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两个含有叠氮根和硫氰根配位单元的 3,4-双咪唑噻吩锰(Ⅱ)配位聚合物的合成与晶体结构

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摘要:制备了 2 个含有叠氮根和硫氰根配位单元的 3,4-双咪唑噻吩(L)的锰(Ⅱ)配位聚合物$[Mn(L)(N_3)_2(H_2O)]_n$ (**1**)和$[Mn(L)_2(SCN_3)_2]_n$ (**2**)并报道了它们的晶体结构。化合物 **1** 和 **2** 是通过 3,4-双咪唑噻吩与四水醋酸锰反应,同时分别引入过量的线性三原子阴离子(N_3^-和 SCN^-)以取代醋酸根作为抗衡离子制备而得。单晶结构分析表明 **1** 和 **2** 具有相同的无限二维链状空间结构,但是由不同的 44 元的$[Mn_6(L)_4(2N_3)_2]$和 36 元的$[Mn_4L_4]$大环单元结构组成。此外,配位聚合物 **1** 中的叠氮根分别采用端基单齿和桥联双齿的配位方式,而配位聚合物 **2** 中的硫氰根仅以端基氮原子与 Mn(Ⅱ)离子配位。

关键词:锰(Ⅱ)配合物;3,4-双咪唑噻吩;叠氮根;硫氰根;晶体结构
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Syntheses and Crystal Structures of Two Manganese(Ⅱ) Coordination Polymers Having 3,4-Diimidazol-Thiophene Ligand Coordinated by Azide and Thiocyanate Counterions

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Abstract: Two manganese(Ⅱ) complexes having V-Shaped 3,4-diimidazol-thiophene ligand formulated as $[Mn(L)(N_3)_2(H_2O)]_n$ (**1**) and $[Mn(L)_2(SCN_3)_2]_n$ (**2**) have been synthesized and structurally compared. The treatment of 3,4-diimidazol-thiophene with $Mn(CH_3COO)_2\cdot 4H_2O$ in the presence of excess three-atom anions (N_3^- and SCN^-) gives 2D coordination polymers **1** and **2** composed of 44-membered $[Mn_6(L)_4(2N_3)_2]$ and 36-membered $[Mn_4L_4]$ metallocyclic units, respectively, where linear N_3^- and SCN^- anions serve as conterions in the replacement of acetate anion. X-ray single-crystal diffraction analyses reveal that N_3^- anions have two kinds of coordination fashions (monodentate and bidentate) in **1**. In contrast, all the SCN^- anions in **2** act as only monodentate N-coordinating mode. CCDC: 994733, **1**; 994734, **2**.

Key words: manganese(Ⅱ) complex; 3,4-diimidazol-thiophene; azide; thiocyanate

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0 Introduction

During the past several decades, thiophenes and their derivatives have attracted much attention in the field of molecular-based materials[1] such as organic light-emitting diodes[2] and field-effect transistors[3], because they are claimed to be ideal functional elements and building blocks in the research of molecular electronics. Particularly, specific attention has been paid to the syntheses and properties of novel π-conjugated copolymers with different electron-attracting N-containing heterocycles and electron-donating thiophene units[4-6]. The use of a variety of metal ions and multi-functional thiophene based ligands in the self-assembly of metal coordination polymers (MCPs) has been an especially active area, because of their intriguing molecular topologies and many potential applications[7]. However, some other factors may affect the structural topologies of such coordination frameworks, since the final chemical structures are also controlled by the reaction temperature[8], pH value[9], solvent system[10], counterion[11], and the conformation and shape of organic building blocks[12].

In many cases, subtle changes of ligand configurations or counterions can generate different supramolecular architectures, so the rational design and synthesis of suitable ligands are very important and interesting issues for constructing novel functional MCPs[13]. For example, bent organic ligands with V-shaped molecular conformation can be used as building blocks for building supramolecular cages, helixes, and other novel polymeric structures, which differ greatly with corresponding linear ligands[14]. In our previous work, some linear and V-shaped isomeric aromatic heterocyclic ligands with thiophene or bithiophene centers and imidazole or triazole terminal groups have been used for constructing of a series of Ag(Ⅰ), Zn(Ⅱ) and Cd(Ⅱ) coordination polymers with d^{10} electronic structurers[15]. However, other transition-metal ions have not been explored in the coordination chemistry of this family of thiophene-centered compounds.

