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Cluster Compounds

Directed Assembly of Cluster-Based Supramolecules into One-Dimensional Coordination Polymers**

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In memory of Ekatherina Anokhina

The directed assembly of solids of various dimensions by using carefully chosen molecular building units allows for remarkable control over the structural and physicochemical properties of materials at the molecular level.[1] Among the building units being investigated, octahedral metal clusters are especially attractive because of their atomlike behavior, stability, availability of multiple coordination sites through the presence of six apical labile ligands, and electronic flexibility resulting from the presence of metal–metal bonds.[2–6] The $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster as well as metal complexes have recently been used as building units for supramolecular assemblies and coordination polymers.[6] Complexes $[Mn(L_s)]^+$ of Mn^{III} ions with tetradentate salen-type ligands (L_s; salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion) have been used to prepare cluster-based materials in which the complex directs the assembly of metal clusters into supramolecular assemblies through the availability of two axially located coordination sites.[6] Some $[Mn(L_s)]^+$ complexes are efficient homogeneous catalysts for the conversion of achiral olefins into chiral epoxides, and their inclusion as building blocks of solids can potentially lead to novel heterogeneous catalysts.[7] The $[Mn(L_s)]^+$ complexes exist in solution as an equilibrium between monomeric species and the phenoxo-bridged dimeric species $[Mn_2(L_s)_2]^{2+}$, while the solid-state structure depends on the steric characteristics of the salen-type ligand.[8] These dimers generally exhibit antiferromagnetic interactions, but ferromagnetic behavior has also been observed.[9]

Recently we reported a neutral heteropentameric supramolecular assembly in which the $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster is linked to four $[Mn(L_s)]^+$ complexes through four CN ligands (Figure 1).[6b] Here we report the assembly of the clusters into extended 1D frameworks. A one-pot reaction between solutions of $[Nb_6Cl_{12}(CN)_6]^{4-}$ and $[Mn(L)]^+$ (H_2L = 7-Me-salen) led to the formation of the 1D coordination polymer $\{[Mn(L)]_2[Mn(L)(EtOH)]_2[Nb_6Cl_{12}(CN)_6]\}$ (**1**), which is composed of heteropentamers linked through phenoxo bridges between the $[Mn(L)]^+$ complexes. Addition of the ligand *trans*-1,2-bis(4-pyridyl)ethylene (bpe) resulted in the formation of $\{[(Mn(L)(bpe)Mn(L)][\{Mn(L)(H_2O)\}_2\{Nb_6Cl_{12}(CN)_6\}]\}$ (**2**) in which the heteropentamers are linked through the bpe ligand to form neutral 1D chains. The chains in **2** are expanded analogues of those found in **1**.

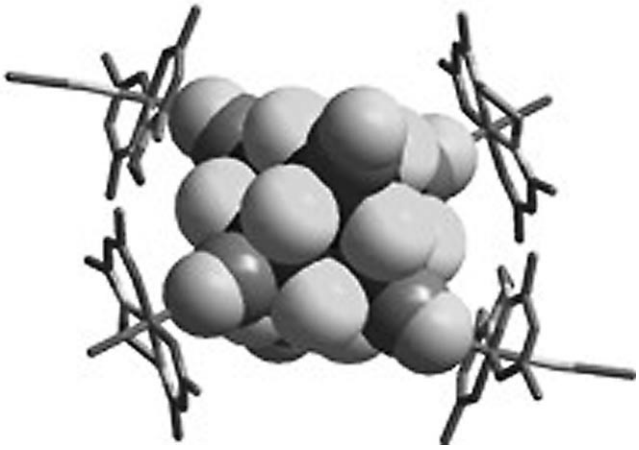

Figure 1. Structure of the pentameric supramolecular assembly $[Mn(acacen)(MeCN)]_2[Mn(acacen)(H_2O)]_2[Nb_6Cl_{12}(CN)_6]$.

