Two New Coordination Polymers Based on Hexanuclear Metal Cluster Cores

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Two new coordination polymers based on hexanuclear metal cluster cores, $Zn_6(HCOO)_6(DBrTPA)_3(DMF)_6$ (**1**) and $Mn_6(HCOO)_6(BTC)_2(DMF)_6$ (**2**) have been solvothermally synthesized. It is noteworthy that the formic ligands were in situ generated by the hydrolysis of DMF solvent under the solvothermal conditions and incorporated into these two compounds. The temperature-dependence of magnetic susceptibility for **2** shows antiferromagnetic interactions between metal centers.

Design and synthesis of coordination polymers are of great current interest for their intriguing topologies and fascinating properties.[1] This class of complexes contains two central components, inorganic units (single metal atoms or metal clusters), and organic ligands. The versatility of organic ligands and the diversity of inorganic units have led to a wide array of functions of coordination polymers. The recent introduction of polynuclear clusters into the coordination polymers has increased the range of their possible applications as functional materials. Many transition-metal clusters with very high ground-state spins, such as manganese, iron, cobalt, and nickel clusters can be used as magnetic building units to construct multi-functional coordination polymers combining magnetism with porosity.[2] Such materials will have enormous interest in the near future as their use as magnetic sensors. On the other hand, in clusters with terminal ligands (usually labile ligands, such as water, methanol, and DMF molecules), the reactivity of the metal site can be studied through the removal of these ligands, which frees a coordination site.[3] The open metal sites played very important roles in molecular recognition in catalysis, hydrogen storage, and biological systems.[4]

In this work, we have synthesized two new coordination polymers, $Zn_6(HCOO)_6(DBrTPA)_3(DMF)_6$ (**1**) and Mn_6-$(HCOO)_6(BTC)_2(DMF)_6$ (**2**) (DBrTPA = 2,5-dibromoterephthalate, BTC = 1,3,5-benzenetricarboxylate) by solvothermal reactions.[5] The interest of Mn and Zn lies in their facile construction of their unusual clusters with polyhedra linked by edges, vertices, or faces in the presence of polycarboxylic acid.[6]

It is worth noting that the formic ligands are incorporated into these two compounds although the absence of added formic acid during the reaction. As we known, when employing wet DMF as solvent in the solvothermal reaction, it is often hydrolyzed into formic acid and dimethylamine. Dimethylamine molecule often acts as a counter cation to balance charge of system and formic acid serves as an anionic ligand to construct metal cluster. When $Zn(NO_3)_2 \cdot 6H_2O$ and DBrTPA were heated in fresh DMF, the product was obtained as a mixture of a small amount of single-crystals of **1** and unidentified powder. Interestingly, the synthesis of **2** relies on subtle control over various hydrothermal parameters, particularly the solvent and temperature. In the absence of H_2O and EtOH, different phases were obtained

rather than compounds **2**. Obviously, the EtOH and H_2O play a key role in the synthesis of **2**. Besides, similar solvothermal reactions at higher temperatures could not produce **2**. When the reactions were carried out by addition of formic acid, the powder of **1** and **2** showing the same X-ray powder diffraction patterns of the corresponding crystalline forms were obtained.

