

Research Article

Self-Assembly of Cluster-Based Nanoscopic Supramolecules into One-Dimensional Coordination Polymers

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Octahedral metal clusters $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$, $(\text{Mn}(\text{Salen}))^+$ (or $(\text{Mn}(7\text{-MeSalen}))^+$) ($\text{Salen} = N, N'$ -ethylene-bis-(salicylidene)iminate) and ditopic organic linkers (4,4'-*bpe* (*trans*-1, 2-bis(4-pyridyl)-ethylene) or 4,4'-*dpyo* (4,4'-dipyridyl N, N' -dioxide)) self-assemble to form three cluster-based 1D coordination polymers: $[\text{Mn}(\text{Salen})(\text{MeOH})_2]\{4,4'\text{-dpyo}[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 2\text{MeOH}$ (**1**), $\{(4,4'\text{-bpe})[(\text{Mn}(7\text{-MeSalen}))_2(\text{Mn}(7\text{-MeSalen})(\text{H}_2\text{O}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 1.5\text{MeCN} \cdot 8\text{H}_2\text{O}$ (**2**), and $\{(4,4'\text{-bpe})(\text{Mn}(\text{Salen})(\text{H}_2\text{O}))_2\}\{4,4'\text{-bpe}_2[(\text{Mn}(\text{Salen})(\text{MeOH}))_2(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)][(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 16\text{H}_2\text{O}$ (**3**). Single crystal X-ray diffraction analyses show that the frameworks of the three coordination polymers are built of heterotrimeric and/or heteropentameric supramolecular species linked by ditopic organic ligands. The framework of **1** consists of anionic chains built of heterotrimeric dianions $[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]^{2-}$ (T) linked by 4,4'-*dpyo*. The chains run along two directions ($[0\ 2\ -2]$ and $[0\ 3\ 3]$) leading to the formation of channels along the crystallographic (*a*) direction where the cations $[\text{Mn}(\text{Salen})(\text{S})_2]^+$ and solvent molecules are located. Also, **2** was reported earlier, it possesses a neutral 1D chain built of neutral heteropentameric supramolecules: $[(\text{Mn}(7\text{-MeSalen}))_2(\text{Mn}(7\text{-MeSalen})(\text{S}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]$ (P) linked by 4,4'-*bpe* ligands. Hydrogen bonds between non-bridging cyanide ligands and coordinated solvent molecules connect the chains into 2D hydrogen-bonded frameworks. Finally, **3** features an anionic chain, built of alternating heterotrimers $[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]^{2-}$ and heteropentamers $[(\text{Mn}(\text{Salen})(\text{S}))_2(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]$ linked by the organic spacer 4,4'-*bpe*. The anionic charge is compensated by the in situ-assembled $[\text{Mn}(\text{Salen})(\text{S})(4,4'\text{-bpe})\text{Mn}(\text{Salen})(\text{S})]^{2+}$ dimers. Magnetic measurements reveal that the Mn(III) ions are well isolated and only weak magnetic interactions are observed. The thermal stability of the three compounds was investigated.

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1. Introduction

Hybrid inorganic-organic materials, coordination polymers, and metal organic frameworks have received considerable attention in recent years [1–8]. These materials generally possess polymeric structures based on metal ions connected through inorganic and/or organic bridging ligands [9, 10]. The topology and function of these materials can, in principle, be controlled through judicious choice of their molecular components. A number of metal-organic frameworks (MOFs) have been prepared and are being actively investigated for their potential use in gas storage [11–16], catalysis [17, 18], magnetic materials [19–21], electronics, and optics [22–25]. The initial work focused on the use of single metal atoms as nodes, and quickly evolved toward

the use of polynuclear metal complexes and metal clusters containing metal-metal bonds as nodes [26–29].

Octahedral face-capped $\text{M}_6\text{L}_8^i\text{L}_6^a$ (M are metals of Groups 6 and 7; $L^i =$ halide, chalcogenide) or edge-capped $\text{M}_6\text{L}_{12}^i\text{L}_6^a$ (M are metals from Groups 4 and 5) clusters are characterized by their variety of electronic states and interesting properties arising from the metal-metal bonds [30–33]. The most prominent series of cluster compounds are the *Chevre*-*Sergent* phases, which exhibit superconductivity at high critical magnetic fields, catalytic activity, and good characteristics as solid-state electrode materials [34–38]. However, M_6L_8^i or $\text{M}_6\text{L}_{12}^i$ inner core has an atom- or ion-like behavior, is stable in solution, and can be subjected to a variety of ligand substitution reactions. The cyanosubstituted hexanuclear clusters are analogous to hexacyanomellates

and are being studied as building blocks for diverse structural assemblies ranging from discrete supramolecular assemblies to polymeric frameworks [39–70].

