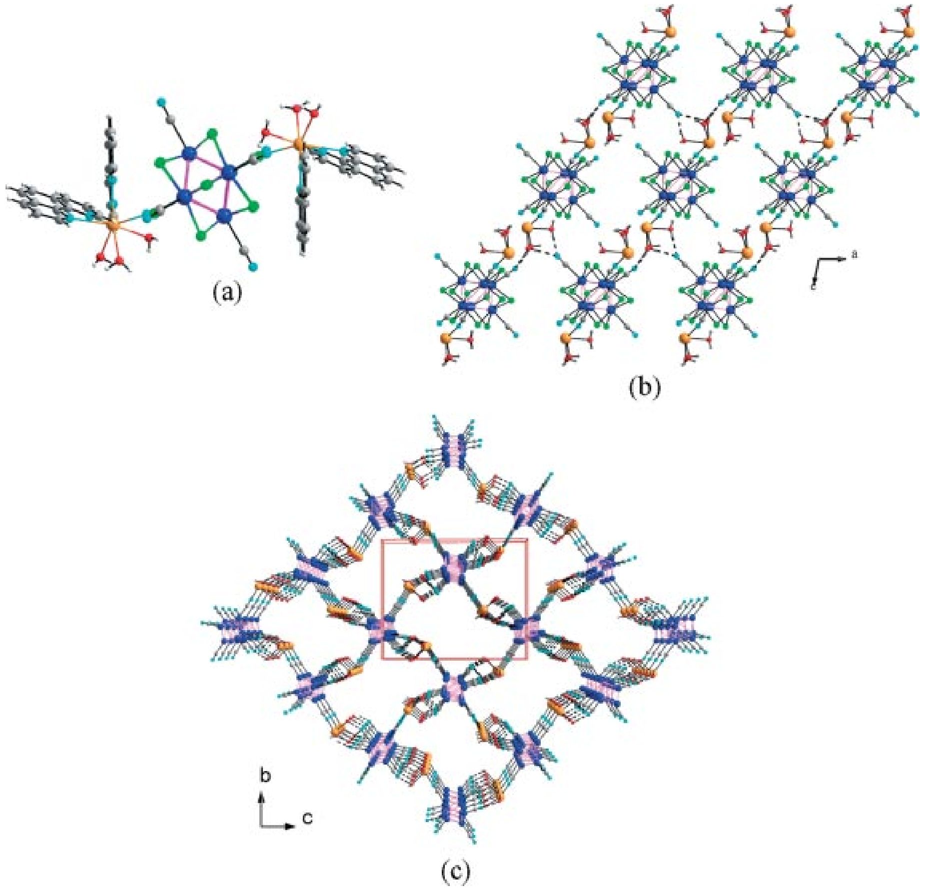


Figure 5. (a) The neutral trimeric unit $\{[Ca(phen)(H_2O)_3]_2[Nb_6Cl_{12}(CN)_6]\}$ in which each cluster is coordinated by two $[Ca(phen)(H_2O)_3]^{2+}$ complexes in a *trans* fashion. (b) Projection along the *b* axis of the neutral layer in which each trimeric unit links four trimeric units through hydrogen bonding. phen Ligand and all hydrogen atoms except those involved in hydrogen bonding are omitted. (c) Perspective view along the *a* axis, which shows the 3D framework of **5**. Inner chloride ligands are omitted.

2128 cm^{-1} was observed for the C≡N stretching frequency. Each trimer is linked to four neighboring trimers by hydrogen bonds between the aqua ligand in $[Ca(phen)_2(H_2O)_3]^{2+}$ and the cyanide ligands to afford layers (Figure 5b). The layers are further connected by hydrogen bonds between calcium complexes and cluster units from neighboring layers to form a 3D framework (Figure 5c). Hydrogen-bonded frameworks built from similar trimeric units in which mononuclear hexacyanometalates such as $[Fe(CN)_6]^{3-}$ and Ca-phen complexes have been reported, as is the case in $\{[Ca(phen)_2(H_2O)_2][Fe(CN)_6][Ca(phen)_2(H_2O)(NO_3)]\}$- (**III**).[36,37]

4.4 Heteropentamers

Slow evaporation of a solution of $[Me_4N]_4[Nb_6Cl_{12}(CN)_6]$ and a sixfold excess of $[Mn(L1)]Cl$ in partially dried acetonitrile resulted in crystals of $\{[Mn(L1)(MeCN)]_2[Mn(L1)(H_2O)]_2[Nb_6Cl_{12}(CN)_6]\}$ (**6**).[26] In **6**, each cluster uses four CN ligands to connect to four solvated manganese complexes: two $[Mn(L1)(MeCN)]^+$ complexes and two $[Mn(L1)(H_2O)]^+$ complexes to form neutral heteropentamers (Figure 6a). The complexes are located opposite to each other across the cluster and are related by an inversion center. The average bond length of the bridging cyanide ligands is 1.148(4) Å, which is close to that of nonbridging cyanide ligands [1.145(5) Å]. In the IR spectrum, only one broad absorption band at 2142 cm^{-1} is observed. The bond length Mn–N_{CN} [2.26(2) Å] is slightly shorter than that found in **3** and **4**. The pentamers link to each other through hydrogen bonds between the cyanide and aqua ligands from adjacent assemblies and form chains (Figure 6b) that run parallel to each other and interact through acetonitrile solvent molecules.

Pentameric units of this type have been found in compounds built from hexacyanometalate and Mn Schiff-base complexes such as $\{[Mn(saltmen)(H_2O)]_4[Fe(CN)_6]\}(ClO_4)$[27] in which the pentamers are hydrogen bonded to each other, and $\{[Mn_2(saltmen)_2]_2[Fe(CN)_6]\}(ClO_4)\cdot H_2O$ (**IV**)[29] which is a 2D coordination polymer built from the pentamers $\{[Mn(saltmen)]_4[Fe(CN)_6]\}^+$ linked through phenoxo bridges between the manganese complexes.

In the synthesis of **6**, it was observed that a small amount of water in the acetonitrile plays an important role in its formation. When dry acetonitrile was used and extra care was taken to reduce inadvertent exposure to moisture, a 3D coordination polymer $[Me_4N]\{[Mn(L1)]_3[Nb_6Cl_{12}(CN)_6]\}$ (**12**) was obtained (vide infra).[38] Despite the availability of two cyanide ligands, attempts to increase the nuclearity of the supramolecular assemblies by using a tenfold excess of $[Mn(L1)]Cl$ were not successful. Only when the reaction was performed in a $MeOH/H_2O$ mixture were heptameric assemblies containing a cluster connected to six manganese complexes isolated (vide infra).

4.5 Heteroheptameric and Heterodimeric Supramolecules

When **2** was mixed with $[Mn(L1)]Cl$ in a $MeOH/H_2O$ mixture, $\{[Mn(L1)(H_2O)]_4[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}\{[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}$ (**7**) was isolated. Its structure consists of the heptamers $\{[Mn(L1)(H_2O)]_4[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}^{2+}$ (Figure 7a) and trimers $\{[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}^{2-}$ (Figure 7b). The cation assembly consists of $[Nb_6Cl_{12}(CN)_6]^{4-}$ linked to six Mn complexes by way of Nb–C≡N–Mn linkages. Two complexes are pentacoordinate, two oxygen atoms and two nitrogen atoms from the Schiff-base ligand and one nitrogen atom from the cyanide ligand, which leads to a distorted square-pyramidal coordination geometry. The complexes are related to each other by an inversion centre. The other four manganese ions are coordinated by two oxygen atoms and two nitrogen atoms from the tetradentate ligand, one nitrogen from the cyanide ligand, and one oxygen from the solvent molecule, which leads to the formation of a distorted octahedral environment. The overall shape of the heptameric cation can be described as a large flattened sphere with a diameter of about 2.1 nm. The anionic trimer is built from $[Nb_6Cl_{12}(CN)_6]^{4-}$ complexes coordinated by two pentacoordinate manganese complexes that are similar to those observed in the heptamer. The trimers are similar to those found in **4** except that the manganese ions in **4** are hexacoordinate because of the presence of a solvent molecule as a ligand. Hydrogen bonds between the CN$^-$ ligand from the

