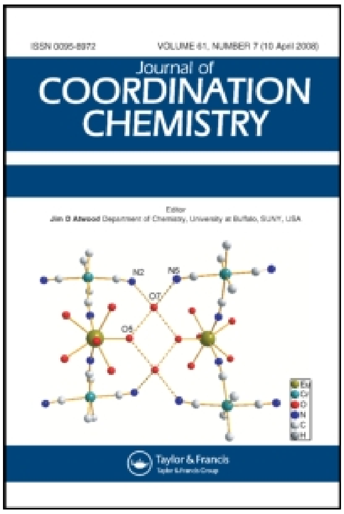

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Note

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURES OF THE COORDINATION POLYMERS [Cu(II)$(NO_3)_2$(BBMB) and [Mn(II)$Cl_2$$(BBMB)_2$] [BBMB = 1,4-BIS(1-BENZIMIDAZOLYLMETHYL) BENZENE]

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Two novel coordination polymers, $[Cu(II)(NO_3)_2(bbmb)]_n$ (**1**) and $[Mn(II)(Cl_2)(BBMB)_2]$ (**2**) [bbmb = 1,4-bis(1-benzimidazolylmethyl)benzene], were synthesized and characterized by IR and thermal analyses. Single-crystal X-ray diffraction analysis shows that Polymer **1** exhibits a distorted metal tetrahedron in its structure, involving two nitrogen atoms from bbmb ligands and two oxygen atoms from NO_3 groups. Each $Cu(II)(NO_3)_2$ unit is bridged by bbmb to form a zigzag chain structure. Polymer **2** possesses a two-dimensional network. The coordination environment around Mn(II) is a distorted octahedron and its solid-state structure exhibits a layered packing mode. In the polymers the two coordinating nitrogen atoms on bridging bbmb ligands are trans to the central benzene plane.

Keywords: 1,4-Bis(1-benzimidazolylmethyl)benzene; X-ray structue; Polymer; Linear ligand

INTRODUCTION

The construction of solid-state coordination polymers has become an area of increasing interest in recent years because of their specific properties in magnetic materials, non-linear optical materials and catalysis [1]. A great number of ligands can be used for the preparation of coordination polymers with metals, especially those linear ligands containing pyridine rings such as 4,4′-bipyridine [2], 1,2-bis(4-pyridyl)ethane [3], *N*,*N*-bis(4-pyridylmethyl)piperazine [4], 1,4-bis(4-pyridylmethoxyl)benzene [5] and so on. Studies of such ligands with imidazole as a substitute for pyridine rings in complexes with divalent metals have been reported [6–12]. 1-Substituted benzimidazole derivatives have not been investigated as analogs of ligands of imidazole derivatives. Recognizing this we are exploring the design and preparation of 1,4-bis(1-benzimidazolylmethyl)benzene (bbmb), a ligand with rigid backbone. In this article, two new

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coordination polymers [Cu(II)$(NO_3)_2$(bbmb)]$_n$ (**1**) and [Mn(II)Cl_2(bbmb)$_2$]$_m$ (**2**) are reported. By comparison with 1,4-bis(1-imidazolylmethyl)benzene (bix), which forms a one-dimensional coordination polymer with Cu(II) [8] a *quasi*-two-dimensional coordination polymer with Mn(II) with bix acting as both a terminal and a bridging ligand [9] and an interpenetrating network with both Zn(II) and Ag(I) [6,7]. The ligand bbmb forms a one-dimensional zigzag coordination polymer with Cu(II) with bbmb as a bridging ligand and a two-dimensional planar network structure of rhombohedral grids with Mn(II), completely different to the complexes of bix with Cu(II), Mn(II), Zn(II) and Ag(I).

EXPERIMENTAL

All materials were purchased and used without further purification. IR spectra were recorded on a Perkin-Elmer FTIR1750 spectrophotometer with KBr pellets in the region 400–4000 cm^{-1}. Carbon, hydrogen and nitrogen analyses were carried out on a Carlo-Erba 1106 instrument. Thermal analyses were carried out with a Rigaku instrument in a nitrogen atmosphere from room temperature to 800°C.

1,4-Bis(1-benzimidazolylmethyl)benzene

Benzimidazole (5 g, 42 mmol) was dissolved in acetone (50 mL), then potassium carbonate (12 g) and potassium iodide (0.5 g) were added. After stirring for 30 min α,α'-dichloro-*p*-xylene (3.5 g, 20 mmol) was added dropwise. The mixture was refluxed for 8 h with vigorous stirring. After cooling, the solution was filtered and the filtrate evaporated to dryness. The residue was recrystallized from alcohol/water (1:1) to give 5.05 g (70.5% of pale-yellow, crystalline 1,4-bis(1-benzimidazolylmethyl)benzene, m.p: 195–197°C. Anal. Calc. for $C_{22}H_{18}N_4$ (%): C, 78.11; H, 5.32; N, 16.56. Found: C, 78.41; H, 5.48; N, 16.42. ^{1}H NMR: δ 5.34(s, 4H, $2CH_2$), 7.14(s, 4H, benzene ring), 7.24 ~ 7.30(m, 6H, benzimidazole at 5,6,7-positions), 7.82(d, 2H, benzimidazole at 4-position), 7.94(s, 2H, benzimidazole at 2-position).