Manganese(III) complexes with tetradentate *Salen*-type Schiff-base ligands $[\text{Mn}(\text{Ls})]^+$ have been widely used as functional units for the preparation of 1D magnetic coordination polymers due to the availability of two axial coordination sites at about 180° from each other, and magnetic anisotropy of the d^4 Mn^{3+} ions [71–75]. These complexes have been used to prepare cluster-based materials in which the complex directs the assembly of metal clusters into supramolecular assemblies by acting as bridging metal ligand. Moreover, some $[\text{Mn}(\text{Ls})]^+$ complexes are used as efficient homogeneous catalysts for the conversion of achiral olefins into chiral epoxides, thence their inclusion as building blocks of solids can potentially lead to novel heterogeneous catalysts [76].

We have previously reported that reactions between $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$ and $[\text{Mn}(\text{L})]^+$ complexes result in the assembly of supramolecular species in which the cluster is coordinated by 1, 2, 3, 4, or 6 metal complexes [66]. As the number of metal complexes per cluster increases, the charge and size of these functionalized nanosized molecules increases (Table 1).

Here, we show that some of these supramolecules can be used as building blocks for the assembly of 1D coordination polymers. Thus, the heterotrimeric dianions $[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]^{2-}$ have been connected via 4,4'-*dpyo* to form an anionic 1D coordination polymer $[\text{Mn}(\text{Salen})(\text{MeOH})_2]_2\{(4,4'\text{-dpyo})[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 2\text{MeOH}$ (**1**). The neutral heteropentamers have been assembled into neutral 1D coordination polymers $\{(4,4'\text{-bpe})[(\text{Mn}(7\text{-MeSalen}))_2(\text{Mn}(7\text{-MeSalen})(\text{H}_2\text{O}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 1.5\text{MeCN} \cdot 8\text{H}_2\text{O}$ (**2**) using the ditopic ligand (4,4'-*bpe*) as bridging ligand, and 1D coordination polymer $[(4,4'\text{-bpe})(\text{Mn}(\text{Salen})(\text{H}_2\text{O}))_2]\{(4,4'\text{-bpe})_2[(\text{Mn}(\text{Salen})(\text{MeOH}))_2(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)][(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 16\text{H}_2\text{O}$ (**3**) in which the chains are built of alternating heterotrimers and heteropentamers connected via 4,4'-*bpe* that has been synthesized and characterized.

2. Experimental Section

2.1. General. Note that $(\text{Me}_4\text{N})_4[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6] \cdot 2\text{MeOH}$ [65], $[\text{Mn}(\text{Salen})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ [77], and $[\text{Mn}_2(7\text{-MeSalen})_2(\text{OAc})]\text{ClO}_4$ [78] were synthesized according to literature methods. Also, LiCl (99%), NbCl_5 (99%, metal basis), Nb powder (99.8%, metal basis), KCN (96%), Me_4NCl (98%), and *o*-hydroxyacetophenone (98%) were purchased from Alfa Aesar, while $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (98%) and ethylenediamine (99%) were purchased from ACROS. *Trans*-1, 2-bis(4-pyridyl)-ethylene (97%) (4,4'-*bpe*) and 4,4'-dipyridyl $\text{N,N}'$ -dioxide hydrate (98%) (4,4'-*dpyo*) were purchased from Aldrich. Finally, NaClO_4 and salicylic aldehyde were purchased from Fisher. All chemicals were used as received. Acetonitrile and methanol were used as received.

2.2. Syntheses

2.2.1. $[\text{Mn}(\text{Salen})(\text{MeOH})_2]_2\{(4,4'\text{-dpyo})[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 2\text{MeOH}$ (**1**). 0.0627 g (0.16 mmol) $[\text{Mn}(\text{Salen})]\text{ClO}_4$ and 0.1204 g (0.64 mmol) 4,4'-*dpyo* are dissolved in 20 mL MeOH to get red-brown solution (A). To 4.0 mL of solution A was added 4.0 mL of 4.0 mM aqueous solution of $(\text{Me}_4\text{N})_4[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]$ (B). Dark brown plate-like crystals formed after 4 hours. The crystals were isolated by filtration, washed with two 5 mL portions of water and two 5 mL portions of MeOH, and then dried in air (Yield: 17.4 mg, 77.68%; Analytical Calculation for $\text{C}_{86}\text{H}_{88}\text{Cl}_{12}\text{Mn}_4\text{N}_{16}\text{Nb}_6\text{O}_{16}$: C, 36.83; H, 3.16; N, 7.99%; Found: C, 36.26; H, 3.11; N, 8.01%. $\nu_{\text{CN}} = 2137; 2117 \text{ cm}^{-1}$).

2.2.2. $[(4,4'\text{-bpe})(\text{Mn}(\text{Salen})(\text{H}_2\text{O}))_2]\{(4,4'\text{-bpe})_2[(\text{Mn}(\text{Salen})(\text{MeOH}))_2(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)][(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]\} \cdot 16\text{H}_2\text{O}$ (**3**). 0.0627 g (0.16 mmol) $[\text{Mn}(\text{Salen})]\text{ClO}_4$ and 0.1166 g (0.64 mmol) 4,4'-*bpe* are dissolved in 20 mL MeOH to get red-brown solution (C). To 4.0 mL of solution C was added 4.0 mL of solution (B). Dark brown plate-like crystals formed after several hours. The crystals were filtered, washed with water and MeOH, then dried in air (Yield: 18.0 mg, 77.9%; Analytical Calculation for $\text{C}_{178}\text{H}_{186}\text{Cl}_{24}\text{Mn}_8\text{N}_{34}\text{Nb}_{12}\text{O}_{36}$: C, 36.97; H, 3.24; N, 8.24%, found: C, 36.12; H, 2.99; N, 8.41%. $\nu_{\text{CN}} = 2125 \text{ cm}^{-1}$).