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction. Compound **1** is a 1D coordination polymer based on pentameric supramolecular units $\{[Mn(L)]_2[Mn(L)(EtOH)]_2[Nb_6Cl_{12}(CN)_6]\}$ connected through phenoxo bridges between the nonsolvated manganese complexes $[Mn(L)]^+$ (Figure 2a).[10] Each pentamer is comprised of an octahedral cluster $[Nb_6Cl_{12}(CN)_6]^{4-}$ connected to two $[Mn(L)]^+$ and two $[(Mn(L)(EtOH)]^+$ complexes through four CN ligands located in equatorial positions. The remaining two cyanide ligands point between the chains. The $[Nb_6Cl_{12}(CN)_6]^{4-}$ cluster is composed of an octahedral Nb_6 core surrounded by 12 edge-bridging Cl ligands and 6 apical cyanide ligands. The average Nb–Nb (2.926(3) Å), Nb–Cl (2.465(7) Å), Nb–C (2.268(6) Å), and C≡N (1.14(1) Å) bond lengths as well as Nb-C≡N bond angle (176.24(2)°) are similar to those found in the cluster precursor (Nb–C (2.282(1) Å), C≡N (1.13(1) Å), and Nb-C≡N (178.3(6)°). The Nb–Nb bond lengths confirm the presence of the diamagnetic $[Nb_6Cl_{12}]^{2+}$ cluster core with 16 valence electrons available for metal–metal bonding. The Mn^{III} ion in the $[Mn(L)]^+$ complex is coordinated by two nitrogen and two oxygen atoms from the 7-Me-salen ligand (Mn–O = 1.870(5) Å and Mn–N = 1.984(6) Å), one nitrogen atom

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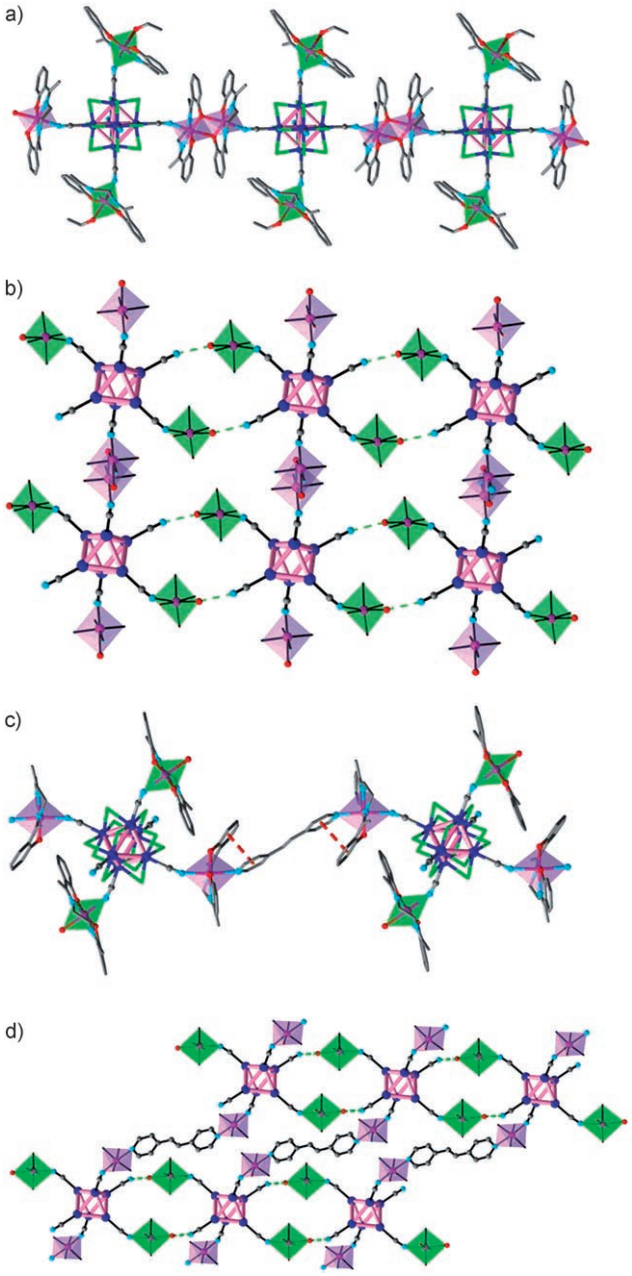

