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Octahedral Niobium Chloride Clusters as Building Blocks of Templated Prussian Blue Framework Analogues

Bangbo Yan, Huajun Zhou, and Abdessadek Lachgar*

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109

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The preparation, structure, and magnetic properties of the first three-dimensional framework containing octahedral niobium cyanochloride clusters as building units are reported. Reactions of aqueous solutions of $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]$ (**2**) with aqueous solutions of $MnCl_2$ result in the precipitation of the compound $(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ (**3**). The structure of **3** was determined from single-crystal X-ray diffraction study (crystal data: cubic, $Fm\bar{3}m$ (No. 225), $a = 15.513(4)$ Å, $V = 3733.2(12)$ Å^3, $Z = 4$). Its 3D framework is based on edge-bridged $[Nb_6Cl_{12}]^{2+}$ clusters and Mn^{2+} ions bridged by cyanide ligands to form a cfc lattice $[MnNb_6Cl_{12}(CN)_6]^{2-}$ in which all tetrahedral sites are occupied by the cations $(Me_4N)^+$ which act as charge compensating template. The structure of **3** can be considered as an expansion of the Prussian blue framework in which $[Fe(CN)_6]^{4-}$ is replaced by the cluster $[Nb_6Cl_{12}(CN)_6]^{4-}$. Magnetic susceptibility measurements indicate that Mn^{2+} is present in a high spin d^5 configuration. No magnetic ordering is observed.

Introduction

Open-framework materials enjoy widespread contemporary interest, due to their potential applications as ion exchangers, molecular sieves, and shape-selective catalysts, as well as in gas separation.[1] The scope of such materials is no longer limited to oxide systems, but it includes non-oxide materials with microporous frameworks. Using self-assembly and crystal engineering methodologies, new classes of inorganic open-framework materials in which metal centers are linked through chalcogenides, polychalcogenides, pnictides, cyanides, and thiopnictides, as well as multitopic organic ligands, have been developed.[2] Unfortunately, predicting and controlling the structures of such materials remains a significant challenge. Recent advances in supramolecular chemistry have demonstrated that it is feasible to pursue a molecular building block approach, referred to as a “bottom up” design, to the assembly of solids with specific skeletal topologies.[3] The building blocks in engineering open-framework materials have recently been extended from mononuclear metal centers to molecular cluster subunits on the basis of the rationale that the large size, versatile topologies, and electronic flexibility of multinuclear species may lead to novel structural and physical−chemical properties.[4,5] A number of cluster-based materials have been assembled by standard solution chemistry techniques[4] or under hydrothermal conditions.[5] For example, the mixed silver−copper germanium sulfide, $(Me_4N)[(Ag_2,Cu_2)Ge_4S_{10}]$, has an open framework built up from the connection of $[Ge_4S_{10}]^{4-}$ clusters through Ag or Cu atoms,[5a] and $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$ represents a framework material composed of well-defined vanadium oxide clusters.[4d]

Cyanometalate anions have been extensively used as building blocks of coordination polymers due to their ability

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* To whom correspondence should be addressed. E-mail: Lachgar@wfu.edu.

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to form strong bonds with transition metal cations, leading to the formation of solids with diverse structures and unique properties.[6] Examples include Prussian blue,[7] and Hofmann clathrates and their analogues.[8] Recently, face-capped octahedral metal cluster chalcocyanides $[M_6X_8(CN)_6]^{n-}$ (M = Mo, W, Re; X = S, Se, Te) have been prepared and used to build solids with extended structures.[9−14] Reactions of $[M_6X_8(CN)_6]^{n-}$ (M = W, Re) with transition metal cations or metal complexes led to the preparation of solids with extended one-,[12c,e] two-,[12c,14b] or three-dimensional networks.[10b,11,12g−i,14c] Two fascinating examples should be mentioned: (i) the framework of $M_4[Re_6X_8(CN)_6]_3\cdot xH_2O$ (M = Ga^{3+}, Fe^{3+}; X = Se, Te)[11c,d] which is an expansion of the Prussian blue structure; and (ii) the compound $A_2M_3[Re_6Se_8(CN)_6]_2\cdot nH_2O$ (A = Na^+, Cs^+, $[H_3O]^+$; M = Mn^{2+}, Co^{2+}, Zn^{2+})[11e,12h] whose structure is an expansion of the porous compound $Na_2Zn_3[Fe(CN)_6]_2\cdot 9H_2O$.[15] In both cases the cluster $[Re_6X_8(CN)_6]^{4-}$ replaces the anion $[Fe(CN)_6]^{4-}$ as the basic building unit.