X-ray single-crystal structure analysis[7] revealed that the two compounds have the same inorganic building units, hexanuclear metal cluster cores with crystallographic $\bar{3}$ symmetry, M_6-$(HCOO)_6(-CO_2)_6(DMF)_6$ (M = Zn (**1**) and Mn (**2**)) (Figure 1). The six carboxylate carbon atoms in the hexanuclear metal cluster serve as points-of-extension that define the vertices of a hexangular building unit. **1** crystallizes in trigonal, space group $P\bar{3}$. The Zn1 ion has a slightly distorted octahedral coordination sphere: three formate oxygen atoms (O(4), O(5A) ($x - y$, $x - 1$, $-z + 2$), O(5B) ($-y + 1$, $x - y - 1$, z)) from three formic ligand, two carboxylate oxygen atoms (O(1), O(2A) ($x - y$, $x - 1$, $-z + 2$)) from two DBrTPA ligands, and one oxygen atom (O(3)) from terminal DMF molecule. Six Zn^{2+} ions are linked together through six formate bridges and six carboxylate groups from DBrTPA ligands to give the hexanuclear $Zn_6(HCOO)_6$-$(DMF)_6(-CO_2)_6$ cluster core, in which carboxylate groups of formic ligands exhibit triatomic carboxylate bridging (μ_3-COO) with three Zn ions, while the carboxylate groups of DBrTPA ligands adopt monoatomic oxygen bridging (*syn–syn*) of two Zn ions. Each hexanuclear cluster core is connected
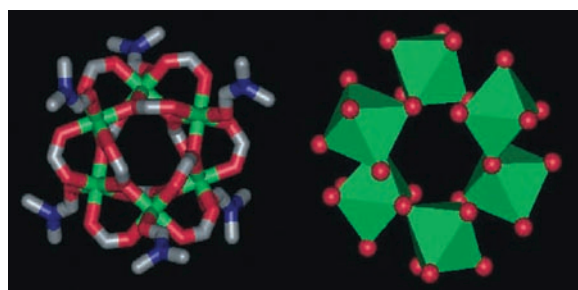
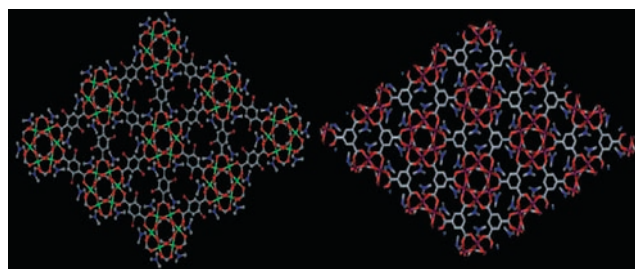

Figure 1. Hexanuclear metal cluster core.

Figure 2. View of the 2D networks of compounds **1** (left) and **2** (right) along the *c* axis.
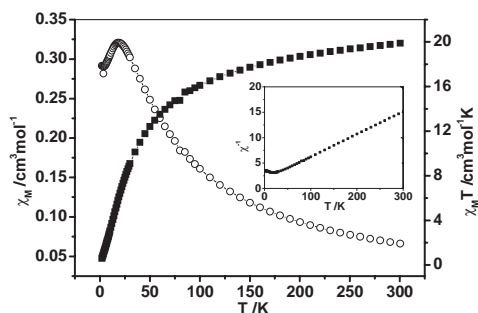
Figure 3. Temperature dependences of the magnetic susceptibility χ_M and the $\chi_M T$ product for **2** under an applied field of 1 T.

to six adjacent cluster cores through six $-C_6H_4Br_2-$ groups of DBrTPA ligands forming a 2D network (Figure 2 left). The 2D network of **1** can be rationalized to be a (3, 6) topological net when the hexanuclear $Zn_6(HCOO)_6(DMF)_6(-CO_2)_6$ cluster is treated as a hexagonal node and 2,5-BrTPA as a linear linker.

Compound **2** also crystallizes in trigonal, space group $P\bar{3}$.[7] Mn1 is in a six-coordinate environment: three formate oxygen atoms (O(2), O(4A) $(x - y, x, -z)$, O(4B) $(-y, x - y, z)$) from three formic ligands, two carboxylate oxygen atoms (O(3), O(1A) $(x - y, x, -z)$) from two BTC ligand, and one oxygen atom (O(5)) from terminal DMF molecule. The Mn^{2+} center adopts a slightly distorted octahedral geometry with *cis* angles ranging from 83.26(4) to 95.36(4)°. Bond length of Mn–O is in the range of 2.1084(9)–2.2254(10) Å. Six Mn^{2+} ions are linked together through six formate bridges and six carboxylate groups from BTC ligands to give the hexanuclear $Mn_6(HCOO)_6$-$(DMF)_6(-CO_2)_6$ cluster core, in which carboxylate groups of formate ligands bridge three Mn ions in the μ_3-mode, while the carboxylate groups of BTC ligands bridge two Mn ions in the *syn–syn* mode. The nearest Mn$\cdots$Mn distance is 3.676 Å. The connection of hexanuclear clusters and BTC links results in a 2D network parallel to the *ab* plane (Figure 2 right).