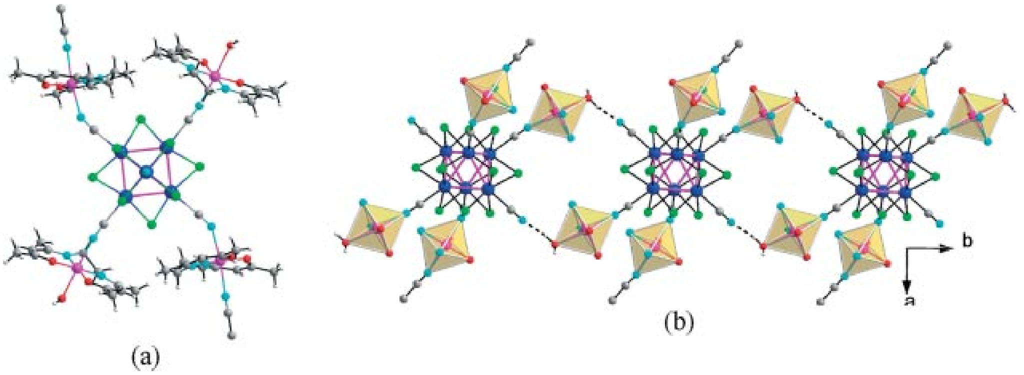


Figure 6. (a) The heteropentamers $\{[Mn(L1)(MeCN)]_2[Mn(L1)(H_2O)]_2[Nb_6Cl_{12}(CN)_6]\}$ in which each cluster is coordinated by two $[Mn(L1)(MeCN)]^+$ complexes and two $[Mn(L1)(H_2O)]^+$ complexes. (b) Neutral chains extending along the *b* axis in which heteropentameric units are connected to each other through hydrogen bonding.

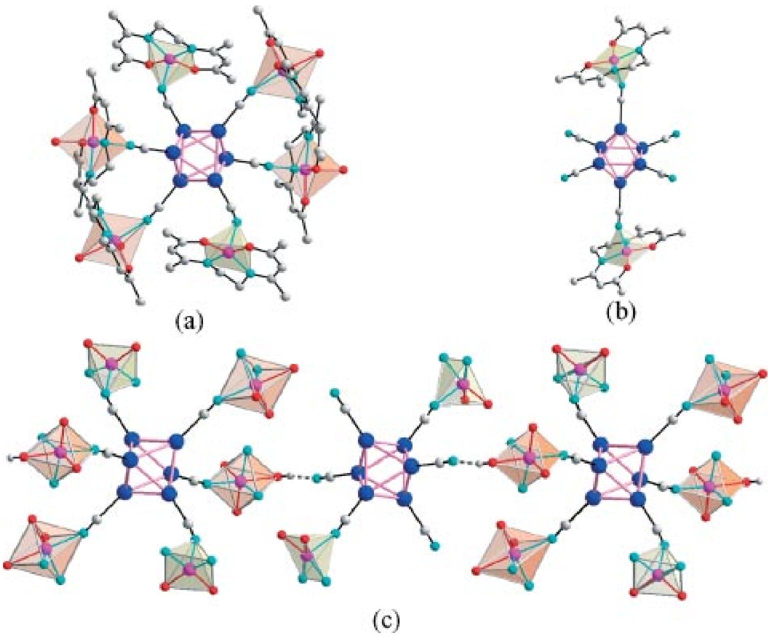


Figure 7. (a) The heteroheptamer $\{[Mn(L1)(H_2O)]_4[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}^{2+}$ complex where each cluster is coordinated by four $[Mn(L1)(H_2O)]^+$ complexes and two $[Mn(L1)]^+$ complexes. (b) The heterotrimer $\{[Mn(L1)]_2[Nb_6Cl_{12}(CN)_6]\}^{2-}$ where each cluster is linked to two $[Mn(L1)]^+$ complexes in the *trans* position. (c) Chains built from hydrogen bonding between coordinated water molecules from cations and cyanide ligands from anions.

anions and the coordinated H_2O molecules from the cations lead to the formation of chains (Figure 7c). The C≡N bond length [1.146(4) Å] for the ligands coordinated to the hexacoordinate Mn complex is longer than that for the CN ligand coordinated to the pentacoordinate manganese [1.137(4) Å]. The average bond length of $Mn–N_{CN}$ for the pentacoordinate Mn complex [2.150(3) Å] is significantly shorter than that found in the hexacoordinate Mn complex [2.287(3) Å] as a result of the solvent coordination effect.

The structure of compound **7** is interesting in terms of the coexistence of the cationic heteroheptamers and anionic heterotrimers as well as penta- and hexacoordinate Mn ions. However, both penta- and hexacoordinate Mn ions have been observed in $[Mn(L2)]_4[Re_6Te_8(CN)_6]$[17a] in which two $[Mn(L2)]^+$ complexes bridge the cluster units to give a 2D framework whereas two other complexes are attached to one cluster unit only through the N_{CN} atom. Similar cationic–anionic assemblies have been observed in compounds containing hexacyanometalates $[M(CN)_6]^{3-}$ (M = Fe^{3+}, Cr^{3+}) as building units.[39,40] For example, $\{[Mn(L2)(H_2O)]_6[Fe(CN)_6]\}[Fe(CN)_6]$ (**V**)[41] is built from $[Fe(CN)_6]^{3-}$ complex anions coordinated by six solvated $[Mn(L2)(H_2O)]^+$ complex cations to form the heptamer $\{[Mn(L2)(H_2O)]_6[Fe(CN)_6]\}^{3+}$.

5. Coordination Polymers Built from $[Nb_6Cl_{12}(CN)_6]^{4-}$ and Metal Complexes

The species described in Section 4 can be described as octahedral clusters ligated by one, two, four, and six metal complexes to form larger supramolecular assemblies. In most cases, the solvent completes the preferred octahedral coordination environment for Mn^{III}, which prevents the formation of coordination polymers. Judicious choice of the synthetic conditions such as cations, solvents, stoichiometries, metal complexes, and salen-type ligands led to the preparation of coordination polymers with 1D, 2D, and 3D frameworks. The framework dimension depends on the cluster/metal complex ratio and the connectivity mode between the two building units. The clusters in all the coordination polymers are similar to those found in supramolecular assemblies in terms of bond lengths and angles.

5.1 One-Dimensional Coordination Polymers

Two coordination polymers with one-dimensional frameworks built from $[Nb_6Cl_{12}(CN)_6]^{4-}$ and $[Mn(L)]^+$ connected by cyanide ligands have been characterized. The salen-type ligand and the solvent system determine which one of these two compounds forms.

$[Me_4N]_3\{[Mn(L1)][Nb_6Cl_{12}(CN)_6]\}$ (**8**) cocrystallized with $[Me_4N]_2[MnNb_6Cl_{12}(CN)_6]$ from the reaction of equimolar amounts of **2** and [Mn(*L1*)]Cl in dry MeCN. It crystallizes in the tetragonal symmetry (space group: $I4_1/a$) and is formed from two sets of chains related to each other by a 4_1 screw axis (Figure 8a). In **8**, each cluster is coordinated by two $[Mn(L1)]^+$ complex cations through Nb–C≡N–Mn linkages, and each $[Mn(L1)]^+$ complex connects two clusters to give anionic zigzag chains $\{[Mn(L1)][Nb_6Cl_{12}(CN)_6]\}_\infty^{3-}$ (Figure 8b) that extend along the crystallographic *a* and *b* axes. The chains are bent with ∠Mn–N≡C of 152.9(2)° and 156.5(3)°. The Nb–C bond length associated with the bridging cyanide ligands [2.301(3) Å] is larger than that of a nonbridging cyanide ligand [2.268(3) Å]. The bond length for a

