Anion effect on the topological frameworks of a series of manganese coordination polymers based on 1,4-bis(imidazol-1-yl)-benzene: Syntheses, crystal structures and magnetic properties

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ARTICLE INFO

ABSTRACT

In this work, the rod-like ligand 1,4-bis(imidazol-1-yl)-benzene (**bib**) has been utilized as a building block to perform counterion researches on the structural diversities of coordination polymers. A series of new manganese compounds, $\{[Mn(\mathbf{bib})_3(ClO_4)_2](CHCl_3)_2\}_n$ (**1**), $[Mn(\mathbf{bib})_2(N_3)_2]_n$ (**2**), $[Mn(\mathbf{bib})_2(HCO_2)_2]_n$ (**3**), $[Mn(\mathbf{bib})_2(Ac)_2]_n$ (**4**), $\{[Mn(\mathbf{bib})_2(CF_3SO_3)_2](CH_2Cl_2)_4\}_n$ (**5**), and $[Mn(\mathbf{bib})_2(SO_4)]_n$ (**6**) have been successfully synthesized. Compound **1** shows a 3D interpenetrating α-Po network only based on the **bib** linker. Compounds **2** and **3** exhibit a 2D (4,4) layer with parallel and incline interpenetration, respectively. Compounds **4** and **5** display a parallel-packing 2D (4,4) layer with the porosity of 23.4% and 61.4%, respectively. Compound **6** furnishes a 3D α-Po framework with a 2D (4,4) layer pillared by the μ_2-SO_4^{2-} ion. The structural diversities among **1**–**6** have been carefully discussed, and the roles of counterions (from coordination affinity and molecular size) in the self-assembly of coordination polymers have also been well documented. Furthermore, magnetic properties of **6** have been carefully studied.

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1. Introduction

Coordination polymers have attracted a great deal of recent attention, which is propelled by the aesthetic structure and topological feature as well as the potential applications in the gas storage, molecular magnet and so on [1]. The rapid growth in this area continues to provide a large number of functional materials with various fascinating topologies, and also has witnessed many comprehensive discussions on the control over the topological framework [2]. However, it is still a great challenge to rationally construct coordination polymers with predicted structures, especially characteristic elements closely related to the functionality, such as the porosity, entanglement and magnetic coupling mediator. The ligand backbone seems to be most important for the final structure [3], but factors affecting the topological framework are intricate and diverse in the formation of coordination polymers, including the coordination nature of metal node [4], solvent [5] and so on.

As an indispensable part of coordination polymers, the counterion has a great effect on the structure owing to the discrepancy of coordination affinity and molecular size [6]. The counterion with strong coordination ability could be viewed as a specific ligand, and thus it is significant for the extension of metal node, directly related to the topology and dimensionality. Furthermore, the coordinated counterion obviously exerts an influence on the volume of coordination sphere of metal node, which is closely relevant to the entanglement and porosity. Therefore, it is necessary to investigate the correlation between the counterion and topological structure, which is beneficial to interpret the law of self-assemble in coordination polymers.

Because of the strong coordinating ability of imidazole, the research of imidazole-containing ligands has experienced a drastic development [7]. The coordination chemistry of rigid bis(imidazole) ligands have been continuously explored in our group, and they are good candidates for the construction of porous or interpenetrating architecture due to the rod-like long backbone [8]. In this paper, compound 1,4-bis(imidazol-1-yl)benzene (**bib**) is chosen as the ligand to react with a series of manganese salts by employing different counterions. Via the above parallel processing method, six coordination polymers, $\{[Mn(\mathbf{bib})_3(ClO_4)_2](CHCl_3)_2\}_n$ (**1**), $[Mn(\mathbf{bib})_2(N_3)_2]_n$ (**2**), $[Mn(\mathbf{bib})_2(HCO_2)_2]_n$ (**3**), $[Mn(\mathbf{bib})_2(Ac)_2]_n$ (**4**), $\{[Mn(\mathbf{bib})_2(CF_3SO_3)_2]$

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$(CH_2Cl_2)_4\}_n$ (**5**) and $[Mn(\textbf{bib})_2(SO_4)]_n$ (**6**) have been obtained. All compounds have been characterized by elemental analysis and IR, and their crystal structures are elucidated by X-ray crystallography. The structural correlation has been carefully discussed to give a systematic research on the effect of counterion. In addition, compound **6** shows a 1D $[-SO_4-Mn-]_\infty$ magnetic unit, and magnetic properties have been well studied by fitting the experimental data.