In this work, 3,4-diimidazol-thiophene was used as an organic μ_2-bridging ligand to react with Mn$(CH_3COO)_2\cdot 4H_2O$ in the presence of excess N_3^- and SCN^- anions. As a result, two novel manganese(Ⅱ) coordination polymers, formulated as $[Mn(L)(N_3)_2(H_2O)]_n$ (**1**) and $[Mn(L)_2(SCN_3)_2]_n$ (**2**), have been obtained by the solvent diffusion method. They are further structurally and spectrally characterized and compared, where N_3^- anions have two kinds of coordination fashions (monodentate and bidentate) in **1** and SCN^- anions act as only monodentate N-coordinating mode in **2**.

1 Experimental

1.1 Materials and instruments

All reagents and solvents were of analytical grade and used without any further purification. 3,4-Diimidazol-thiophene (L) was prepared via a previously reported approach[16]. Elemental analyses (EA) for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Fourier transform infrared (FT-IR) spectra (4 000~400 cm^{-1}) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. UV-Vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm.

1.2 Synthesis of $[Mn(L)(N_3)_2(H_2O)]_n$ (1)

A buffer layer of a NaN_3 (13 mg, 0.2 mmol) solution (10 mL) of methanol/water (2∶1, *V*/*V*) was carefully layered over a solution of $Mn(CH_3COO)_2\cdot 4H_2O$ (25 mg, 0.1 mmol) in water (5 mL). Then a solution of 3,4-diimidazol-thiophene (21 mg, 0.1 mmol) in methanol (5 mL) was layered over the buffer layer. Grey crystals of **1** were isolated after two weeks in a yield of 22 mg (59%). Anal. Calcd. for $C_{10}H_{10}MnN_{10}OS$ (%): C: 32.18, H: 2.70, N: 37.53%. Found (%): C: 32.12; H: 2.77; N: 37.45. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3 414 (b), 2 135 (w), 2 052 (m), 1 578 (m), 1 414 (m), 1 059 (m). UV-Vis in methanol: λ_{max}=247 nm.

1.3 Synthesis of $[Mn(L6)_2(SCN_3)_2]_n$ (2)

MCP **2** was prepared in a similar way to that used for **1**, except that excess KSCN was used instead

of NaN_3. Yield, 39 mg (65%). Anal. Calcd. for $C_{22}H_{16}MnN_{10}S_4$ (%): C: 43.77, H: 2.67, N: 23.20%. Found(%): C: 43.94; H: 2.73; N: 23.14%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3 417 (b), 3 125 (m), 3 072 (m), 2 047 (s), 1 573 (m), 1 537 (m), 1 523 (m), 1 499 (s), 1 338 (m), 1 319 (m), 1 236 (m), 1 109 (m), 1 097 (m), 1 067 (m), 1 043 (m), 929 (m), 833 (s), 805 (s), 738 (s), 651 (s) and 631 (m). UV-Vis in methanol: λ_{max}=247 nm.

1.4 X-ray crystallography

Both single-crystal samples of **1** and **2** were covered with glue and mounted on glass fibers for data collection with Mo $K\alpha$ radiation (λ=0.071 073 nm) on a Bruker SMART 1000 diffractometer equipped with a CCD camera. Data collection was performed by using SMART program and cell refinement and data reduction were made with the SAINT program[17]. All the structures were solved by directed method and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 6.10[18]. All non-H atoms were anisotropically refined, and all hydrogen atoms except two water protons in **1** were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. Two water protons were located in the difference synthesis first and their positions were fixed geometrically and the distances to oxygen atom were set as 0.082 and 0.085 nm. Furthermore, the two protons were assigned fixed isotropic thermal parameters at 1.5 times the equivalent isotropic U of the oxygen atom. All calculations were carried out on a PC computer with the SHELXTL PC program package and molecular graphics were drawn by using DIAMOND software. The summary of the crystal data, experimental details and refinement results for complex **1** and **2** is listed in Table 1, while selected bond distances and bond angles related to the central Mn(Ⅱ) ion are given in Table 2.