Compounds containing edge-bridged octahedral metal clusters $[M_6L_{12}]^{n+}$ have been known for almost a century, and their excision from polymeric materials as well as their ligand substitution reactions have been investigated.[16,17] However, their use as building blocks of solids with extended frameworks remains largely unexplored. In the course of our investigation of the use of edge-bridged octahedral metal clusters containing a combination of ligands as building units of extended solids, we have prepared a new hybrid inorganic−organic material that has the formula $(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ (**3**) from reaction of aqueous solutions of $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]$ (**2**) and $MnCl_2$. Compound **3** has a three-dimensional framework formed of $[Nb_6Cl_{12}]^{2+}$ and Mn^{2+} bound to each other via cyanide ligands to produce an open-framework that is an expansion of that of Prussian blue, organically templated by $[Me_4N]^+$ cations.

Experimental Section

Synthesis. The compounds $Li_2Nb_6Cl_{16}$, and $[Mn(salen)]ClO_4\cdot 2H_2O$ were prepared as described previously.[18,19] Water was distilled and deionized with a Milli-Q filtering system. All other reagents were used as purchased. Product identity and purity were verified by elemental analysis and by comparing the observed powder X-ray diffraction pattern with that simulated from the single-crystal X-ray analysis.

$(Me_4N)_3[Nb_6Cl_{18}]\cdot 2MeCN$ (1). Solid Me_4NCl (0.210 g, 1.918 mmol) was added to a solution of $Li_2Nb_6Cl_{16}$ (0.383 g, 0.336 mmol) in 20 mL of EtOH. The solution was stirred for 2 h to form a green precipitate, which was collected by filtration, washed with EtOH, and dried in a vacuum. The cluster compound was extracted with hot MeCN using water bath to form a dark brown solution. The product was recrystallized using diethyl ether, and the dark brown precipitate was collected by filtration and dried in a vacuum to yield 0.272 g (ca. 54% yield). Dark-brown platelike crystals of **1** suitable for single-crystal X-ray diffraction were obtained by vapor diffusion of Et_2O in a concentrated solution of **1** in CH_3CN.

$(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]\cdot 6MeOH$ (2). Aqueous KCN (30 mL) (0.895 g, 13.74 mmol) was added to 40 mL of $(Me_4N)_3[Nb_6Cl_{18}]\cdot 2MeCN$ (0.975 g, 0.650 mmol) in MeCN. Upon addition of the aqueous KCN solution, a small amount of gas evolved. The color of the solution changed slowly from brown to green, and the reaction was complete after stirring for 1 h. After the solvent was removed under vacuum, the green solid was extracted in hot MeCN, recrystallized using diethyl ether, collected by filtration, and dried under vacuum to yield 0.769 g (ca. 76%) of the product. Dark-green platelike crystals of **2** suitable for single-crystal X-ray diffraction were obtained by vapor diffusion of Et_2O in a concentrated methanolic solution of **2**. IR(KBr): $\nu_{CN} = 2123\ cm^{-1}$ (broad).

$(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ (3). Compound **3** was obtained quantitatively by mixing an aqueous solution of $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]$ with an aqueous solution of $MnCl_2\cdot 4H_2O$. In a typical synthesis, 15 mL of an aqueous solution of $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]$ (0.140 g, 0.10 mmol) was added to an aqueous

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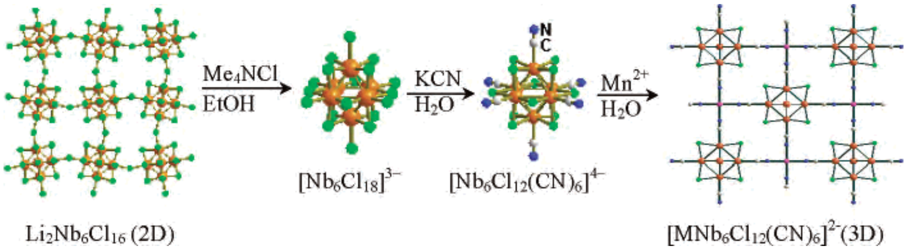
Scheme 1