2. Experimental section

2.1. Materials and general methods

All the starting materials and reagents were commercially obtained and used without any further purification. The ligand **bib** was synthesized according to the reported procedure [9]. Elemental analyses of C, H and N were performed on a Perkin-Elmer 240 C analyzer. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffract-ometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromater. Magnetic data were collected on a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer equipped with a 5T magnet using crushed crystals of the sample. The diamagnetic corrections were calcu-lated using Pascal's constants.

2.2. Synthesis of complexes

2.2.1. $\{[Mn(\textbf{bib})_3(ClO_4)_2](CHCl_3)_2\}_\infty$(**1**)

A mixture of CH_3OH and $CHCl_3$ (8 mL, 1:1 v/v), as a buffer layer, was carefully layered over a solution of **bib** (31.5 mg, 0.15 mmol) in $CHCl_3$ (6 mL). A solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (18 mg, 0.05 mmol) in CH_3OH (6 mL) was then layered over the buffer layer. The resultant solution was left to stand at room temperature for about three weeks. Then colorless block crystals suitable for X-ray crystal analysis were obtained by filtration. Yield: ~65% based on **bib**. Elemental analysis (%): calcd for $C_{38}H_{32}Cl_8MnN_{12}O_8$: C, 40.63; H, 2.87; N, 14.96. Found: C, 40.42; H, 2.80; N, 14.85. IR (KBr, cm^{-1}): 3552s, 3508s, 3446s, 3412s, 3129m, 3031w, 2027w, 1639m, 1617m, 1531s, 1306m, 1265m, 1245w, 1089s, 1066m, 961w, 930w, 833m, 759m, 740m, 623m, 546w, 490w.

2.2.2. $[Mn(\textbf{bib})_2(N_3)_2]_n$(**2**)

The mixture of $MnCl_2 \cdot 4H_2O$ (11.9 mg, 0.06 mmol), NaN_3 (5.9 mg, 0.09 mmol), and **bib** (25.2 mg, 0.12 mmol) was dissolved in 14 mL component solvent ($H_2O:C_2H_5OH=3:4$). Consequently, the resulting mixture was transferred and sealed in a 25 mL Teflon-lined autoclave, which was sealed and heated at 140 °C for three days, and then, followed by slow cooling (a descent rate of 2.5 °C h^{-f}) to room temperature. Colorless crystals were obtained with a yield of about 45% based on **bib**. Anal. Calcd for $C_{24}H_{20}MnN_{14}$: C, 51.53; H, 3.60; N, 35.05. Found: C, 51.28; H, 3.52; N, 34.94. IR (KBr, cm^{-1}): 3945w, 3485m, 3465s, 3419s, 3361s, 3242w, 3126m, 3030m, 2053s, 1911m, 1617m, 1531s, 1495s, 1440m, 1315s, 1244s, 1123s, 1094m, 1062s, 827s, 736m, 548m, 470w.

2.2.3. $[Mn(\textbf{bib})_2(HCO_2)_2]_n$(**3**)

The similar synthetic method as described above for compound **1**, except that $Mn(ClO_4)_2 \cdot 6H_2O$ was replaced by $Mn(HCO_2)_2 \cdot 2H_2O$. Yield: ~60% based on **bib**. Anal. Calcd for $C_{26}H_{22}MnN_8O_4$: C, 55.23; H, 3.92; N, 19.82. Found: C, 55.01; H, 3.84; N, 19.70. IR (KBr, cm^{-1}): 3969w, 3529s, 3481s, 3452s, 3150m, 2921m, 2785m, 2602w, 2093w, 1763w, 1591m, 1530s, 1440m, 1354s, 1301s, 1126m, 1062s, 960m, 829m, 751m, 648m, 549m, 409w.