2.3. Single Crystal X-Ray Structure Determinations. Intensity data for all compounds were measured at 193(2) K on a Bruker SMART APEX CCD area detector system. Data were corrected for absorption effects using the multiscan technique (SADABS). All structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package. A summary of the most important crystal and structure refinement data for all compounds is given in Table 2.

For **1**, the integration of the data using a triclinic cell yielded a total of 44244 reflections to a maximum θ angle of 27.50° , of which 11634 were independent ($R_{\text{int}} = 5.21\%$), and 9654 (82.98%) were greater than $2\sigma(F^2)$. The structure was solved and refined in the space group $P2_1/n$ (No. 14), with $Z = 2$. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms on C atoms were generated and refined isotropically. The hydroxylic hydrogen atoms from the coordinated methanol molecules were located from electron density map while the one from the free methanol molecule could not be located. The final anisotropic full-matrix least-squares refinement on F^2 with 637 variables converged to $R_1 = 5.77\%$ for observed data and $wR_2 = 10.92\%$ for all data. The largest residual peak on the final difference electron density map was $0.887 \text{ e}^-/\text{\AA}^3$ (0.89 \AA from Nb2) and the largest hole was $-0.690 \text{ e}^-/\text{\AA}^3$ (1.26 \AA from Nb1).

For **3**, the integration of the data using a triclinic cell yielded a total of 27232 reflections to a maximum θ angle of 22.0° , of which 12018 were independent ($R_{\text{int}} = 2.80\%$), and 10350 (86.12%) were greater than $2\sigma(F^2)$. The structure was solved and refined in the space group P-1 (number 2),

TABLE 1: The six supramolecular assemblies in which the cluster $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]$ is linked to one, two, three, four, and six $[\text{Mn}(\text{III})(\text{ACEN})]$. $[\text{Nb}_6]$ refers to the cluster $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$ and $[\text{Ta}_6]$ refers to the cluster $[\text{Ta}_6\text{Cl}_{12}(\text{CN})_6]^{3-}$; $\text{Mn} = [\text{Mn}(\text{III})(\text{ACEN})]^+$. (ACEN = bis(acetylacetonato)ethylenediamine).

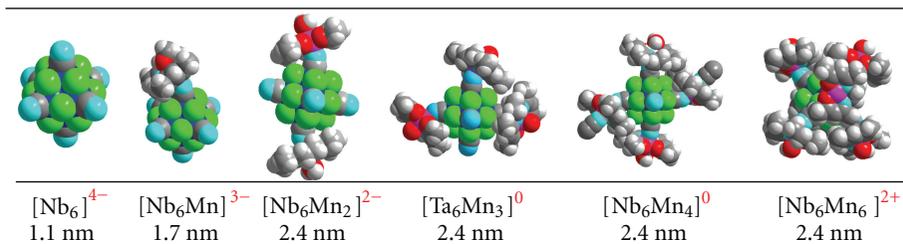


TABLE 2: Crystal data and structure refinement for the complexes.

	1	2	3
Formula	$\text{C}_{86}\text{H}_{88}\text{Cl}_{12}\text{Mn}_4\text{N}_{16}\text{Nb}_6\text{O}_{16}$	$\text{C}_{93}\text{H}_{106.50}\text{Cl}_{12}\text{Mn}_4\text{N}_{17.50}\text{Nb}_6\text{O}_{18}$	$\text{C}_{178}\text{H}_{186}\text{Cl}_{24}\text{Mn}_8\text{N}_{34}\text{Nb}_{12}\text{O}_{36}$
Mr.	2804.34	2960.08	5782.89
Cryst. System	Monoclinic	Triclinic	Triclinic
space group	P2(1)/n	P-1	P-1
a/Å	16.1629(10)	13.1923(16)	16.9662(17)
b/Å	21.2740(13)	14.2188(17)	17.6917(18)
c/Å	16.4062(10)	16.3598(19)	18.0631(18)
α/deg	90	97.737(2)	74.184(2)
β/deg	115.7020(10)	100.990(2)	74.198(2)
γ/deg	90	102.532(2)	75.567(2)
V (Å ³)/Z	5083.1(5)/2	2890.7(6)/1	4928.9(9)/1
d_{calc} , g/cm ³	1.832	1.700	2.745
F(000)	2788	1481	3780
θ range (°)	3.80 ~ 27.50	3.83 ~ 27.50	3.76 ~ 22.00
Reflections collected/unique	44244/11634	25667/13079	27232/12018
R(int)	0.0521	0.0327	0.0280
Goodness-of-fit on F ²	1.159	1.028	1.048
$R_1, *wR_2^{**}$			
I > 2 σ (I)	$R_1 = 0.0577, wR_2 = 0.1046$	$R_1 = 0.0435, wR_2 = 0.1049$	$R_1 = 0.0974, wR_2 = 0.2674$
all data	$R_1 = 0.0743, wR_2 = 0.1092$	$R_1 = 0.0581, wR_2 = 0.1130$	$R_1 = 0.1081, wR_2 = 0.2764$
Max/mean shift in final cycle	0.001/0.000	0.001/0.000	0.309/0.023