solution (15 mL) of $MnCl_2{\cdot}4H_2O$ (0.020 g, 0.10 mmol). Green precipitate appeared immediately. After stirring for 3 h, the green solid was separated by filtration, washed with water (3 × 30 mL), and dried in air at 50 °C to yield 0.094 g (ca. 70%) of **3**. Black crystals of **3** suitable for single-crystal X-ray diffraction analysis were grown by layering an aqueous solution of $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]$ with a methanolic solution of $[Mn(salen)]ClO_4{\cdot}2H_2O$ in a narrow-diameter tube (i.d.: 7 mm); cubelike crystals formed at the interface between the two solutions after 2 days. Elemental analysis (%): calcd for $C_{14}H_{24}Cl_{12}MnN_8Nb_6$ (found): C 11.53 (11.04), H 1.80 (1.92), N 8.35 (8.62). IR(KBr): $\nu_{CN} = 2157$ cm^{-1} (sharp).

X-ray Structure Determination. Intensity data were collected at −55 °C on a Bruker P4 diffractometer using an ω scan on crystals of **1** and **2** selected in Paratone oil, and attached to quartz fibers. Single crystals of **3** were selected in air and attached to quartz fibers using epoxy, and intensity data were collected at room temperature using $\theta/2\theta$ scan mode. Lattice parameters were initially determined from least-squares refinement of 25 centered reflections. Intensity data were corrected for background, and Lorentz and polarization effects, and converted to structure factor amplitudes and their esd's using the Shelxtl 5.1 software package.[20] An empirical absorption correction based on 20 ψ-scans was applied. All structures were solved by direct methods, and positional parameters and temperature factors for all atoms were refined with successive full-matrix least-squares cycles. The positions of the hydrogen atoms of the Me_4N^+ were located from a difference Fourier map and were included in the final cycles of the refinement. All atoms (except hydrogens) were refined anisotropically. The most pertinent crystallographic data for all three compounds are listed in Table 1. Positional parameters and equivalent isotropic thermal parameters and additional crystallographic results are given in the Supporting Information.

Magnetic Susceptibility Measurements. Magnetic susceptibility of **3** was measured using a Quantum Design MPMS XL SQUID magnetometer. Loose crystals of **3** were placed into a gelatin capsule, which was placed inside a plastic straw. Samples were measured under both zero field cooled (zfc) and field cooled (fc) conditions. In both cases, the magnetization was measured in the temperature range 2−300 K at an applied field of 5 kG. In addition, field sweeps at applied fields between −40 and 40 kG were measured at 5 K. The very small diamagnetic contribution of the gelatin capsule containing the sample had a negligible contribution to the overall magnetization, which was dominated by the sample signal.

Other Physical Measurements. X-ray powder diffraction data were collected on a Norelco automated X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Thermogravimetric analyses were performed on a 10.34 mg sample of **3** under a flow of nitrogen (40 mL/min) at a ramp rate of 5 °C/min, using a Perkin-Elmer Pyris 1 TGA system. Infrared spectra were recorded on a Mattson Infinity System FTIR spectrometer.

Table 1. Crystal Data and Structure Refinements for $(Me_4N)_3[Nb_6Cl_{18}]{\cdot}2MeCN$ (**1**), $(Me_4N)_2K_2[Nb_6Cl_{12}(CN)_6]{\cdot}6MeOH$ (**2**), and $(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ (**3**)

	1	**2**	**3**
formula	$C_{16}H_{42}N_5Nb_6Cl_{18}$	$C_{20}H_{48}N_8K_2Nb_6Cl_{12}O_6$	$C_{14}H_{24}N_8MnNb_6Cl_{12}$
fw (g/mol)	1500.11	1557.82	1342.21
T, K	218	218	293
cryst syst	monoclinic	monoclinic	cubic
space group	$C2/c$	$P2_1/n$	$Fm\bar{3}m$ (No. 225)
a, Å	22.731(3)	11.640(1)	15.513(4)
b, Å	9.1692(11)	14.385(2)	
c, Å	23.901(3)	16.494(3)	
β, deg	109.906(3)	105.26(1)	
V, Å^3	4684.0(9)	2664.5(8)	3733.2(12)
Z	4	2	4
ρ_{calcd}, g cm^{-3}	2.127	1.942	2.388
μ, mm^{-1}	2.467	2.044	2.99
λ, Å	0.71073	0.71073	0.71073
R1[a]	0.053	0.057	0.046
wR2[b,c]	0.077	0.132	0.073
GOF	0.979	1.019	1.12

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]]^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (0.0101P)^2$ ($P = (\max(F_o^2, 0) + 2F_c^2)/3$).