2.2.4. $[Mn(\textbf{bib})_2(Ac)_2]_n$(**4**)

The procedure was the same as compound **1** except that Mn $(ClO_4)_2 \cdot 6H_2O$ was replaced by $Mn(Ac)_2 \cdot 4H_2O$. Yield: ~55% based on **bib**. Anal. Calcd for $C_{28}H_{26}MnN_8O_4$: C, 56.66; H, 4.41; N 18.88. Found: C, 56.45; H, 4.32; N, 18.76. IR (KBr, cm^{-1}): 3734w, 3452m, 3408s, 3236w, 3072m, 2362m, 1927w, 1723w, 1577s, 1526s, 1509s, 1431s, 1396m, 1360s, 1315w, 1276s, 1241m, 1129s, 1060s, 959m, 660m, 519m, 411w.

2.2.5. $\{[Mn(\textbf{bib})_2(CF_3SO_3)_2](CH_2Cl_2)_4\}_n$(**5**)

A mixture of C_2H_5OH and CH_2Cl_2 (8 mL, 1:1 v/v), as a buffer layer, was carefully layered over a solution of **bib** (25.2 mg, 0.12 mmol) in CH_2Cl_2 (6 mL). A solution of $Mn(CF_3SO_3)_2$ (21.2 mg, 0.06 mmol) in C_2H_5OH (6 mL) was then layered over the buffer layer, and the resultant solution was left to stand at room temperature for about four weeks. Then Colorless block crystals suitable for X-ray crystal analysis were obtained by filtration. Yield: ~50% based on **bib**. Anal. Calcd for $C_{30}H_{28}Cl_8F_6MnN_8O_6S_2$: C, 32.37; H, 2.54; N, 10.07. Found: C, 32.13; H, 2.47; N, 9.95. IR (KBr, cm^{-1}): 3552s, 3475s, 3420s, 3162m, 3131m, 2526w, 2308w, 1902w, 1638m, 1618m, 1529s, 1493m, 1441w, 1287s, 1265s, 1246s, 1174s, 1120m, 1030m, 839w, 740w, 640m, 550w, 517w, 488w.

2.2.6. $[Mn(\textbf{bib})_2(SO_4)]_n$(**6**)

A mixture of C_2H_5OH and H_2O (8 mL, 1:1 v/v), as a buffer layer, was carefully layered over a solution of $MnSO_4 \cdot H_2O$ (10.14 mg, 0.06 mmol) in H_2O (6 mL). A solution of **bib** (25.2 mg, 0.12 mmol) in C_2H_5OH (6 mL) was then layered over the buffer layer, and the layered solution was left to stand at room temperature for about three weeks. Then colorless block crystals suitable for X-ray crystal analysis were obtained by filtration. Yield: ~65% based on **bib**. Anal. Calcd for $C_{24}H_{20}MnN_8O_4S$: C, 50.44; H, 3.53; N, 19.61. Found: C, 50.22; H, 3.45; N, 19.49. IR (KBr, cm^{-1}): 3691m, 3500w, 3438m, 3115s, 3068s, 2362m, 1795w, 1616m, 1531s, 1490m, 1303s, 1254m, 1156s, 1111s, 1072s, 959m, 927m, 880w, 841m, 792m, 658m, 548m, 492w.

2.3. X-ray data collection and structure determinations

Suitable X-ray single crystals diffraction data of **1–6** were selected and mounted on a Rigaku MM-007/Saturn 70 with graphite mono-chromatic Mo-$K\alpha$ radiation ($\lambda=0.71073$ Å). The program SAINT was used for integration of the diffraction profiles [10]. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [11]. Metal atoms in each complex was located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically. Further details for structural analysis are summarized in Table 1, and selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. $\{[Mn(bib)_3(ClO_4)_2](CHCl_3)_2\}_\infty$ (**1**)

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/n$, and the Mn^{II} ion locates at the inversion center. As show in Fig. 1a, the Mn^{II} ion lies in a distorted octahedral coordination environment, which is surrounded by six imidazole rings of distinct **bib** ligands. The lengths of equatorial bonds are 2.258(5) Å, with an elongation to