* $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$, ** $wR_2 = \{\sum w[(F_o^2 - F_c^2)] / \sum w[(F_o^2)]\}^{0.5}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. 1, $a = 0.0322, b = 15.5540$; 2, $a = 0.0598, b = 0.8822$; 3, $a = 0.1589, b = 80.8760$.

with $Z = 1$. All nonhydrogen atoms in the framework were located from Fourier difference map while the free solvent molecules and hydrogen atoms could not be located. No attempt was made to locate hydrogen atoms on C atoms. The final anisotropic full-matrix least-square refinement on F² with 1217 variables converged to $R_1 = 9.74\%$ for observed data and $wR_2 = 27.64\%$ for all data.

2.4. Other Physical Measurements. Elemental analyses were carried out by Atlantic Microlab, Inc. Thermogravimetric analyses were performed on ~14 mg samples under a flow of argon or air (40 mL/min) at a ramp rate of 5°C/min, using a Perkin-Elmer Pyris 1 TGA system. Infrared spectra were recorded as KBr pellets on a Mattson Infinity System FTIR spectrometer. The magnetic susceptibility data were collected using a Quantum Design MPMS SQUID mag-

netometer. Approximately, 15 mg samples were packed in gelatin capsules between cotton plugs. The data obtained have been corrected for the diamagnetic contribution of the sample holder, the diamagnetism of the closed shell octahedral $\{\text{Nb}_6\}$ cluster [79] and diamagnetic contribution of all other atoms using Pascal's constants [80].

X-ray powder diffraction data was collected at room temperature using a BRUKER P4 general-purpose four-circle X-ray diffractometer equipped with a GADDS/Hi-Star detector positioned 20 cm from the sample. The goniometer was controlled using the GADDS software suite [81]. The sample was mounted on tape and data was recorded in transmission mode. The data was reduced by area integration methods to produce a single powder diffraction pattern for each frame. Individual powder diffraction patterns were merged and analyzed with the program EVA [82].

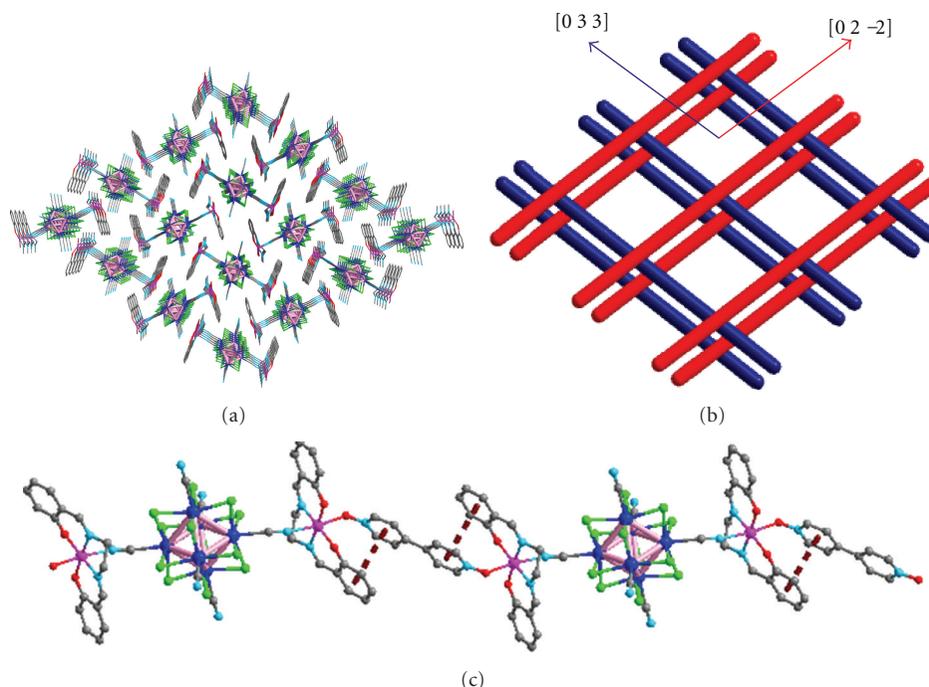


FIGURE 1: (a) A perspective view of the structure of **1**. Note that $[\text{Mn}(\text{Salen})(\text{MeOH})_2]^+$ cations are represented as space-filling mode and some cations are omitted to show the size and shape of the channel. (b) Schematic diagram showing the packing mode of the chains along $[0\ 2\ -2]$ and $[0\ 3\ 3]$ directions. (c) A projection of one anionic chain showing the linkages between the three components and π - π interaction between *dpyo* and the *Salen* ligand represented as dotted brown line.