χ_M vs T and $\chi_M T$ vs T plots for compound **2** are shown in Figure 3. Magnetic measurements were carried out on powdered sample of **2** under an applied field of 1 T in the temperature range of 2–300 K. $1/\chi_M$ vs T plot of **2** is linear above 30 K and obeys the Curie–Weiss law with $C = 22.57$ cm^3 K mol^{-1} and $\theta = -41.07$ K. The value of $\chi_M T$ product at room temperature (19.88 cm^3 K mol^{-1}) is lower than the expected value for six magnetically independent Mn^{2+} ions with $S = 5/2$ (26.25 cm^3 K mol^{-1} for $g = 2.00$). $\chi_M T$ decreases gradually from 19.88 to 14.35 cm^3 K mol^{-1} between 300 and 70 K and then decreases more steeply to reach 0.58 cm^3 K mol^{-1} at 2 K. This behavior and the negative Weiss constant indicate the operation of an antiferromagnetic interaction between Mn^{2+} ions. The χ_M vs T plot of **2** shows Néel point at 19 K.

In conclusion, two new coordination polymers based on hexanuclear metal cluster cores, have been solvothermally synthesized. The co-ligand, formate in both compounds was in situ generated from DMF during the reactions and plays a significant role to form hexanuclear core structure. The cryomagnetic results of compound **2** show overall antiferromagnetic interaction between metal centers through μ_3-formate and *syn–syn* type BTC bridges.

References and Notes
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5 Typical procedure: **$Zn_6(HCOO)_6(DBrTPA)_3(DMF)_6$ (1)**. $Zn(NO_3)_2 \cdot 6H_2O$ (0.149 g, 0.5 mmol), 2,5-dibromoterephthalic acid (0.162 g, 0.5 mmol) were dissolved in DMF (10 mL) with stirring. The solution was then sealed in a 25 mL Teflon-lined stainless container, which was heated to 120 °C for 2 days. After slow cooling of the sample to room temperature, colorless hexagonal prism-like single crystals together with white unknown powder indicated by powder diffraction were obtained. Yield: 20%. Elemental analysis (%) for **1** ($C_8H_9BrNO_5Zn$): calcd: C, 27.87; H, 2.61; N, 4.06%. Found: C, 28.03; H, 3.02; N, 3.94%. **$Mn_6(HCOO)_6(BTC)_2(DMF)_6$ (2)**. $MnCl_2 \cdot 4H_2O$ (0.198 g, 1.0 mmol), 1,3,5-benzenetricarboxylic acid (0.210 g, 1.0 mmol) were dissolved in DMF/EtOH/H$_2$O (8 mL/1 mL/ 1 mL) with stirring. The solution was sealed in a 25 mL Teflon-lined stainless container, which was heated to 70 °C for 2 days. After slow cooling of the sample to room temperature, light yellow single crystals for **2** were separated by filtration. Yields: 82%. Elemental analysis (%) for **2** ($C_7H_9NO_5Mn$): calcd: C, 34.70; H, 3.72; N, 5.78%. Found: C, 34.54; H, 3.53; N, 5.62%.
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7 Single-crystal X-ray data were collected at 293 K on a Rigaku Mercury diffractometer with Mo Kα radiation ($\lambda = 0.7101$ Å). The structures were solved by direct methods (SIR97), and refined by full-matrix least-squares on F^2. Crystal data for **1**. $C_8H_9BrNO_5Zn$ (293 K). $M_r = 344.44$, trigonal, space group $P\bar{3}$, $a = b = 16.0568(11)$ Å, $c = 7.6324(10)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1704.2(3)$ Å^3, $Z = 6$, $D_{calcd} = 2.014$ g/cm^3, absorption coefficient 5.682 mm^{-1}, total reflections collected 13525, unique 2603 ($R_{int} = 0.064$), GOF = 1.159, $R1 = 0.0461$, $Rw = 0.1114$ ($I > 2\sigma(I)$). Crystal data for **2**. $C_7H_9NO_5Mn$ (293 K). $M_r = 242.09$, trigonal, space group $P\bar{3}$, $a = b = 14.2146(10)$ Å, $c = 8.1976(8)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1434.5(2)$ Å^3, $Z = 6$, $D_{calcd} = 1.681$ g/cm^3, absorption coefficient 1.375 mm^{-1}, total reflections collected 11189, unique 2151 ($R_{int} = 0.0367$), GOF = 1.134, $R1 = 0.0262$, $Rw = 0.0675$ ($I > 2\sigma(I)$). CCDC reference numbers, 602073 and 602074.