Results and Discussion

Synthesis. Compound **3** was prepared at room temperature in a stepwise fashion (Scheme 1). The cluster was excised from $Li_2Nb_6Cl_{16}$, a layered cluster compound prepared at high temperature. This step was followed by substitution of the outer chloride ligands with cyanide groups. The final step involved bringing together the building blocks (cluster and metal cation) to form the anionic 3D framework in a self-assembly process.

$$\text{step 1: } 10LiCl + 14NbCl_5 + 16Nb \xrightarrow{700\ ^\circ C} 5Li_2Nb_6Cl_{16}$$

$$\text{step 2: } Li_2Nb_6Cl_{16}/EtOH + Me_4NCl \rightarrow (Me_4N)_3[Nb_6Cl_{18}]$$

$$\text{step 3: } [Nb_6Cl_{18}]^{3-} + 7CN^- \rightarrow [Nb_6Cl_{12}(CN)_6]^{4-} + 1/2(CN)_2 + 6Cl^-$$

$$\text{step 4: } [Nb_6Cl_{12}(CN)_6]^{4-} + Mn^{2+} \rightarrow [MnNb_6Cl_{12}(CN)_6]^{2-}$$

Single crystals of **3** could be obtained only when a methanolic solution of the complex $[Mn(salen)]ClO_4$ was used. The slow reduction of Mn(III) in $[Mn(salen)]ClO_4$ in methanol and subsequent release of Mn(II) during the self-assembly process presumably lead to the growth of crystals suitable for single-crystal X-ray diffraction. Similar findings were reported in the case of one-dimensional bimetallic assemblies, $[Mn(en)_2]_3[M(CN)_6]_2{\cdot}2H_2O$,[21] where the slow

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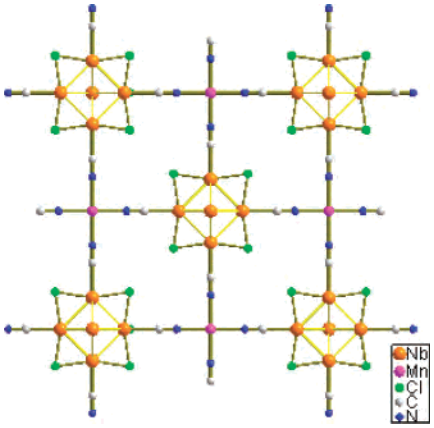

Figure 1. A projection of a unit cell for the anionic framework of $(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ showing the cfc nature of the framework: Nb, gray; Mn, red; Cl, green; N, blue; C, black. The $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster sites are fully occupied; selected bond lengths (Å): Nb−Nb = 2.939(3), Nb−Cl = 2.468(3), Nb−C = 2.272(2), Mn−N = 2.242(2), C−N = 1.155(3).

dissociation of $[Mn(en)_3]^{2+}$ into $[Mn(en)_2]^{2+}$ in aqueous solution leads to the growth of large single crystals. Notably, reactions of $[Mn(salen)]ClO_4$ with $Na_4[Re_6Te_8(CN)_6]$ containing the face capped octahedral cluster $[Re_6Te_8(CN)_6]^{4-}$ lead to the formation of either $[Mn(salen)]_4[Re_6Te_8(CN)_6]$[14b] or $Na[Mn(salen)]_3[Re_6Te_8(CN)_6]$[14c] in which the rhenium cyanotelluride clusters are bridged through the $[Mn(salen)]^+$ to form 2D or 3D frameworks, respectively.

Crystal Structure. The structure of **1** contains discrete octahedral cluster anion, $[(Nb_6Cl_{12}{}^{i})Cl_6{}^{a}]^{3-}$ (where i and a denote “inner” and “outer” ligands, respectively), which consists of a Nb_6 octahedron with 12 edge capping chloride ligands and six terminal chloride ligands. The average Nb−Nb bond length (2.981 Å) and the average Nb−Cl distances for inner (2.442 Å) and outer (2.529 Å) ligands are in good agreement with other compounds containing $[Nb_6Cl_{18}]^{3-}$.[22a] Reaction of **1** with aqueous KCN produced compound **2**, in which all six outer chlorines were substituted by CN ligands and the cluster was reduced by one electron to form $[Nb_6Cl_{12}(CN)_6]^{4-}$. The Nb−C (2.255−2.291 Å) and C−N (1.125−1.158 Å) bond lengths are in normal range.[17] The mean Nb−Nb distance (2.932 Å) in **2** is shorter than that in **1** while the mean Nb−Cl^i distance (2.468 Å) is longer than that for **1**. This can be attributed to the difference in the number of valence electrons per cluster between these two compounds (VEC = 16 for **2** and 15 for **1**).[22a,23]