CCDC: 994733, **1**; 994734, **2**.

Table 1 Crystal data and structure refinement parameters for complex 1 and 2

Complex	**1**	**2**
Empirical formula	$MnC_{10}H_{10}N_{10}OS$	$MnC_{22}H_{16}N_{10}S_4$
Formula weight	373.28	603.67
Crystral size / mm	0.10×0.12×0.14	0.16×0.16×0.16
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Cmca$
a / nm	1.219 9(1)	1.867 2(5)
b / nm	0.793 1(1)	1.709 3(5)
c / nm	1.634 3(2)	0.796 7(2)
β / (°)	111.138(1)	
V / nm^3	1.474 9(2)	2.542 8(12)
Z	4	4
D_c / ($g\cdot cm^{-3}$)	1.681	1.577
F(000)	756	1 228
μ(Mo $K\alpha$) / mm^{-1}	1.058	0.882
Max. / min. transmission	0.901 6 / 0.866 0	0.871 7 / 0.871 7
h_{min} / h_{max}	−14 / 14	−22 / 22
k_{min} / k_{max}	−5 / 9	−20 / 11
l_{min} / l_{max}	−19 / 15	−8 / 9
Parameters	208	92
Reflections collected	7 125	5 984
Independent reflections (R_{int})	2 601 (0.058)	1 162 (0.083)
Observed reflections ($I>2\sigma(I)$)	2 168	1 106

Continued Table 1

R_1, wR_2 ($I>2\sigma(I)$)[a]	0.034 2, 0.087 5	0.041 3, 0.101 0
R_1, wR_2 (all data)[a]	0.042 2, 0.092 6	0.042 6, 0.102 0
Goodness of fit on F^2	1.05	1.16
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / ($e\cdot nm^{-3}$)	440, −480	470, −430

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=[\sum[w(F_o^2-F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

Table 2　Selected bond distances (nm) and angles (°) for complex 1 and 2

		1			
Mn1-O1	0.218 3(2)	Mn1-N4[a]	0.222 9(2)	Mn1-N5	0.228 2(2)
Mn1-N8	0.219 5(2)	Mn1-N2	0.224 6(2)	Mn1-N7[b]	0.228 9(2)
O1-Mn1-N8	88.6(1)	N4[a]-Mn1-N5	87.0(1)	O1-Mn1-N7[b]	87.3(1)
O1-Mn1-N4[a]	92.3(1)	N1-Mn1-N5	88.8(1)	N1-Mn1-N7[b]	87.0(1)
N8-Mn1-N4[a]	91.1(1)	O1-Mn1-N1	91.8(1)	N8-Mn1-N7[b]	175.7(1)
O1-Mn1-N5	178.2(1)	N1-Mn1-N8	94.4(1)	N4[a]-Mn1-N7[b]	87.9(1)
N8-Mn1-N5	93.1(1)	N4[a]-Mn1-N1	173.3(1)	N5-Mn1-N7[b]	91.1(1)
		2			
Mn1-N3	0.223 3(3)	Mn1-N1	0.224 6(2)		
N3[a]-Mn1-N1	89.9(1)	N1[a]-Mn1-N3	89.9(1)	N1-Mn1-N1[c]	91.1(1)
N3-Mn1-N1	90.1(1)	N1-Mn1-N1[b]	180.00		
N3-Mn1-N3[a]	180.00	N1-Mn1-N1[a]	88.9(1)		

Symmetry code: [a] 3/2−x, −1/2+y, 1/2−z; [b] 1−x, −y, −z for **1**; [a] x, −y, −z; [b] −x, −y, −z; [c] −x, y, z for **2**.