Figure 2. a) The neutral coordination chain of **1**. b) The packing diagram of **1** viewed along the *b* direction. c) The neutral coordination chain of **2**. The intrachain, offset face-to-face π–π interaction is represented as red dotted lines. d) The packing diagram of **2** viewed along the *c* direction. The 7-Me-salen ligand, chlorine atoms, and free solvent molecules are omitted for clarity in (b) and (d). The hydrogen bonds are represented by dotted green lines.

from the cyanide ligand with Mn–N_{CN} = 2.222(6) Å, and one phenolic oxygen atom with Mn–$O_{phenoxo}$ = 2.363(4) Å. The Mn^{III} ion in the $[(Mn(L)(EtOH)]^+$ complex is tetracoordinated by the salen ligand, one cyanide ligand (Mn–N_{CN} = 2.291(6) Å), and one ethanol ligand (Mn–O = 2.262(6) Å). The Mn-N≡C angles of 153.2(6)° and 159.5(6)° are different to those of 165.75(3)° and 148.56(2)° in the heteropentamer containing the $[Mn(acacen)]^+$ complex (acacen = *N*,*N*′-bis(acetylacetone)ethylenediamine) as a result of differences in the interactions between the supramolecular assemblies. The heteropentamers are linked through phenoxo bridges between the manganese complexes, thereby leading to 1D chains running along the [110] direction. The phenoxo bridged dimers $[Mn_2(L)_2]^{2+}$ have a relatively short Mn···Mn distance of 3.346(1) Å and the Mn-O-Mn angle (102.9(2)°) is similar to that observed in other $[Mn_2(L_s)_2]$ dimers.[11] Hydrogen bonds between nonbridging cyanide groups and the ethanol ligands connect the chains into layers that stack perpendicular to the *b* axis (Figure 2b). Adjacent layers are related to each other by an inversion center and are separated by MeCN molecules.

Compound **2** is built from heteropentamers $\{Mn_4(Nb)_6\}$ with similar bond lengths and bond angles as those found in **1**. The heteropentamers are linked by the bpe ligand to form neutral chains running along the [−111] direction. The 7-Me-salen ligand in the bridged manganese complexes is distorted because of an intrachain, offset face-to-face π–π interaction between the salen ligand and the bpe with a ring···ring distance of 3.72 Å. The dihedral angle between the two benzene rings of the ligand is 42.3°, compared with 15.2° in **1**. Compound **2** can be treated as an expanded analogue of **1** with the connectivity $\{Nb_6\}$-C≡N-Mn-bpe-Mn-N≡C-$\{Nb_6\}$ (Figure 2c), which is different from the connectivity $\{Re_6\}$-bipy-M-bipy-$\{Re_6\}$ reported for a series of Re_6-based materials.[3] The location of the cyanide and bpe ligands on the same side of the N_{CN}-Mn-N_{bpe} axis leads to chains with sinusoidal wavelike structures. Hydrogen bonds between nonbridging cyanide groups and aqua ligands connect the chains into layers (Figure 2d). The layers are held together through hydrogen bonding with the disordered water molecules located between the layers. Although the simultaneous use of a CN and a ditopic nitrogen ligand has been reported for coordination polymers based on mononuclear cyanometalate nodes,[11] similar structures have never been reported in cluster-based coordination networks. The intrachain distance between the closest Nb_6 clusters is expanded from 18.25 Å in **1** to 27.29 Å in **2**, compared with the closest intrachain Fe···Fe distance of about 12.81 Å in $(NEt_4)[Mn_2(5\text{-MeOsalen})_2Fe(CN)_6]$, which is a mononuclear analogue of **1**.[13] The distance between the intrachain manganese centers in **2** is about 13.79 Å, which is longer than those in the 1D complexes $[Mn(salen)Ag(CN)_2]$ (10.43 Å) bridged by $[Ag(CN)_2]^-$ ions and [Mn(salen)(dca)] (8.56 Å) bridged by dicyanamide (dca).[14]