X-ray analysis of a crystal of **3** revealed the compound to have a three-dimensional cubic face-centered framework that represents a direct expansion of the Prussian blue structure (Figure 1). The framework is built of $[Nb_6Cl_{12}]^{2+}$ units and Mn^{2+} connected by cyanide ligands to form Nb−C≡N−Mn−N≡C−Nb linkages leading to an extended lattice structure. No linkage isomerism of the type Nb−C≡N−Mn/Nb−N≡C−Mn was observed consistent with the IR spectra which show a single sharp band due to the C≡N stretching vibration. Each cyanochloride cluster is surrounded by six Mn^{2+} ions, and each Mn^{2+} ion is linked to six clusters.

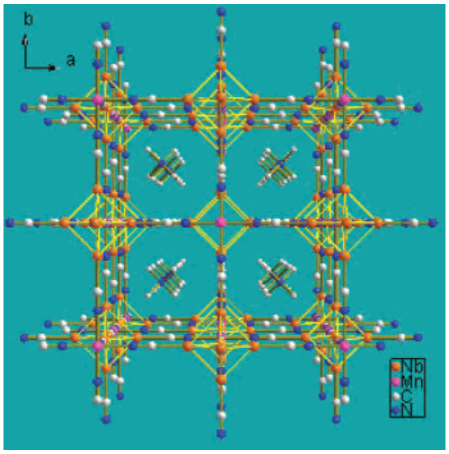

Figure 2. A perspective view of the structure of $(Me_4N)_2[MnNb_6Cl_{12}(CN)_6]$ showing the 3D nature of the anionic framework and the location of the $[Me_4N]^+$ counterions, which occupy all tetrahedral sites of the cfc lattice. Chlorine and hydrogen atoms have been omitted for clarity.

The Nb_6 unit of the $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster in **3** forms an ideal octahedron, in agreement with the essential octahedral metal array of other $[Nb_6Cl_{12}]^{n+}$ systems.[22] The Nb−Nb bond length, 2.939(3) Å, agrees with that reported for a $[Nb_6Cl_{12}]^{2+}$ core.[23] Each vertex is bound by a cyanide ligand with C−N distance 1.155(3) Å, which is comparable to those found in the starting material **2** (1.125−1.158 Å). The Nb−C distances of 2.272(2) Å for **3** are close to those found in most niobium cyanide compounds,[24] but shorter than those found in niobium cyanooxychlorides.[17] With an equivalent arrangement of the cyanide ligands, the $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster represents an enlarged analogue of $[Fe(CN)_6]^{4-}$, wherein the mean trans-N···N distance has increased from 6.17(1) to 11.030(3) Å.[25]

The Mn^{2+} sites exhibit an ideal octahedral geometry, which receives contributions from the nitrogen atoms of six cyanide ligands, with Mn−N distance 2.242(2) Å. According to the charge balance, the +2 oxidation state of Mn atoms is confirmed by the bond valence sum calculations[26] which gives 2.21 as the calculated value for the oxidation state of Mn.

In contrast to Prussian blue, in which the $[Fe(CN)_6]^{4-}$ sites are only 75% occupied, the structure of **3** consists of a fully occupied cubic face centered lattice of alternating Mn^{2+} ions and $[Nb_6Cl_{12}(CN)_6]^{4-}$ clusters, with $[Me_4N]^+$ cations occupying all interstitial tetrahedral cavities as shown in Figure 2. The $[Me_4N]^+$ ions fit well into the tetrahedral cages, with hydrogen atoms pointing toward inner chloride ligands.