2　Results and discussion

2.1　Syntheses and spectral characterizations

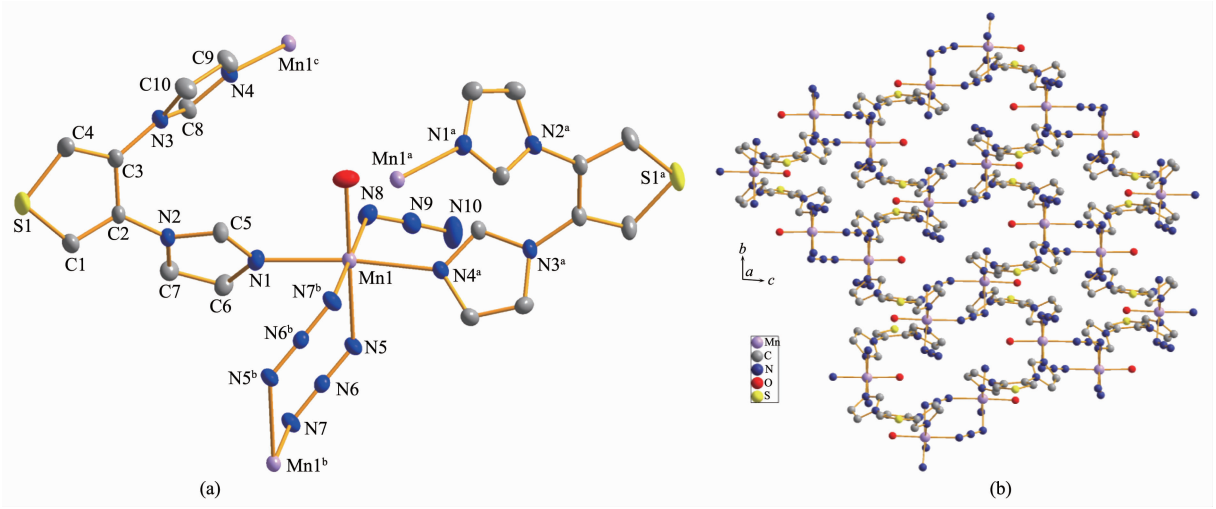
As we know, acetate ion has weak coordination ability, but linear three-atom N_3^- and SCN^- anions have much stronger coordination ability and they are often used as bridging counterions to connect adjacent metal centers in the process of self-assembly. In our experiments, excess linear N_3^- or SCN^- anion was added in the process of reaction between 3,4-diimidazol-thiophene and Mn $(CH_3COO)_2\cdot 4H_2O$, in order to replace the original acetate anion and coordinate with the central Mn(Ⅱ) ion. By using this synthetic strategy, 2D Mn(Ⅱ) coordination polymers **1** and **2** have been produced, respectively, where N_3^- and SCN^- anions take part in the coordination with Mn(Ⅱ) ions and exhibit different coordination modes.

The methanol solutions of MCPs **1** and **2** with the same concentration of 1.0×10^{-5} mol·L^{-1} have the same UV-Vis absorption peak at 247 nm corresponding to the π-π* transitions between the heterocyclic aromatic rings of 3,4-diimidazol-thiophene. The peak is different from the free ligand at 240 nm, indicative of the alteration of molecular conformation after metal-ion complexation. The formation of above-mentioned N_3^- and SCN^- included MCPs **1** and **2** can be easily verified from their FT-IR spectra. In **1**, there are two peaks at 2 135 and 2 052 cm^{-1}, respectively, while **2** only displays one peak at 2 047 cm^{-1}. In comparison with the free N_3^- and SCN^- anions at 2 130/2 107 cm^{-1} and 2 051 cm^{-1}, shifts of 5/55 cm^{-1} and 4 cm^{-1} have been found, indicative of the formation of coordinative bonds. Furthermore, the existence two peaks in **1** and one peak in **2** reveals two possible coordination modes for N_3^- anion and one coordination fashion for SCN^- anion, respectively, which can be further supported by the following X-ray single-crystal structure studies.

2.2　Crystal structures

2.2.1　$[Mn(L)(N_3)_2(H_2O)]_n$ (**1**)

The molecular structure of **1** with the atom-numbering scheme is shown in Fig.1a, there is only one crystallographically independent manganese (Ⅱ)