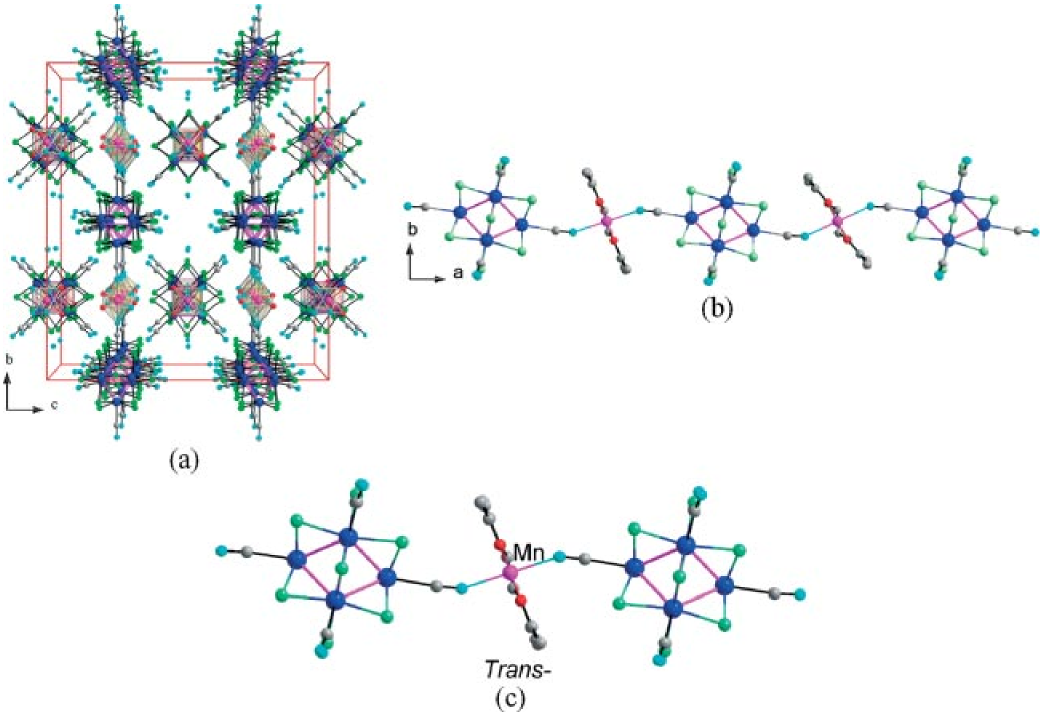


Figure 8. (a) Perspective view of the 1D coordination polymer $[Me_4N]_3\{[Mn(L1)]\ [Nb_6Cl_{12}(CN)_6]\}$ (**8**); (b) The anionic zigzag chain extending along the *a* axis. (c) Each Mn complex is coordinated by two cluster units in a *trans* conformation. The Mn complexes are shown as $\{MnN_4O_2\}$ octahedra.

bridging C≡N ligand [1.145(4) Å] is slightly longer than that for a nonbridging C≡N group [1.139(4) Å]. Two Mn–N_{CN} bond lengths are observed [2.332(3) and 2.382(3) Å] and they are longer than those found in all supramolecular assemblies described above. The chains belong to the 2,2-TT type because each cluster is *trans* coordinated by two Mn complexes and each Mn complex is connected to two clusters in a *trans* conformation (Figure 8c).[42] The chains are stacked parallel to each other along the *ac* and *ab* planes and are separated by solvent molecules and ammonium ions (Figure 8a).

$[Me_4N]_3\{[Mn(L3)][Nb_6Cl_{12}(CN)_6]\}$ (**9**) was obtained from reaction of **2** with $[Mn(L3)(MeOH)](ClO_4)$ in methanol (mol ratio $[Nb_6Cl_{12}(CN)_6]^{4-}:[Mn(L3)]^+ \approx 1.0$).[38] It is a 1D coordination polymer with the same cluster complex connectivity as that observed for **8**. Each cluster is connected to two complexes through two cyanide ligands on opposite sides, and each complex connects two clusters to afford anionic zigzag chains $\{[Mn(L3)][Nb_6Cl_{12}(CN)_6]\}_\infty^{3-}$ that extend along the crystallographic *c* axis. The chains stack parallel to each other along the *a* axis (Figure 9a) to form layers parallel to the *ac* plane. Ammonium ions and solvent molecules are located between the chains. The Nb–C bond lengths for the bridging C≡N ligands are 2.278(8) and 2.288(8) Å, slightly larger than those for nonbridging CN ligands [2.25(1)–2.271(9) Å]. The bond lengths of the bridging C≡N ligand [1.129(9) and 1.126(9) Å] are significantly smaller than those for nonbridging cyanide ligands [1.15(1) Å]. Yet only one broad asymmetric band is observed in the IR spectrum at 2128 cm^{-1}. The Mn–N≡C

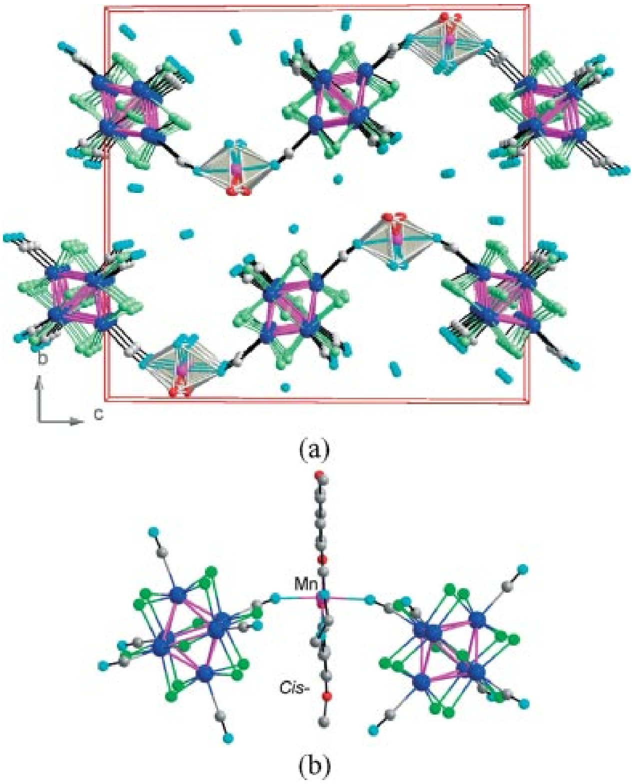


Figure 9. (a) Perspective view of the structure of 1D coordination polymer $[Me_4N]_3\{[Mn(L3)]\ [Nb_6Cl_{12}(CN)_6]\}$ (**9**) along the crystallographic *a* axis; (b) each Mn complex is coordinated by two cluster units in the *cis* conformation.

linkage [$\angle$Mn–N≡C = 148.59(8)°] is bent to a greater extent than in **8**. The N_{CN}–Mn–N_{CN} linkage [$\angle N_{CN}$–Mn–N_{CN} = 174.2(2)°] is also slightly more bent compared to that observed in **8**. The geometric conformation of the metal complex dictates the topology of the chains in **8** and **9**. In **8**, each manganese is linked to two clusters located on opposite sides of the N_{CN}–Mn–N_{CN} axis (*trans* conformation), whereas in **9**, each Mn complex is linked to two clusters located on the same side of the N_{CN}–Mn–N_{CN} axis (*cis* conformation) (Figure 9b). Complex **9** is an expanded analogue of $[Et_4N]_2\{[Mn(L1)][Fe(CN)_6]\}$ (**VI**) in which $[Mn(L1)]^+$ and $[Fe(CN)_6]^{3-}$ are linked by CN ligands to afford chains.[43]

Reactions between $[Et_4N]_3[Fe(CN)_6]$ and $[Mn(L3)(H_2O)]^+$ in methanol led to the formation of $[Et_4N]\{[Mn_2(L3)_2][Fe(CN)_6]\}$ built from phenoxo-bridged dimers $[Mn_2(L3)_2]^{2+}$ and $[Fe(CN)_6]^{3-}$ linked by the cyanide ligand to form one dimensional coordination polymers.[44] The formation of the dimeric Mn complexes is most likely due to the relative stability of the monomer versus the dimer, which depends on the solvent used.