3. Results and Discussion

3.1. Structure of Compound 1. Compound **1** features 1D anionic chains with $[\text{Mn}(\text{Salen})(\text{MeOH})_2]^+$ as charge compensating ions (Figure 1). The chains are built of heterotrimer $[(\text{Mn}(\text{Salen}))_2(\text{Nb}_6\text{Cl}_{12}(\text{CN})_6)]^{2-}$ building blocks which are connected to each other by 4,4'-*dpyo* ditopic linkers. Within the heterotrimer, the cluster $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$ is characterized by its octahedral $\{\text{Nb}_6\}$ metal core equipped with 12 edge-bridging Cl ligands and 6 terminal CN^- ligands, with bond lengths ($\text{Nb}-\text{Nb} = 2.934(8)\text{ \AA}$) and angles typical for niobium hexacyanochloride clusters with 16 valence electrons per cluster [34–43]. Each cluster uses the nitrogen ends of two cyanide ligands located opposite to each other to connect to two Mn complexes in *trans*-mode with $\text{Nb}-\text{C} = 2.271(5)\text{ \AA}$ and $\text{C}\equiv\text{N} = 1.140(6)\text{ \AA}$. Two of the four non-bridging cyanide ligands engage in extensive hydrogen bonding with the methanol ligand of the $[\text{Mn}(\text{Salen})(\text{MeOH})_2]^+$ cations with $\text{O}\cdots\text{N}$ separation of $2.771(6)\text{ \AA}$ and $\text{O}-\text{H}\cdots\text{N}$ angle of $170(8)^\circ$. The remaining two cyanide ligands are linked to niobium only, with bond lengths $\text{Nb}-\text{C} = 2.271(5)\text{ \AA}$ and $\text{C}\equiv\text{N} = 1.151(6)\text{ \AA}$. Although there are three kinds of cyanide groups in the structure, only two absorption bands related to the CN stretching vibrational mode ($2137, 2117\text{ cm}^{-1}$) are observed in the IR spectrum. The 2137 cm^{-1} band is assigned to the CN which is attached to the cluster only, and the 2117 cm^{-1} band is assigned to the CN ligand that acts either as a linker to Mn or is involved in hydrogen bonding with the methanol ligand.

The Mn^{3+} ions within the chains have a distorted octahedral coordination environment with two N and two O from the *Salen* ligand (average $\text{Mn}-\text{O} = 1.88(2)\text{ \AA}$ and $\text{Mn}-\text{N} = 1.986(2)\text{ \AA}$, compared to $1.88(3)\text{ \AA}$ and $1.983(2)\text{ \AA}$ found in $[\text{Mn}(\text{Salen})\text{Cl}(\text{H}_2\text{O})]$ [83]. The two axial sites are occupied by one N from a cyanide ligand from the cluster with $\text{Mn}-\text{N}_{\text{CN}} = 2.263(4)\text{ \AA}$ and $\angle\text{C}\equiv\text{N}-\text{Mn} = 153.6(4)^\circ$, and one O from the 4,4'-*dpyo* with $\text{Mn}-\text{O}_{\text{dpyo}} = 2.217(4)\text{ \AA}$, $\angle\text{N}_{\text{dpyo}}-\text{O}_{\text{dpyo}}-\text{Mn} = 119.2(3)^\circ$. The cluster unit and the 4,4'-*dpyo* linker are located on the same side of the $\text{N}_{\text{CN}}-\text{Mn}-\text{O}_{\text{dpyo}}$ axis leading to zig-zag wave-like chains. To the best of our knowledge, this is the first example where the $[\text{Mn}(\text{Salen})]^+$ complex uses its two open axial sites to coordinate to two different bridging ligands to form an extended structure.

The 4,4'-*dpyo* ligand connects the heterotrimers into a 1D coordination polymer via a coordination bond between its oxygen ends and $[\text{Mn}(\text{Salen})]^+$ complexes. Intrachain offset face-to-face π - π interactions between the *Salen* ligand and 4,4'-*dpyo* with ring \cdots ring distance of 3.70 \AA are observed. The chains run along $[0\ 3\ 3]$ and $[0\ 2\ -2]$ crystallographic directions and are packed into alternating layers. The packing leads to the formation of channels along the *a* direction where the cations and free solvent molecules are located.