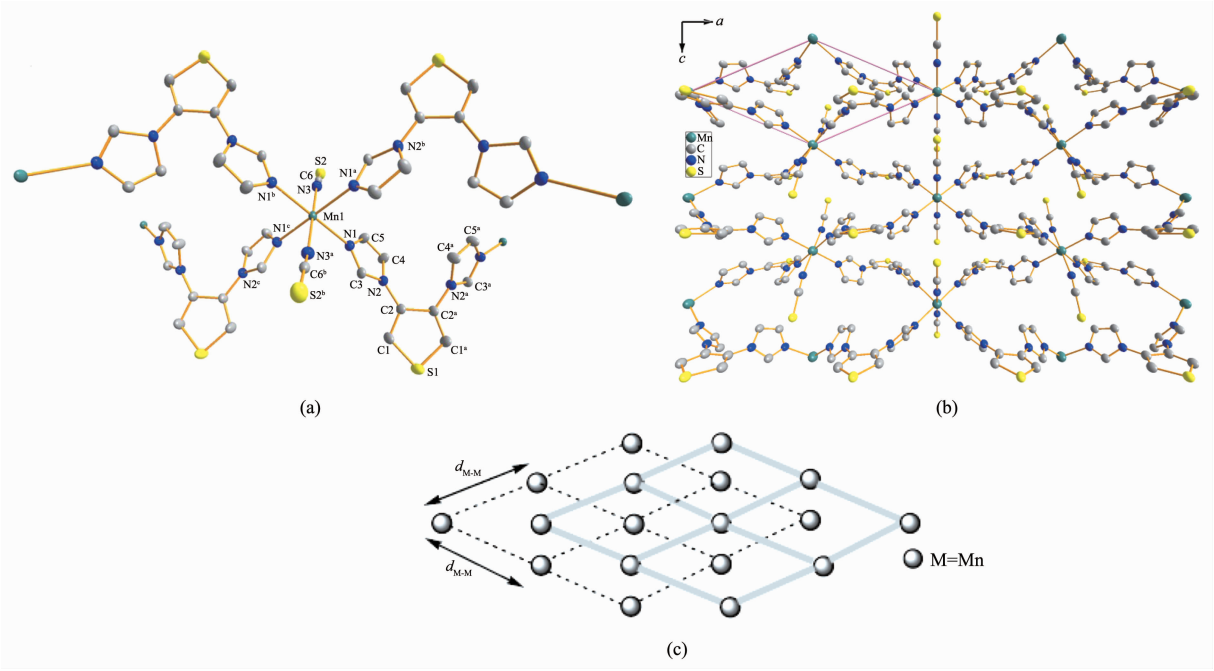
Symmetry codes: [a] 3/2−*x*, −1/2+*y*, 1/2−*z*; [b] 1−*x*, −*y*, −*z*; [c] 3/2−*x*, 1/2+*y*, 1/2−*z* in (a)

Fig.1 (a) ORTEP drawing with 30% probability displacement ellipsoids of complex **1**; (b) View of 2D polymeric structure of complex **1**

atom in distorted octahedral geometry, which is coordinated by two nitrogen atoms (N2 and N4^a, 3/2−*x*, −1/2+*y*, 1/2−*z*) from two different 3,4-diimidazol-thiophene ligands, one nitrogen atom (N7^b, 1−*x*, −*y*, −*z*) from one of bridging azide anion (N_3^-) and one nitrogen atom (N8) of the terminal N_3^- ion comprising the basal coordination plane. The axial coordination sites are occupied by one nitrogen atom (N5) of the bridging azide group and the oxygen atom (O1) of one coordination water molecule. The measured Mn-N and Mn-O bond distances are in the range of 0.218 3(2)~0.228 9(2) nm. The N_3^- ions adopt two different coordination modes in this structure: one acts as a terminal ligand, the other serves as a μ_2-1,3 (end-to-end, EE) bridge to link neighboring metal centers. The 3,4-diimidazol-thiophene ligand here also adopts a trans conformation, as shown in Fig.1a, and the two imidazole rings are also not coplanar to the central thiophene ring. They are staggered at each side of the thiophene plane with the dihedral angles of 44.7(1)° and 51.2(1)°, respectively. In addition, the dihedral angle between two coordinated imidazole rings around the Mn(Ⅱ) ion is 50.0 (1)°. One double EE-N_3 bridge and two continuous L bridges alternatively link the metal ions forming a 44-membered $[Mn_6(L)_4(2N_3)_2]$ macrocyclic framework. Such a metallomacrocyclic unit repeats along the *bc*-plane to generate a 2D neutral layer as shown in Fig.2b. The Mn ⋯ Mn separation linked by the double bridging *EE*-N_3 is 0.525 8(2) nm and that across the bridging 3,4-diimidazol-thiophene ligand is 0.559 3(2) nm. There are intralayer O−H ⋯ N hydrogen bonds between the hydrogen atoms of coordinated water and the terminal nitrogen atom of N_3^- anion, further stabilizing the 2D layer structure.