Magnetic susceptibility data for **1** and **2** were measured from 300 to 5 K at 1 kG. At room temperature **1** has μ_{eff} = 4.74 μ_B, thus confirming the presence of a high-spin Mn^{III} center (4.90 μ_B for $S = 2$). The value of μ_{eff} remains nearly constant as the temperature is decreased to about 70 K, when it gradually decreases to reach 3.99 μ_B at 5 K. The plot of χ_m^{-1} versus T follows the Curie–Weiss law, with C = 11.22 emu $mol^{-1}K^{-1}$ and $\theta = -2.07$ K. The negative θ value and the decrease in the value of μ_{eff} below 70 K indicate antiferromagnetic coupling. The Heisenberg dimer model with the Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ was used to model the magnetic data for **1**. The best fit gave: g = 1.937, $J = -0.645$ cm^{-1}, which are close to those reported for dimeric Mn^{III}–salen-type complexes with antiferromagnetic interactions.[12] The

Mn–O* (axial phenolic oxygen) bond length, stereoelectronic character of the ligand, and Jahn–Teller distortion present in the d^4 Mn^{3+} ion play an important role in determining the type of magnetic coupling in the dimers. The intradimer antiferromagnetic coupling observed for **1** originates from a relatively short Mn–O* bond length (2.363(4) Å).[12] For **2**, the room-temperature μ_{eff} value of 4.89 μ_B remains constant to 50 K, when it decreases smoothly to 4.43 μ_B at 5 K, thus suggesting weak magnetic coupling interactions arising from the large diamagnetic bridging groups between the Mn^{III} ions, as confirmed by the small θ value ($C = 3.78$ emu mol^{-1} K^{-1}; $\theta = -0.79$ K). Molecular field theory[15] was used to estimate the coupling interaction between the Mn^{III} ions, and the data fit was obtained with $g = 2.003(1)$ and $zj' = -0.044(1)$ cm^{-1}, which indicates that **2** is a paramagnet. The values obtained are comparable to those reported for 1D chains built of $[Mn(salen)]^+$ complexes bridged by long linkers.[14]

Thermogravimetric analysis (TGA) of **1** performed under flowing air shows two distinct weight losses: The first (5.61 %) involves loss of all solvent molecules below 150 °C (calcd: 6.43 %) and the second corresponds to the decomposition of the compound above 700 °C to form $MnNb_2O_6$ and Mn_3O_4, as confirmed by powder X-ray diffraction (PXRD; obs loss: 61.53 %; calcd loss: 59.91 %).[16] The thermal behavior of **2** involves loss of 1.5 MeCN molecules and 3 H_2O molecules (obs loss: 3.69 %, calcd loss: 3.90 %) before 180 °C. The final product obtained above 700 °C was found to be a mixture of $MnNb_2O_6$ and Mn_3O_4 (obs loss: 61.59 %, calcd loss: 62.41 %). It is worth noting that the preparation of $MnNb_2O_6$, which is useful for applications in dielectric resonators and filters, usually requires temperatures higher than 1000 °C for more than ten days.[16]

The assembly of nanometric molecular structures (ca. 2 nm) into extended frameworks using a one-pot reaction indicates that it is possible to link these units through coordination bonds using ditopic ligands. The findings provide tremendous opportunities in terms of the design and synthesis of complex materials and their functionalization by judicious choice of the metal cluster, the complex, and the organic ligand. Work is underway to investigate the use of the 15- and 14-electron clusters and study their effect on the magnetic properties of these materials.