5.2 Two-Dimensional Coordination Polymers

Direct mixing of dilute methanolic solutions of **2** and $[Mn(L2)](ClO_4)$ (mol ratio complex:cluster = 2) led to quantitative formation of $[Me_4N]_2\{[Mn(L2)]_2[Nb_6Cl_{12}(CN)_6]\}$ (**10**).[19] Polymer **10** can be obtained as a microcrystalline powder when the molar ratio $[Mn(L2)]^+$:$[Nb_6Cl_{12}(CN)_6]^{4-}$ ranges from 1.0 to 4.0. In **10**, each cluster is coordinated by four $[Mn(L2)]^+$ complexes through Nb–C≡N–Mn linkages and each $[Mn(L2)]^+$ complex connects two $[Nb_6Cl_{12}(CN)_6]^{4-}$ anionic complexes to generate anionic layers $\{[Mn(L2)]_2[Nb_6Cl_{12}(CN)_6]\}_\infty{}^{2-}$ that are parallel to the *bc* plane (Figure 10b). The Nb–C bond lengths associated with bridging cyanide ligands are about 2.29 Å and longer than those associated with nonbridging cyanides (2.27 Å). In contrast, the C≡N bond lengths are all about 1.13 Å, which is consistent with the observation of only one absorption band in the IR spectrum at 2134 cm^{-1} for the C≡N stretch. The Mn–N_{CN} bond lengths are significantly different from each other and vary between 2.23 and 2.36 Å owing to the bowl-shaped salen-type ligand *L2* with the longer Mn–N_{CN} linkages on the concave side of the ligand. The Mn–N≡C bond angles are also significantly different, 144.2(3) and 155.0(3)°, respectively. The two phenyl groups of the *L2* ligand in **10** are located in a *cis* fashion with respect to the basal N_2O_2 plane; in contrast, the phenyl groups in $[Mn(L2)](ClO_4)$[45], which is used as a precursor, are located in a *trans* fashion.[46] The layers are stacked in a staggered fashion along the crystallographic *a* axis and are separated by ammonium ions that are found in the vicinity of the uncoordinated cyanide ligands (Figure 10a). Similar layers have been observed in $[Mn(L2)]_4[Re_6Te_8(CN)_6]$[17a] in which Re_6 clusters are coordinated by six $[Mn(L2)]$, two of which are dangling. Polymer **10** represents a cluster-expanded analogue of the compound $[Et_4N]\{[Mn(L2)]_2[Fe(CN)_6]\}$ (**VII**)[47] in which each $[Fe(CN)_6]^{3-}$ is linked to four complexes and each complex links two ferricyanides to form anionic layers that stack perfectly on top of each other contrary to the stacking in **10**.

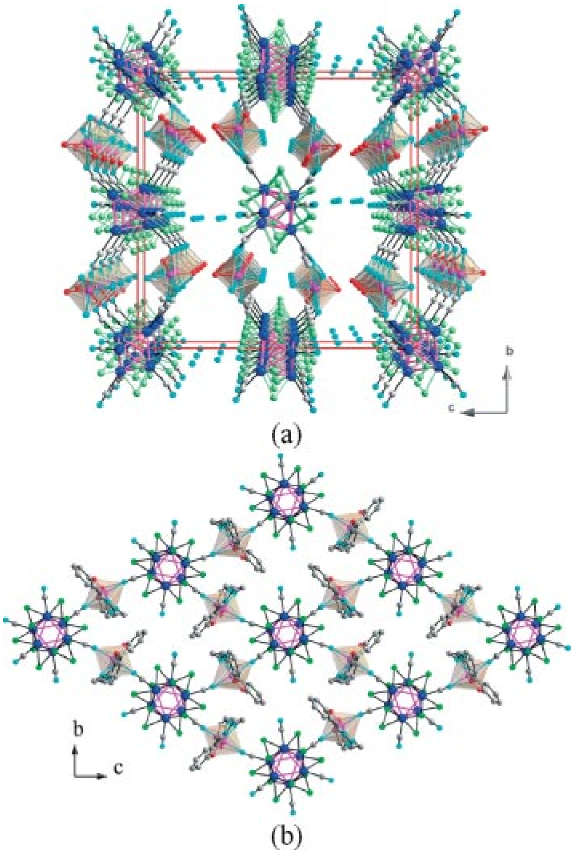


Figure 10. (a) Perspective view of the structure of 2D coordination polymer $[Me_4N]_2\{[Mn(L2)][Nb_6Cl_{12}(CN)_6]\}$ (**10**) along the crystallographic *a* axis; (b) A projection of the anionic layer parallel to the crystallographic *bc* plane along the *a* axis.

5.3 Effect of the Metal Complex Coordination Requirements: The Layered Framework of $[Zn(en)]_2[Nb_6Cl_{12}(CN)_6]$

The topology, dimension, and properties of frameworks built from clusters and metal complexes presumably depend on the metal complex and the coordination preferences of the metal ion. The use of $[Zn(en)]^{2+}$ and the cluster as building units led to the formation of $[Zn(en)]_2[Nb_6Cl_{12}(CN)_6]$ (**11**) which has a layered framework and was obtained from the reaction between an aqueous solution of $Na_4[Nb_6Cl_{12}(CN)_6]$ and an ethanolic solution containing equimolar amounts of $Zn(ClO_4)_2\cdot 6H_2O$ and en.[48] The structure of **11** consists of neutral layers in which each cluster $[Nb_6Cl_{12}(CN)_6]^{4-}$ is coordinated by six $[Zn(en)]^{2+}$ complexes through Nb–C≡N–Zn linkages and each $[Zn(en)]^{2+}$ is connected to three cluster units to afford layers parallel to the *ab* plane (Figure 11a). Although the C≡N bond lengths are all found at ca. 1.15 Å, not much different from that observed in **10**, the C≡N IR bond stretch frequency appears at 2167 cm^{-1}, which is much higher than that observed for **10**. The Zn–N bond length [2.051(8) Å] is shorter than that of the Mn–N bond found in compounds containing supramolecular assemblies and coordination polymers and reflects the smaller ionic radius of Zn^{2+}. The Zn–N≡C bond angle is 172.5(9)°, which is close to those found for Ca–N≡C in **5** [172.9(8)°] but larger than the Mn–N≡C bond angles in **3**, **4**, and **6**–**9** [144.2(3)–165.8(3)°]. The layers stack on top of each other along the *c* axis and are held together only through weak Van der Waals interactions. Projection along the crystallographic *b* axis indicates that [Zn(en)] complexes are alternatively located above and below the plane (Figure 11b).

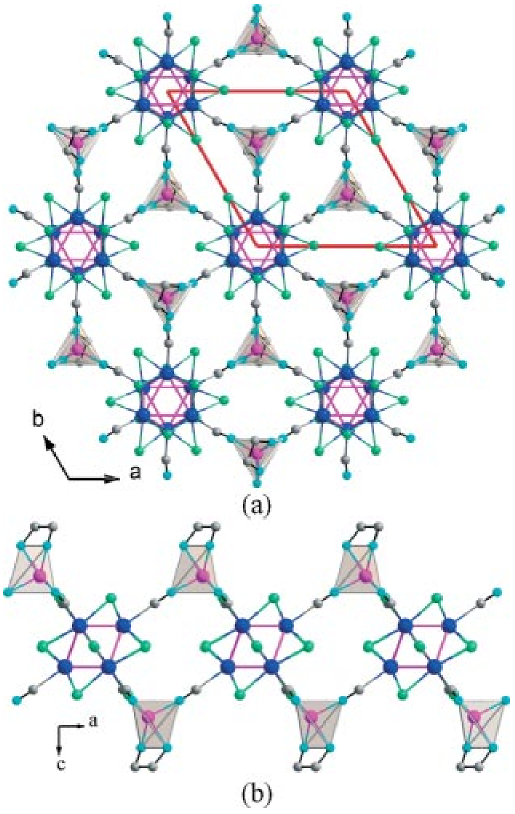


Figure 11. (a) A projection of the layer in $[Zn(en)]_2[Nb_6Cl_{12}(CN)_6]$ (**11**) along the *c* axis. (b) A projection of the layer along the crystallographic *b* axis, which shows that the [Zn(en)] complexes are alternatively located above and below the plane.