2.2.2 $[Mn(L)_2(SCN_3)_2]_n$ (**2**)

The X-ray structure analysis shows that MCP **2** crystallizes in the orthorhombic space group Cmca with one Mn (Ⅱ) ion, two 3,4-diimidazol-thiophene ligands, and two thiocyanate ions in the asymmetric unit (Fig.2a). Each Mn(Ⅱ) metal center is located on a symmetric center with six-coordinate octahedral geometry, formed equatorially by four nitrogen atoms of imidazole rings (N1, N1^a, N1^b, , N1^c, Symmetry codes: [a] *x*, −*y*, −*z*; [b] −*x*, −*y*, −*z*; [c] −*x*, *y*, *z*) from four 3,4-diimidazol-thiophene ligands and axially by two nitrogen atoms (N3 and N3^a, Symmetry codes: [a] *x*, −*y*, −*z*) from two thiocyanate anions. The thiocyanate anion here acts as a monodentate N-bounding ligand with an end-on coordination mode. It is noted that each 3,4-diimidazol-thiophene ligand is bound to two adjacent metal ions adopting the trans conformation and the dihedral angle between the thiophene ring and the two side imidazole rings is equal to 45.2(1)°



Symmetry codes: [a] $x, -y, -z$; [b] $-x, -y, -z$; [c] $-x, y, z$ in (a)

Fig.2　(a) ORTEP drawing with 30% probability displacement ellipsoids of complex **2**; (b) View of 2D polymeric structure of complex **2**; (c) Metal arrangement between 2D flat layers

and the dihedral angle between planes of the two coordinated imidazole rings is 48.9 (1)°. It is worthwhile to point out that four metal ions connect four 3,4-diimidazol-thiophene bridging ligands forming a 36-membered $[Mn_4L_4]$ metallocyclic ring in the structure of **2**. Each Mn(Ⅱ) ion is linked by four equivalent 3,4-diimidazol-thiophene ligands and vice versa. Resultantly, a 2D MCP with puckered rhombohedral grid units is constituted along the ac plane, as illustrated in Fig.2b, where each rhombohedral grid is organized by four 3,4-diimidazol-thiophene ligands as the four edges and four Mn(Ⅱ)ions as the four vertexes. The grid has a length of 1.015 0(2) nm with two diagonals of 0.796 7(2) nm and 1.867 2(2) nm and interior angles of 46.2(1)° and 133.8(1)°, respectively. All Mn(Ⅱ) ions are strictly coplanar in every layer with the interlayer distance of 0.499 0(2) nm. The space between the neighboring layers is occupied by the mono-coordinated SCN^- groups. Moreover, adjacent layers are arranged in an offset manner, where every Mn(Ⅱ) ion of one layer is rightly positioned between the vicinal centers of rhombus-type grids (Fig.2c).

3　Conclusion

In summary, two novel manganese(Ⅱ) coordination polymers, $[Mn(L)(N_3)_2(H_2O)]_n$ (**1**) and $[Mn(L)_2(SCN_3)_2]_n$ (**2**) based on the same V-shaped 3,4-diimidazol-thiophene μ_2-bridging ligand, have been successfully synthesized, spectrally and structurally characterized. An anion exchange and coordination synthetic strategy is used to build these two 2D Mn(Ⅱ) coordination polymers. In complex **1** and **2**, the central manganese(Ⅱ) ions are both in distorted octahedral geometry with 3,4-diimidazol-thiophene and N_3^-/SCN^- anions as ligands. However, the linear three-atom N_3^- and SCN^- anions have different coordination modes in **1** and **2**. Because of the participancy of coordinated N_3^- and SCN^- anions, different 44-membered $[Mn_6(L)_4(2N_3)_2]$ and 36-membered $[Mn_4L_4]$ metallocyclic units are constructed in 2D Mn(Ⅱ) coordination frameworks of **1** and **2**, respectively.

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