The charge of the anionic chain is compensated by two $[\text{Mn}(\text{Salen})(\text{MeOH})_2]^+$ cations in which Mn^{3+} is chelated by a *Salen* ligand and coordinated by two methanol ligands with $\text{Mn}-\text{O} = 2.270(4)$ and $2.233(5)\text{ \AA}$. One of the methanol ligands forms a hydrogen bond with nonbridging cyanide

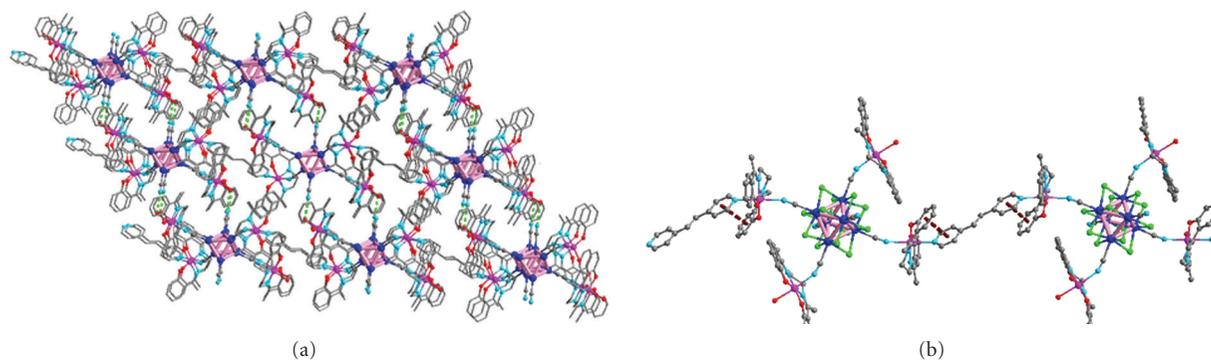


FIGURE 2: The structure of **2**. (a) The packing diagram viewed along the *a* direction. Cl atoms and free solvent molecules are omitted for clarity. Hydrogen bond is represented as a dotted green line. (b) The 1D neutral chain, π - π interaction is represented as a dotted red line.

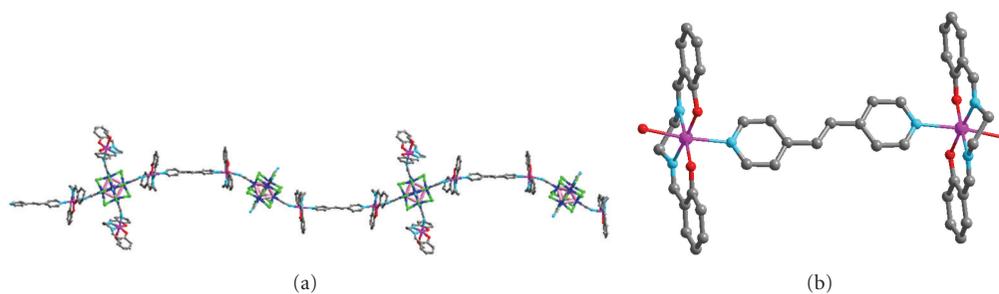


FIGURE 3: The structure of **3** (a) 1D anionic chain. (b) The cation: $\{[\text{Mn}(\text{Salen})(\text{H}_2\text{O})]_2(4,4'\text{-bpe})\}^{2+}$.

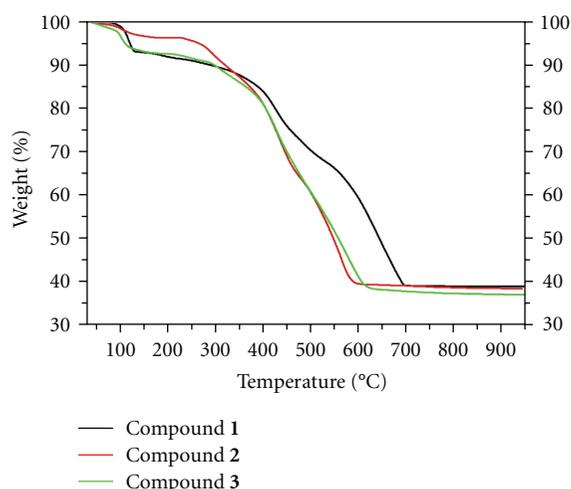


FIGURE 4: TGA plots for compounds **1–3** from 30°C to 950°C at 5°C/min under air flow (40 mL/min).

ligand and the other forms a strong hydrogen bond with the free methanol molecule with $\text{O}\cdots\text{O}$ separation of 2.558(9) Å and $\text{O-H}\cdots\text{O}$ angle of 175(9)°. In addition to hydrogen bonds, the cation is also involved in an edge to face

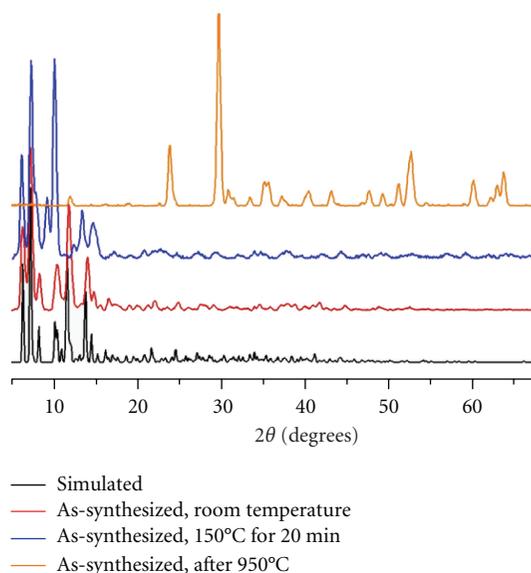


FIGURE 5: Powder X-ray diffraction patterns of **1**: pattern simulated from crystal structure in black; observed pattern at room temperature in red; observed pattern after being heated at 150°C for 20 minutes in blue; observed pattern after being heated to 950°C in orange which corresponds to a mixture of MnNb_2O_6 and Mn_3O_4 .