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However, no hydrogen bonds were found between the framework and the $[Me_4N]^+$ ions. The presence of $[Me_4N]^+$ in the framework is interesting since the inclusion of organic species in frameworks of Prussian blue analogues is rare. Usually, the cavities are filled with water or inorganic moieties such as Li, Na, K, and NH_4^+. The only reported Prussian blue related structure that accommodates organic molecules in its cavities is $\{[Mn(Pr^iOH)_2(H_2O)]_2[Re_6S_8(CN)_6]\}\cdot 2Pr^iOH$.[12i] However, the latter structure is not a direct expansion of Prussian blue, and the Pr^iOH molecules also serve as bridging ligands between Mn atoms. The structure of **3** belongs to the *Elpasolite*[27] structure type which has the formula K_2NaAlF_6 and is built of a cfc lattice of $[AlF_6]^{3-}$ octahedra with Na^+ occupying all octahedral sites and K^+ occupying all tetrahedral sites ($a = 8.118$ Å). The open-framework nature of **3** was investigated by a PLATON analysis of the volume accessible to solvent, which was found to be 1376.5 Å^3 (ca. 36.9% of the unit cell volume).[28] Thermogravimetric analysis of **3** shows a weight loss of ca. 10.4% in the temperature range 220−330 °C, corresponding to the release of $[Me_4N]^+$ ions (calcd 11.0%). A powder X-ray study showed that the framework of **3** remains virtually the same after the powder sample was heated at 300 °C for 3 h in a sealed Pyrex tube under vacuum. The powder diffraction pattern exhibits line shifts that indicate a contraction of the cubic unit cell after removal of the templating ammonium ion. The powder pattern was indexed to give a cubic unit cell with $a = 15.320(4)$ Å. A further weight loss (ca. 11.7%) is observed in the temperature range 330−370 °C and is consistent with loss of CN group (calcd 11.6%). The powder X-ray diffraction of the product obtained after TGA (600 °C) indicates collapse of the framework and formation of a phase that has not been identified yet.

IR Spectra. Several factors are known to affect $\nu_{C\equiv N}$ in metal cyanides.[29] An increase in $\nu_{C\equiv N}$ can be assigned to withdrawal of π^* electron density while a decrease in $\nu_{C\equiv N}$ is generally explained by larger metal to CN π back-donation.[30] IR spectra for **2** show $\nu_{C\equiv N} = 2123$ cm^{-1}, compared to $\nu_{C\equiv N}$ values in the range 2040−2080 cm^{-1} in ionic cyanide salts. On the other hand, **3** shows a band at 2157 cm^{-1}, an increase of 34 cm^{-1} compared to that for **2**. This could be attributed to the coordination of a metal to the nitrogen end of a coordinated cyanide.[31] The increase in the energy of the C≡N stretch is consistent with the electron-withdrawing ability of the cluster moiety which decreases the π^*(CN) electron density, and the bridging mode of the CN ligand. The observation of only a single, sharp band for CN stretch in **3** is consistent with the fact that the compound contains only a single, well-defined cyanide environment.

Magnetic Properties. The magnetic susceptibility data show that the manganese ion is present as Mn^{2+} in high-spin d^5 electronic configuration. The magnetic moment 6.35 μ_B is slightly higher than that calculated on the basis of the spin-only formula (5.92 μ_B). Consistent with the predictions for octahedral Mn^{2+}, compound **3** showed paramagnetic Curie−Weiss behavior with $S = {}^5/_2$. Also in agreement with the predictions for the octahedral Mn^{2+} compound, the g value in **3** was calculated to be 2.09. The paramagnetic manganese centers in **3** are well-separated by the intervening diamagnetic $[Nb_6Cl_{12}(CN)_6]^{4-}$ clusters. No evidence for magnetic ordering was observed in temperatures down to 2 K.

Conclusion

The novel cluster-based hybrid organic−inorganic material described herein demonstrates potential for use of reduced metal clusters as building units for a variety of materials with extended structures. The stepwise preparation of the 3D framework of **3** using the 6−12 type clusters offers possibilities for the design and preparation of novel materials. Investigation of the impact of (i) size and type of the organic templates, (ii) the metal complexes, and (iii) the use of magnetically active cluster units (i.e., $[Nb_6Cl_{12}(CN)_6]^{3-}$) on the structural and physicochemical properties of the products are underway. We have recently applied the same approach to niobium oxychloride cluster compounds, and preliminary crystal structure investigations indicate that different arrangement of inner oxygen and chlorine ligands around the cluster core leads to different topologies. The finding that the use of Mn(III)(salen)ClO_4 was critical in obtaining good quality crystals and the tentative explanation that its in-situ reduction leads to a steady and slow release of Mn^{2+} need to be investigated. In particular, we are investigating the use of Cr(III)(salen)ClO_4 complex as a substitute to Mn(III)(salen)ClO_4 because of its kinetic stability and its d^3 electron configuration.

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Supporting Information Available: One X-ray crystallographic file in CIF format, a plot of the powder X-ray diffraction pattern, one figure showing an IR spectrum, one figure showing the TGA under nitrogen, and a plot of the magnetic susceptibility data. This material is available free of charge via the Internet at http://pubs.acs.org.

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