Similar layers have been observed in $[Zn(H_2O)]_2[Fe(CN)_6]$[49] and in $[Zn(H_2O)]_2[Re_6Se_8Fe(CN)_6]$.[8k] However, in contrast to **11** where Zn^{2+} is coordinated by two N atoms from the chelating en ligand and three N_{CN} atoms from three different clusters to form a distorted square pyramid ZnN_5, in the latter compounds Zn^{2+} is coordinated by one oxygen atom from the aqua ligand and three N_{CN} atoms, which leads to the formation of distorted ZnN_3O tetrahedra. The layers in **11** can be considered as expanded layers of the $CdCl_2$ or CdI_2 structure types[50,51] in which the $[Nb_6Cl_{12}]^{2+}$ cluster core takes the place of Cd^{2+}, and the complex anion $[Zn(en)(CN)_3]^-$ takes the place of the halide; thus the chemical formula can be written as $[Nb_6Cl_{12}][Zn(en)(CN)_3]_2$. However, the layers are stacked on top of each other in **11**, whereas in $CdCl_2$ and CdI_2, the layers are staggered.

5.4 Three-Dimensional Coordination Polymers

$[Me_4N]\{[Mn(L1)]_3[Nb_6Cl_{12}(CN)_6]\}$ (**12**) was obtained from the reaction of **2** with [Mn(*L1*)]Cl (8 equiv.) in dry acetonitrile.[38] In the presence of even trace amounts of water in acetonitrile, compound **7** was obtained instead. In **12**, each cluster is coordinated by six $[Mn(L1)]^+$ complexes and each complex links two cluster units to give an overall 3D framework (Figure 12a). The structure consists of identical but symmetry independent layers parallel to the *bc* plane with the same cluster complex connectivity as that found in **10** (Figure 12b). The layers are linked to each other through manganese complexes, which leads to the formation of cavities where the cation and acetonitrile molecules are located. The C≡N bond lengths range between 1.14 and 1.16 Å and only one peak at 2142 cm^{-1} was observed for the C≡N vibrational stretching frequency. This value is larger than that found in the starting materials (2126 cm^{-1}) and 2D coordination polymer **10** built from [Mn(*L2*)] (2134 cm^{-1}). Two symmetry independent manga-

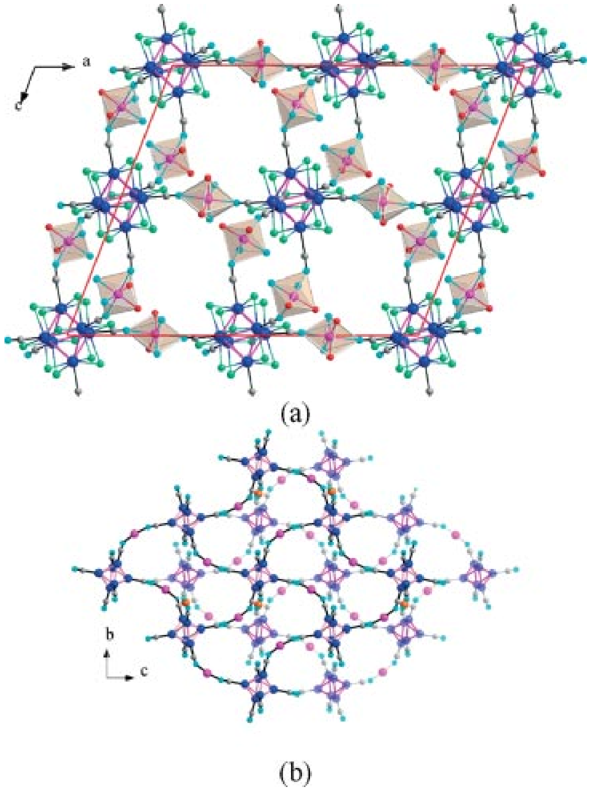


Figure 12. (a) Projection of the structure of the 3D coordination polymer $[Me_4N]\{[Mn(L1)][Nb_6Cl_{12}(CN)_6]\}$ (**12**) along the crystallographic *b* axis; (b) A projection along the *a* direction of two adjacent layers (one is bold and the other is faded), which shows the staggered packing of the layers along the *a* axis. The layers are further connected to each other through an additional set of Mn complexes.

nese complexes are used to connect the clusters within the layers with bond lengths $Mn–N_{CN}$ = 2.34 Å, whereas a third manganese complex links the layers together to form the 3D framework with an average bond length $Mn–N_{CN}$ = 2.296 Å. The compound $Na\{[Mn(L2)]_3[Re_6Se_8(CN)_6]\}$[17a] also features a 3D coordination polymer in which each Re_6 cluster is surrounded by six Mn complexes.

The overall structure can be considered a 3D framework in which layers found in **10** are connected to each other through additional Mn complexes by using the two remaining CN ligands. The compound has been shown to lose almost all solvent molecules after being washed or when evacuated at room temperature without loss of crystallinity. Careful structural analysis reveals that solvent molecules are not involved in hydrogen bonding.

5.5 Effect of the Metal Complex: The 3D Framework of $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (13)

This compound was synthesized in a one-pot reaction by mixing a solution of $BaCl_2$ and phen (mol ratio = 1:2) in H_2O/EtOH with an aqueous solution containing $[Me_4N]_4[Nb_6Cl_{18}]$ and KCN.[32] The cyanochloride cluster was generated in situ. The structure of **13** is a neutral 3D framework built from $[Nb_6Cl_{12}(CN)_6]^{4-}$ and $[Ba(phen)_2(H_2O)]^{2+}$ (Figure 13a). Each cluster unit is linked to six barium complexes through cyanide ligands and each Ba complex links three clusters. Two crystallographically independent Ba complexes are present and arranged in a *mer* conformation around the cluster. Each set of Ba complexes links the cluster units to form ladder-like chains along the *c* and *b* axis (Figure 13b); this generates channels along the crystallographic *a* axis in which the phen ligands are located. The bond length of C≡N is about 1.14 Å yet two C≡N stretches were observed in the IR spectrum (2122, 2131 cm^{-1}). In addition to three N atoms from the cyanide ligands, each barium is additionally coordinated by four N atoms from two phen ligands and one O atom from a water molecule. Extended frameworks containing Ba-phen complexes and hexacyanometalates as building units have been reported. For instance, $\{[Ba_2(phen)_4(H_2O)_6][Fe(CN)_6]\}Cl$ (**VIII**)[52] is built from dimeric unit $[Ba_2(phen)_4(H_2O)_6]^{4+}$ and $[Fe(CN)_6]^{3-}$ and they are connected to each other by CN ligands to form chains. The dimers $[Ba_2(phen)_4(H_2O)_6]^{4+}$ are built from monomers $[Ba(phen)_2(H_2O)_2]^{2+}$ that are connected to each other by two water molecules through Ba–O–Ba linkages. Ba ions are nine-coordinate by four N atoms from two phen ligands, four O atoms from water molecules, and one N atom from a cyanide ligand.