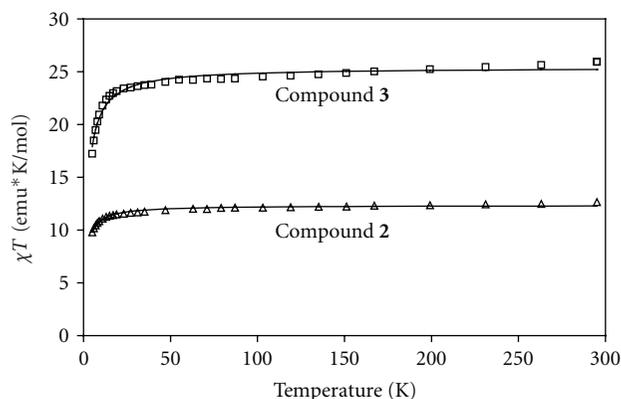


FIGURE 6: Temperature dependence of magnetic susceptibilities for compounds 2 and 3 (5–300 K at 1000 G).

π - π interaction with the anionic chain (H_{5A} -Ring $_{C17-C22}$ = 2.68 Å and H_{2A} -Ring $_{C27-C32}$ = 2.60 Å).

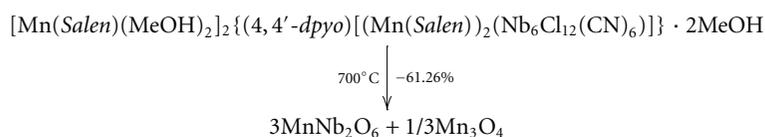
3.2. Structure of Compound 2. Compound 2 was reported earlier by us and is given here for comparison purpose only [68]. The neutral chains in 2 are built of neutral heteropentamers $[(Mn(7-MeSalen))_4(Nb_6Cl_{12}(CN)_6)]$ linked by 4,4'-*bpe* ligands (Figure 2). In each heteropentamer, the $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster uses four of its six cyanide ligands to connect to four Mn complexes through cyanide bridges and the octahedral coordination environment of each Mn(III) ion is completed by one N from a 4,4'-*bpe* ligand, which links the heteropentamers into chains running along the $[-1\ 1\ 1]$ direction. An intrachain offset face-to-face π - π interaction between the 7-MeSalen ligand and 4,4'-*bpe* with ring \cdots ring distance of 3.72 Å leads to the bending of the 7-MeSalen ligand: the dihedral angle between the two benzene rings of the ligand is 42.3°, compared with 19.6° in 1. The location of the cyanide and the *bpe* ligands on the same side of the N_{CN} -Mn- N_{bpe} axis leads to chains with a sinusoidal wave-like structure. Hydrogen bonds between nonbridging cyanides and the aqua ligands further connect the chains into layers (Figure 2(a)) which are held together through hydrogen bonding between disordered water molecules.

3.3. Structure of Compound 3. The reaction of $Mn(Salen)Cl$, $(Nb_6Cl_{12}(CN)_6)^{4-}$ and 4,4'-*bpe* in MeOH-H₂O solvent leads to compound 3, which crystallizes in the triclinic system, space group P-1 with $a = 16.9662(17)$, $b = 17.6917(18)$, $c = 18.0631(18)$ Å, $\alpha = 74.184(2)$, $\beta = 74.198(2)$, $\gamma = 75.567(2)^\circ$, $V = 4928.9(9)$ Å³,

and $Z = 1$. Data collected on three different crystals indicated complex twinning problems that could not be modeled. However, the data was sufficiently good to give the overall framework. The compound consists of 1D anionic chains built of two different nodes: anionic heterotrimers $[(Mn(Salen))_2(Nb_6Cl_{12}(CN)_6)]^{2-}$ and neutral heteropentamers $[(Mn(Salen))_4(Nb_6Cl_{12}(CN)_6)]$ linked to one another by 4,4'-*bpe* ligands (Figure 3). In the heteropentamer, the sixth coordination site of the nonbridged $(Mn(Salen))^+$ complexes are occupied by methanol molecules. No intrachain π - π interactions between the Salen ligand and the aromatic part of the bridging ligand are observed compared to the relatively strong interactions present in 1 and 2. The in situ formed dimeric cation $\{[Mn(Salen)(H_2O)]_2(4,4'-bpe)\}^{2+}$ is used to balance the chains' negative charge. No free solvent molecules could be located from the electron density map and the presence of 16 waters of crystallization was determined based on elemental analysis and TGA data.

The connectivity mode $\{Nb_6\}-C\equiv N-Mn-L_{bridge}-Mn-N\equiv C-\{Nb_6\}$ observed in the three compounds is different from that observed in a series of $\{Re_6\}$ based compounds in which $(\{Re_6\}-L_{bridge}-M-L_{bridge}-\{Re_6\})$ is observed [84–87]. Simultaneous use of CN and ditopic ligands as bridges has been observed in mononuclear cyanometallate-based coordination polymers [88–93], however similar structures have never been reported for cluster-based coordination networks.