Experimental Section

$\{[Mn_2(L)_2][\{Mn(L)(EtOH)\}_2Nb_6Cl_{12}(CN)_6]\}\cdot 2MeCN$ (**1**): A 5.0 mM solution of $[Mn_2(L)_2(OAc)](ClO_4)$[17] (3.0 mL) in MeCN/EtOH (1:1) was layered with a 2.0 mM solution of $(Et_4N)_4[Nb_6Cl_{12}(CN)_6]$[6a] (3.0 mL) in MeCN. Brown platelike crystals were obtained at the interface. The crystals were collected by filtration, washed with EtOH, and dried in air to give the product (7.5 mg, yield: 46.1 %). Elemental analysis calcd for $C_{86}H_{90}Cl_{12}Mn_4N_{16}Nb_6O_{10}$: C 38.11, H 3.35, N 8.27 %; found: C 38.10, H 3.30, N 8.76 %. $\nu_{CN} = 2132$ cm^{-1}.

$\{[(Mn(L)(bpe)Mn(L)][\{Mn(L)(H_2O)\}_2\{Nb_6Cl_{12}(CN)_6\}]\}\cdot 1.5MeCN\cdot 8H_2O$ (**2**): $[Mn_2(L)_2(OAc)](ClO_4)$ (0.0686 g, 0.16 mmol) and bpe (0.1166 g, 0.64 mmol) were dissolved in MeCN (20 mL) and stirred overnight. A 4.0 mM aqueous solution of $[Me_4N]_4[Nb_6Cl_{12}(CN)_6]\cdot 2MeOH$ (4.0 mL) was added to this solution (4.0 mL).[6a] Red-brown elongated platelike crystals began to form after several minutes. The crystals were separated after 24 h, washed with water and methanol, and dried in air; yield: 13.7 mg, 58.1 %. Elemental analysis calcd for $C_{93}H_{106.50}Cl_{12}Mn_4N_{17.50}Nb_6O_{18}$: C 37.73, H 3.62, N 8.28 %; found: C 37.25, H 3.32, N 7.70 %. $\nu_{CN} = 2128$ cm^{-1}.

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[10] Crystal data for **1**: $C_{86}H_{90}Cl_{12}Mn_4N_{16}Nb_6O_{10}$, $M_r = 2710.36$, triclinic, space group $P\bar{1}$, $a = 12.904(2)$, $b = 14.024(2)$, $c = 14.101(2)$ Å, $\alpha = 100.340(2)$, $\beta = 91.070(2)$, $\gamma = 94.313(2)°$, $V = 2502.0(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.799$ g cm^{-3}, $2\theta_{max} = 55.00°$, $T = 193(2)$ K, 22276 measured reflections. $R_1 = 0.0670$ for 9111 reflections ($I > 2\sigma(I)$), $\omega R_2 = 0.1629$ for 11313 independent reflections (all data) and 604 parameters. GOF = 1.132. CCDC-623454 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **2**: $C_{93}H_{106.50}Cl_{12}Mn_4N_{17.50}Nb_6O_{18}$, $M_r = 2960.08$, triclinic, space group $P\bar{1}$, $a = 13.192(2)$, $b = 14.218(2)$, $c = 16.359(2)$ Å, $\alpha = 97.737(2)$, $\beta = 100.990(2)$; $\gamma = 102.532(2)°$; $V = 2890.7(6)$ Å^3, $Z = 1$, $\rho = 1.700$ g cm^{-3}, $2\theta_{max} = 55.00°$, $T = 193(2)$ K, 25667 measured reflections. $R_1 = 0.0435$ for 10437 reflections ($I > 2\sigma(I)$),

$\omega R_2 = 0.1130$ for 13079 independent reflections (all data) and 688 parameters. GOF = 1.028. CCDC-623455 contains the supplementary crystallographic data for this paper.

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