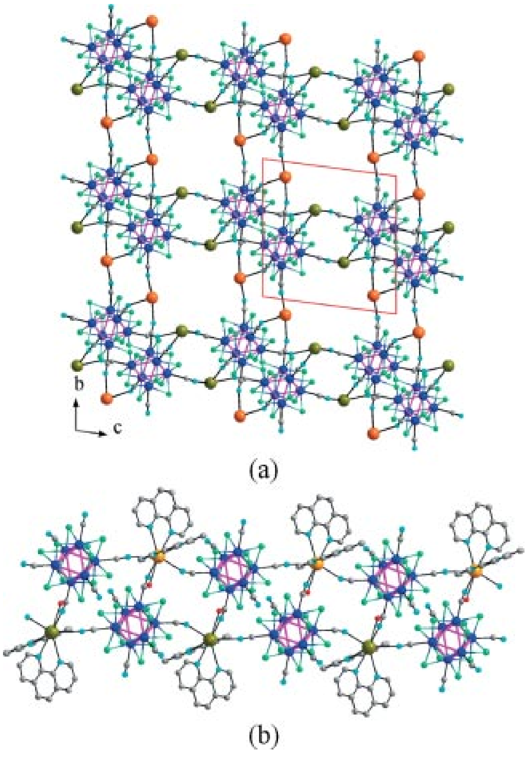


Figure 13. (a) Projection of the 3D framework found in $[Ba(phen)_2(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$ (**13**) along the *a* direction. Water molecules and phen ligands located within the cavities have been omitted for clarity. (b) Ba complexes link cluster units to afford ladder chains along the *c* direction.

6. Properties

6.1 Thermal Stability

The thermal stability of compounds built from cluster units and Mn complexes depends on the nature of their framework. Thus, when heated to 200 °C in air-flow, materials built from supramolecular assemblies lose their crystallinity after losing all solvent molecules essential to the formation of the hydrogen-bonded frameworks. Figure 14 shows typical TGAs for materials based on supramolecular assemblies and coordination polymers. The stability of the

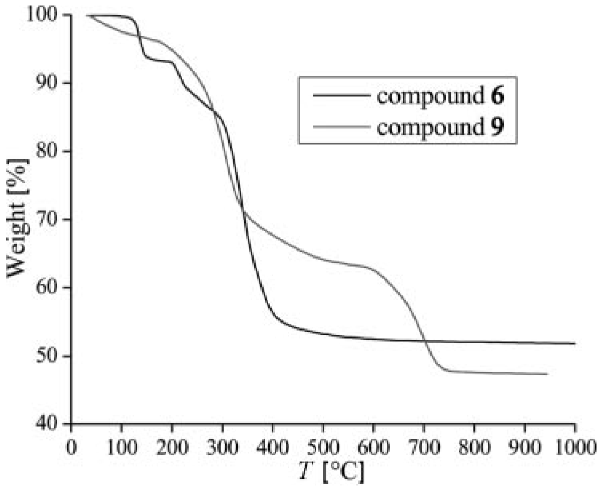


Figure 14. TGA of **6** built from supramolecular assemblies and **9** characteristic of coordination polymer heated from 30 °C to 950 °C at 5 °C /min under air-flow (40 mL/min).

coordination polymers is different because the solvent molecules are not involved in building the frameworks. When heated in air-flow, the product obtained after 700 °C is generally a mixture of metal oxides with compositions determined by the ratio of Mn:Nb_6 in the initial material. When the ratio Mn:Nb_6 = 1 or 2, the product is a mixture of $MnNb_2O_6$ and Nb_2O_5, and when Mn/Nb_6 = 3, only $MnNb_2O_6$ is observed. The thermal decomposition can be described by the following chemical equation:

$\{[Mn(L)]_n[Nb_6Cl_{12}(CN)_6]\} + [(15 + n)/2 + n]O_2 \rightarrow nMnNb_2O_6 + (3 - n)Nb_2O_5$ (n = 1, 2, 3)

It is worth noting that the columbite $MnNb_2O_6$ forms in the temperature range 400–750 °C, much lower than the temperatures (800–1400 °C) at which $MnNb_2O_6$ is prepared through conventional mixed oxide route.[53]

6.2 Magnetic Properties

In all compounds described above, the Nb–Nb bond lengths are characteristic of diamagnetic 16-electron clusters.[18] The effective magnetic moment in **6**, **10**, and **12** are characteristic of high-spin Mn^{III} ions. For example, for **12** the μ_{eff} value at 300 K is 5.17 μ_B, close to the calculated value of the spin-only effective moment of the high-spin Mn^{3+} ion (4.90 μ_B). As the compound is cooled from 300 K to 20 K, the effective magnetic moment remains almost the same and then decreases slowly. The data were fitted with the Curie–Weiss relation $\chi(T) = \chi_0 + C/(T - \theta)$ to give C = 3.36 emu K mol^{-1} and $\theta = -2.02$ K (Figure 15). No evidence of magnetic exchange coupling between the Mn^{III} centers was observed even for the 3D framework of **12**. This is different from the case of the Prussian-blue $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 14H_2O$ in which the Fe^{III} ions are separated from each other by diamagnetic Fe^{II} ions, yet ferromagnetic coupling (T_c = 5.6 K) was observed.[54] Two reasons can account for this: 1) the large size of the cluster units, which separate two Mn^{III} ions, results in a Mn interdistance of 15.1(2) Å for **12**, and 2) the electronic structure of the diamagnetic 16-electron cluster.

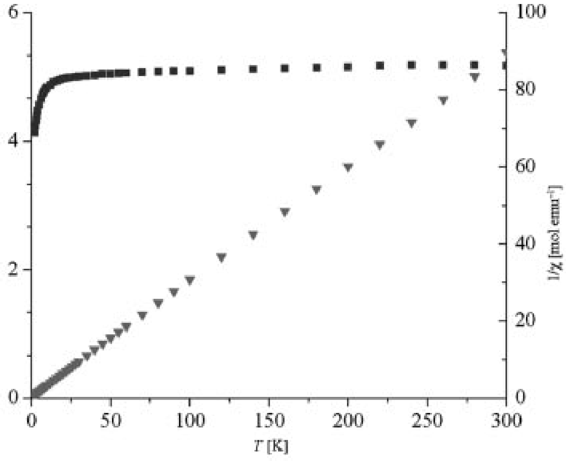


Figure 15. Plot of μ (left) and $1/\chi$ (right) versus T of **12** measured under a 1 kG magnetic field.

7. Conclusion

Octahedral niobium cyanochloride clusters and coordinatively unsaturated metal complexes have been successfully used as components of larger assemblies. Two types of assemblies have been obtained depending on the metal complex chosen, the solvent system, and the molar ratios used. Table 1 summarizes the most important bond lengths and angles, as well as the $\nu(C\equiv N)$ bond stretching frequency of the compounds described here and their analogues based on $[Fe(CN)_6]^{3-}$. The following observations can be made: 1) Supramolecular assemblies in which the cluster is progressively coordinated by one, two, four, and six metal complexes have been obtained. The size of these supramolecules increases from 1.5 to 2.4 nm as the number of metal complexes per cluster increases. The cluster-based supramolecules are about 0.5 to 0.8 nm larger than analogous species built from $[Fe(CN)_6]^{3-}$ and metal complexes, which is consistent with the fact that the size of $[Nb_6Cl_{12}(CN)_6]^{4-}$ is about 0.5 nm larger than $[Fe(CN)_6]^{3-}$. 2) The functionalization of the cluster unit by attaching a different number of metal complexes led to the formation of different species with different charges. 3) The dimension and topology of coordination polymers built from clusters and metal complexes are dictated by the coordination requirements of the metal complex and the connectivity mode between the metal complex and the cluster. Thus, Mn^{III} Schiff-base complexes containing two free coordination sites are used to build 1D, 2D, and 3D coordination polymers as the cluster uses two, four, and six CN ligands to link to the metal complex and the Mn:Nb_6 ratio increases from 1 to 3. Both $[Zn(en)]^{2+}$ and $[Ba(phen)_2(H_2O)]^{2+}$ use three coordination sites to build either 2D and 3D coordination polymers because of the availability of three coordination sites. 4) Though similarities between the compounds reported here and their counterparts that are built from $[Fe(CN)_6]^{3-}$ or Re_6 clusters are observed, the compounds differ from each other in terms of their structural features and properties. The reactivity of $[Nb_6Cl_{12}(CN)_6]^{4-}$ towards metal complexes is also different from that of $[Fe(CN)_6]^{3-}$ and Re_6 clusters. 5) The formation of supramolecular assemblies results from the substitution of ammonium ions with coordinatively unsaturated metal complexes. Di-, tri-, and pentameric supramolecules are formed as the number of Mn complexes attached to the cluster increases. The process can be represented by the following chemical equation:

$[Me_4N]_4[Nb_6Cl_{12}(CN)_6] + n[Mn(L)]+ \rightarrow [Me_4N]_{4-n}\{[Mn(L)]_n[Nb_6Cl_{12}(CN)_6]\} + n[Me_4N]+$ ($0 \le n \le 4$)

6) The formation of 1D, 2D, and 3D coordination polymers is governed by the same chemical equation as above. As n increases from 1 to 3, 1D, 2D, and 3D frameworks are obtained. These coordination polymers can be viewed as supramolecular units connected to each other by additional clusters. Thus, the 1D polymer can be described as being formed from heterotrimers connected to cluster units to form chains, the 2D material can be described as heteropen-

Table 1. Most important bond lengths [Å] and bond angles [°] and the ν(C≡N) [cm^{-1}] for the compounds described in the present review and their iron(III) hexacyanide analogues.[a]

	3	**I**	**4**	**II**	**5**	**III**	**6**	**IV**	**7**	**V**
Nb(Fe)–C	2.279(7)	1.94(4)	2.286(14)	1.933(5)	2.288(7)	1.943(6)	2.286(6)	1.97(8)	2.282(8)	1.941(2)
C≡N	1.140(6)	1.15(1)	1.144(2)	1.164(6)	1.14(2)	1.1531	1.147(2)	1.13(3)	1.142(3)	1.149(2)
Nb(Fe)–C≡N	175.7(13)	177.6(8)	176.7(5)	178.8(4)	177(2)	177(2)	176.7(18)	177.7(17)	177(2)	177.7(2)
Mn–N_{CN}	2.280(5)	2.198(9)	2.295(3)	2.332(3)	2.54(1)[a]	2.50(1)[a]	2.26(2)	2.193	2.150(3), 2.287(3)	2.334(2)
Mn–N_{CN}≡C	150.3(4)	162.4(8)	157.2(3)	146.6(3)	172.9(8)[a]	149(2)[a]	148.6(3), 165.8(3)	156(1)	150.3(3)–161.5(3)	150.7(1)
ν_{CN}	2134	2104	2131	2128, 2110	2128	2118	2143	2118	2140, 2128	2108, 2115

	8	**9**	**VI**	**10**	**VII**	**11**	**12**	**13**	**VIII**
Nb(Fe)–C	2.28(1)	2.27(1)	1.958(6)	2.279(7)	1.941(5)	2.260(8)	2.28(1)	2.286(8)	1.94(1)
C≡N	1.144(5)	1.13(1)	1.147(2)	1.133(4)	1.162(8)	1.15(1)	1.149(8)	1.140(5)	1.150(3)
Nb(Fe)–C≡N	175.6(14)	175(3)	177.1(4)	175.1(3)	177(1)	172.6(9)	175.3(25)	169.7(6)–177.4(7)	176.9(8)
Mn–N_{CN}	2.36(3)	2.345(3)	2.316(4)	2.233(3), 2.365(3)	2.266(3), 2.337(3)	2.051(8)[b]	2.31(3)	2.803(6)–2.864(8)[c]	2.835(7)[c]
Mn–N_{CN}≡C	152.9(2), 156.5(3)	148.59(8)	152.5(3)	144.2(3), 155.0(3)	146.2(2), 167.8(3)	172.5(9)[b]	145.3(7)–158.3(7)	130.5–172.6[c]	157.7(3), 165.8(2)[c]
N_{CN}–Mn–N_{CN}	178.92(3)	174.2(2)	172.0(2)	173.3(1)	169.4(1)	100.16(2)[b]	168.3(2)–176.1(3)	142.3(2)[c]	N/A
ν_{CN}	2127	2127	2124	2131	2106, 2131	2167	2132	2122, 2131	2100, 2104

[a] Compounds **I**–**VIII** are based on $[Fe(CN)_6]^{3-}$ as building units and were used to compare compounds based on mononuclear hexacyanides to their cluster analogues.

tamers linked by way of cluster units, whereas the 3D framework consists of heteroheptamers connected by cluster units.

Further studies are necessary to advance our understanding of this system and to allow the preparation of materials with tailored structural features and properties. The stability of the supramolecular assemblies in solution is of interest in order to study their potential use as larger building units for the preparation of materials with more complex structures. More important are the opportunities these assemblies present in terms of their functionalization by use of different metal complexes and different ligands. The rate-limiting step of advances in this field, as in many other areas of synthesis, is the preparation of single-crystals suitable for structural characterization. The use of powder XRD to solve and refine the crystal structure is in most cases of little use as PXRD patterns are generally dominated by four or five peaks. For instance, in the case of the Prussian-blue analogues, the structure initially determined from PXRD was significantly different from that determined later from single-crystal XRD. Magnetic studies of supramolecular assemblies and coordination polymers show that no magnetic coupling was observed between the cluster units and the metal ions or between the metal ions through cluster units, possibly a result of the diamagnetism and large size of the metal cluster. Oxidation–reduction of the cluster and its use as a building unit may lead to modification of the physical properties of the materials obtained. Recently, the 15-electron cluster $[Nb_6Cl_{12}(CN)_6]^{3-}$ was isolated, and it is being investigated as a building unit in complexes to determine its effect on magnetic properties.

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[1] a) J. Rebek, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 245–255; b) F. Vögtle, *Supramolecular Chemistry*, John Wiley & Sons, New York, **1991**; c) A. Harada, K. Li, M. Kamachi, *Nature* **1994**, *370*, 126–128.

[2] a) J. M. Lehn, *Science* **1993**, *260*, 1762–1763; b) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; c) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; d) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401; e) A. Harada, J. Li, M. Kamachi, *Nature* **1992**, *356*, 325–327.

[3] a) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678; b) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**; c) M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120–126; d) G. R. Desiraju, *Nature* **2001**, *412*, 397–400.

[4] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, *Coord. Chem. Rev.* **1999**, *190–192*, 1023–1047 and references therein.

[5] R. Chevrel, M. Sergent, J. Prigent, *J. Solid State Chem.* **1971**, *3*, 515–519.

[6] a) S. C. Lee, R. H. Holm, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 840–856; b) T. Saito in *Early Transition Metal Clusters with π-Donor Ligands* (Ed.: M. H. Chisholm), VCH, **1995**; c) T. Saito, *Adv. Inorg. Chem.* **1997**, *44*, 45–91; d) N. Prokopuk, D. F. Shriver, *Adv. Inorg. Chem.* **1998**, *46*, 1–49; e) T. Saito, *J. Chem. Soc., Dalton Trans.* **1999**, 97–106; f) J. C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev.* **2001**, *101*, 2037–2066; g)

E. J. Welch, J. R. Long, *Prog. Inorg. Chem.* **2005**, *54*, 1–45 and references therein.

[7] a) T. J. Paskach, G. L. Schrader, R. E. McCarley, *J. Catal.* **2002**, *211*, 285–295; b) S. Kamiguchi, M. Watanabe, K. Kondo, M. Kodomari, T. Chihara, *J. Mol. Catal. A* **2003**, *203*, 153–163; c) S. Kamiguchi, M. Noda, Y. Miyagishi, S. Nishida, M. Kodomari, T. Chihara, *J. Mol. Catal. A* **2003**, *195*, 159–171; d) S. Kamiguchi, S. Iketani, M. Kodomari, T. Chihara, *J. Cluster Sci.* **2004**, *15*, 19–31; e) S. Kamiguchi, S. Nishida, M. Kodomari, T. Chihara, *J. Cluster Sci.* **2005**, *16*, 77–91; f) S. Kamiguchi, A. Nakamura, A. Suzuki, M. Kodomari, M. Nomura, Y. Iwasawa, T. Chihara, *J. Catal.* **2005**, *230*, 204–213.