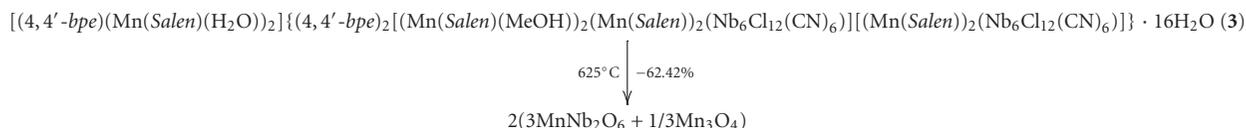
3.4. Thermal Stabilities. Polycrystalline samples of each compound were used to study the thermal stability of the three compounds (Figure 4). TGA of 1 shows two distinct weight losses. The first (6.84%) corresponds to loss of all coordinated and free solvent molecules at temperature below 200°C (cal. 6.85%). The powder X-ray diffraction pattern of samples obtained after heating (1) at 150°C for 20 minutes is virtually the same as that of 1 except for the peak at $2\theta = 8.300^\circ$ which shifts to $2\theta = 9.087^\circ$ indicating minor structural transformations. IR spectra of the materials obtained after being heated at 150°C for 20 minutes was found to be the same as those of the original compound indicating the conservation of all functional components. The compound continues to lose weight after 200°C without any well-defined phase being formed indicating a continuous decomposition until 700°C is reached. The final product obtained after 700°C is a mixture of the oxides $MnNb_2O_6$ and Mn_3O_4 , as confirmed by PXRD (Figure 5) (%loss (obs.) = 61.02%; %loss (calc.) = 61.26%) [94, 95]. The overall chemical equation for this process can be written as



Compound **2** has similar thermal behavior as that observed for **1**. It first loses solvent molecules (1.5 MeCN and 3 H₂O before 180°C (%loss (obs.) = 3.69%, loss (calc.) = 3.90%)) and forms a desolvated phase which is stable up to 300°C as confirmed by PXRD and IR (SI). The compound decomposes to form a mixture of MnNb₂O₆ and Mn₃O₄ at temperatures above 580°C (%loss (obs.) = 61.59%, %loss (calc.) = 62.41%).

Compound **3** loses all its solvent molecules (2 coordinated MeOH, 2 coordinated H₂O, and 16 lattice water

molecules (%loss (obs.) = 7.02%, loss (calc.) = 6.71%) before 150°C. The desolvated phase loses crystallinity as indicated by a decrease in diffraction peaks intensity. IR spectra (SI), however, indicate the presence of CN as well as salen and bridging ligand. The compound continues to decompose after 300°C without any stable phases until it reaches 625°C when it forms a mixture of MnNb₂O₆ and Mn₃O₄ (%loss (obs.) = 63.00%, %loss (calc.) = 62.42%) as confirmed by PXRD (SI). The overall decomposition reaction can be written as follows:



3.5. Magnetic Properties. Magnetic properties of **2** and **3** were measured upon warming from 5 to 300 K in an applied field of 1000 G (Figure 6). Because previous reports have shown that the niobium cluster is diamagnetic with a temperature independent paramagnetism term [96, 97], it is reasonable to model the temperature-dependent paramagnetism as due solely to the Mn(III) centers. The data can be fit to a Curie-Weiss expression for each of the compounds to yield $g_{ave} = 2.03$, $\theta = -1.3$ K, and $g_{ave} = 2.06$, $\theta = -2.1$ K, respectively. These values are consistent with four and eight high-spin Mn(III) centers for compounds **2** and **3**. The slight downturn in the data at low temperatures is probably due to zero field splitting of the $S = 2$ ground state. The values obtained are comparable to those reported for 1D coordination polymer built of well-separated $[Mn(Salen)]^+$ centers [98, 99].

4. Conclusion

In summary, trimeric (T) and pentameric (P) nanoscopic supramolecular species (~2 nm) based on the diamagnetic 16 electron cyanochloride cluster $[Nb_6Cl_{12}(CN)_6]^{4-}$ coordinated by 2 or 4 Mn(III) complexes have been assembled into extended frameworks via bridging ditopic organic ligands (O) through self-assembly processes. The bridging modes can be described as (-T-O-T-O-) in **1**, (-P-O-P-O-) in **2**, and (-T-O-P-O-T-) in **3**. The compounds are chemically and thermally stable and their magnetic properties are consistent with the long distances between the manganese(III) centers. The assembly of such complex materials containing large supramolecular species linked to each other via ditopic organic ligands in a simple one-pot reaction indicates the tremendous opportunities this chemistry provides. We have recently developed synthesis methodologies for the synthesis of the 14 and 15 electron $\{Nb_6\}$ and $\{Ta_6\}$ cyano- and azido-chloride clusters and we are investigating their use as building blocks to study the effect of the metal, the ligand and the electronic structure of the cluster on the properties of these materials.

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