[8] a) S. Jin, F. J. DiSalvo, *Chem. Commun.* **2001**, 1586; b) S. Jin, F. J. DiSalvo, *Chem. Mater.* **2002**, *14*, 3448; c) N. G. Naumov, A. V. Virovets, V. E. Fedorov, *J. Struct. Chem.* **2000**, *41*, 499–520; d) V. E. Fedorov, N. G. Naumov, Y. V. Mironov, A. V. Virovets, S. B. Artemkina, K. A. Brylev, S. S. Yarovoi, O. A. Efremova, U. H. Peak, *J. Struct. Chem.* **2002**, *43*, 669–684; e) Y. V. Mironov, V. E. Fedorov, I. Ijjaali, J. A. Ibers, *Inorg. Chem.* **2001**, *40*, 6320–6323; f) K. A. Brylev, Y. V. Mironov, N. G. Naumov, V. E. Fedorov, J. A. Ibers, *Inorg. Chem.* **2004**, *43*, 4833–4838; g) M. P. Shores, L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **1999**, *121*, 775–779; h) L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772; i) M. V. Bennett, M. P. Shores, L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 6664–6668; j) Y. Kim, S. K. Choi, S. M. Park, W. Nam, S. J. Kim, *Inorg. Chem. Commun.* **2002**, *5*, 612–615, k) L. G. Beauvais, L. G. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783.

[9] B. B. Yan, H. J. Zhou, A. Lachgar, *Inorg. Chem.* **2003**, *42*, 8818–8822.

[10] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–907.

[11] B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043 and references therein.

[12] R. Cortés, K. Urtiaga, L. Lezama, J. L. Pizarro, A. Goñi, M. I. Arriortua, T. Rojo, *Inorg. Chem.* **1994**, *33*, 4009–4015.

[13] M. Monfort, I. Resino, M. S. E. Fallah, J. Ribas, X. Solans, M. Font-Bardia, H. Stoeckli-Evans, *Chem. Eur. J.* **2001**, *7*, 280–287.

[14] H. D. Selby, B. K. Roland, Z. P. Zheng, *Acc. Chem. Res.* **2003**, *36*, 933–944 and references therein.

[15] E. N. Jacoben, *Acc. Chem. Res.* **2000**, *33*, 421–431.

[16] A. Vogler, H. Nikol, *Pure Appl. Chem.* **1992**, *64*, 1311–1317.

[17] a) Y. Kim, S. M. Park, W. Nam, S. J. Kim, *Chem. Commun.* **2001**, 1470–1471; b) Y. Kim, S. M. Park, W. Nam, S. J. Kim, *Inorg. Chem. Commun.* **2002**, *5*, 592–595.

[18] E. V. Anokhina, Ph. D. Thesis, Wake Forest University, **2001** and references therein.

[19] H. J. Zhou, C. S. Day, A. Lachgar, *Chem. Mater.* **2004**, *16*, 4870–4877.

[20] F. W. Koknat, R. E. McCarley, *Inorg. Chem.* **1974**, *13*, 295–300.

[21] N. G. Naumov, S. Cordier, C. Perrin, *Solid State Sci.* **2003**, *5*, 1359–1367.

[22] V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, I. S. Neretin, Y. L. Slovokhotov, *Chem. Commun.* **1998**, 2579–2580.

[23] L. H. Jones, *Inorg. Chem.* **1963**, *2*, 777–780.

[24] V. Marvaud, C. Decroix, A. Sciuller, F. Tuyèras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* **2003**, *9*, 1692–1705.

[25] V. Marvaud, C. Decroix, A. Sciuller, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* **2003**, *9*, 1677–1691.

[26] H. J. Zhou, A. Lachgar, *Cryst. Growth Des.* **2006**, *6*, 2384–2391.

[27] H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi, C. Florián, *Inorg. Chem.* **1998**, *37*, 255–263.

[28] M. I. Fernández, M. Fondo, A. M. García-Deibe, B. Fernández, M. J. Rodríguez, M. R. Bermejo, *Transition Met. Chem.* **2002**, *27*, 416–422.

[29] H. Miyasaka, N. Matsumoto, H. Ōkawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981–994.

[30] H. J. Choi, J. J. Sokol, J. R. Long, *Inorg. Chem.* **2004**, *43*, 1606–1608.

[31] H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani, *Inorg. Chem.* **1997**, *36*, 670–676.

[32] Z. H. Yan, C. S. Day, A. Lachgar, *Inorg. Chem.* **2005**, *44*, 4499–4505.

[33] G. Smith, E. J. O'Reilly, C. H. L. Kennard, A. H. White, *J. Chem. Soc., Dalton Trans.* **1985**, 243–251.

[34] X. M. Chen, T. C. W. Mak, *Polyhedron* **1994**, *13*, 1087–1090.

[35] X. M. Chen, T. C. W. Mak, *Inorg. Chem.* **1994**, *33*, 2444–2447.

[36] A. Datta, N. K. Karan, S. Mitra, E. R. Tiekink, *Polyhedron* **2002**, *21*, 2237–2241.

[37] A. Datta, G. M. Hossain, N. K. Karan, K. M. Malik, S. Mitra, *Inorg. Chem. Commun.* **2003**, *6*, 266–269.

[38] H. J. Zhou, B. Cloix, C. S. Day, A. Lachgar, *Chem. Mater.* **2006**, submitted.

[39] R. J. Parker, L. Spiccia, K. J. Berry, G. D. Fallon, B. Moubarakia, K. S. Murraya, *Chem. Commun.* **2001**, 333–334.

[40] R. J. Parker, L. Spiccia, S. R. Batten, J. D. Cashion, G. D. Fallon, *Inorg. Chem.* **2001**, *40*, 4696–4704.

[41] X. P. Shena, B. L. Lia, J. Z. Zou, H. M. Hu, Z. Xu, *J. Mol. Struct.* **2003**, *657*, 325–331.

[42] J. Černák, M. Orendáč, I. Potočňák, J. Chomič, A. Orendáčová, J. Skoršepa, A. Feher, *Coord. Chem. Rev.* **2003**, *224*, 51–66.

[43] N. Re, E. Gallo, C. Floriani, H. Miyasaka, M. Matsumoto, *Inorg. Chem.* **1996**, *35*, 6004–6008.

[44] M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. I. Sugiura, M. Yamashita, C. Coulon, R. Clerac, *J. Am. Chem. Soc.* **2005**, *127*, 3090–3099.

[45] H. Li, Z. J. Zhong, C. Duan, X. You, T. C. W. Mak, B. Wu, *J. Coord. Chem.* **1997**, *41*, 183–189.

[46] A. Garcia-Deibe, A. Sousa, M. R. Bermejo, P. P. Macrory, C. A. McAuliffe, R. G. Pritchard, M. Hellwell, *J. Chem. Soc., Chem. Commun.* **1991**, 728–729.

[47] H. Miyasaka, H. Ieda, N. Matsumoto, K. I. Sugiura, M. Yamashita, *Inorg. Chem.* **2003**, *42*, 3509–3515.

[48] B. B. Yan, C. S. Day, A. Lachgar, *Chem. Commun.* **2004**, 2390–2391.

[49] H. Siebert, B. Nuber, W. Jentsch, *Z. Anorg. Allg. Chem.* **1981**, *474*, 96–104.

[50] D. E. Partin, M. O'Keeffe, *J. Solid State Chem.* **1991**, *95*, 176–183.

[51] G. K. Chadha, *Z. Kristallogr.* **1974**, *139*, 147–152.

[52] N. K. Karan, S. Mitra, G. Rosair, D. J. Jenkins, K. M. Abdul-Malik, *Inorg. Chem. Commun.* **2001**, *4*, 712–715.

[53] a) H. J. Lee, K. S. Hong, S. J. Kim, I. T. Kim, *Mater. Res. Bull.* **1997**, *32*, 847; b) R. C. Pullar, J. D. Breeze, N. M. Alford, *J. Am. Ceram. Soc.* **2005**, *88*, 2466.

[54] A. Ito, M. Suenaga, K. Ono, *J. Chem. Phys.* **1968**, *48*, 3597.

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