[Cu$(NO_3)_2$(bbmb)]$_n$ (1)

An acetonitrile (3 mL) solution of bbmb (16.9 mg, 0.05 mmol) was added dropwise to an acetonitrile (2 mL) solution of $Cu(NO_3)_2 \cdot 3H_2O$ (6.04 mg, 0.025 mmol) to give a clear blue solution. Bottle-green crystals were obtained the next day. Anal. Calc. for $C_{22}H_{20}N_6O_7Cu$ (%): C, 48.53; H, 3.68; N, 15.44. Found: C, 45.64; H, 3.20: N, 15.36.

[MnCl_2(bbmb)$_2$]$_m$ (2)

A solution of $MnCl_2$ (6.3 mg, 0.05 mmol) in methanol (2 mL) was added slowly to a solution of bbmb (33.8 mg, 0.1 mmol) in methanol (3 mL). The clear yellow solution was left to stand undisturbed at room temperature. The next day, pale-yellow crystals were obtained. Anal. Calc. for $C_{44}H_{36}N_8MnCl_2$ (%): C, 65.84; H, 4.49; N, 13.96. Found: C, 66.00; H, 4.82; N, 14.41.

TABLE I Crystal data and structure refinement details for Complexes **1** and **2**

	Complex (*1*)	*Complex* (*2*)
Empirical formula	$C_{22}H_{20}CuN_6O_7$	$C_{44}H_{36}Cl_2MnN_8$
Formula weight	543.98	802.65
Temperature	293(2) K	457(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, P2(1)/n
Unit cell dimensions	$a = 11.0987(11)$ Å $\alpha = 74.142(2)$	$a = 11.664(3)$ Å
	$b = 11.4587(11)$ Å $\beta = 71.858(2)$	$b = 13.334(3)$ Å $\beta = 90.046(2)$
	$c = 14.1047(14)$ Å $\gamma = 88.120(2)$	$c = 1.664(3)$ Å
Volume	1637.1(3) Å	1814.2(7) Å
Z, Calculated density	3, 1.655 Mg/m^{-3}	2, 1.469 Mg/m^{-3}
Absorption coefficient	1.061 mm^{-1}	0.558 mm^{-1}
$F(000)$	837	830
Crystal size	0.40 × 0.20× 0.20 mm	0.40 × 0.30× 0.30 mm
Theta range for data collection	1.58 to 25.00°	2.32 to 25.00°
Index ranges	$-7 \Leftarrow h \Leftarrow 14$ $-14 \Leftarrow k \Leftarrow 13$	$-11 \Leftarrow h \Leftarrow 15$ $-12 \Leftarrow k \Leftarrow 16$
	$-17 \Leftarrow l \Leftarrow 18$	$-14 \Leftarrow l \Leftarrow 14$
Reflections collected/unique	6827/5653 [R(int) = 0.0345]	7285/3180 [R(int) = 0.1584]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5653/0/428	3180/0/250
Goodness-of-fit on F^2	0.959	1.108
Final R indices [$I > 2\sigma > (I)$]	$R1 = 0.0665$, $wR2 = 0.0889$	$R1 = 0.1052$, $wR2 = 0.2332$
R indices (all data)	$R1 = 0.1070$, $wR2 = 0.0985$	$R1 = 0.1452$, $wR2 = 0.2546$
Largest diff. peak and hole	0.640 and -0.518 e A^3	0.893 and -0.920 e A^3

Crystal Structure Determination

Intensity data for the compounds were collected on a SMART-APEX X-ray diffractometer. Graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω–2θ scan mode was used. The structures were solved directly and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were constrained at estimated positions. All calculations were performed using the SHELXL-97 crystallographic software package [13]. Crystal data for the two complexes are listed in Table I. Selected bondlengths and angles are given in Table II. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

IR Specta

Selected IR data for the ligand and complexes are given in Table III. Bands from 3031 to 3143 cm^{-1} are associated with Ar–H stretching. Bands characteristic of ligand vibration ($\nu_{C=N}$ $\nu_{C=C}$ stretching) observed at 1610 and 1488 cm^{-1} are shifted towards higher energy (*ca.* 4–40 cm^{-1}) by complexation to copper and manganese ions. These indicate that benzimidazole rings participate in the formation of complexes. Peaks at 1463, 1384 and 1291 cm^{-1} in Complex **2** are assigned to $\nu_{N–O}$ modes of the nitrate groups, suggesting coordinated nitrate [14].

TABLE II Selected bondlengths (Å) and angle (°) for Complexes **1** and **2**

	Atoms	*Distance*	*Atoms*	*Angle*
Complex **1**	Cu(1)–N(3)	1.946(3)	N(1)–Cu(1)–O(3)	157.53(14)
	Cu(1)–O(3)	2.015(3)	N(3)–Cu(1)–N(1)	92.31(14)
	O(3)–N(6)	1.287(4)	N(1)–Cu(1)–O(5)	94.17(13)
	Cu(1)–O(2)	2.463	N(3)–Cu(1)–O(5)	163.62(14)
	Cu(1)–N(1)	1.960(3)	O(5)–Cu(1)–O(3)	86.87(12)
	N(7)–O(6)	1.220(4)	N(3)–Cu(1)–O(3)	92.85(13)
	N(6)–O(1)	1.216(4)	O(1)–N(6)–O(2)	123.3(5)
	Cu(1)–O(4)	2.456	O(1)–N(6)–O(3)	119.6(4)
	Cu(1)–O(5)	1.980(3)	O(2)–N(6)–O(3)	117.1(4)
	N(7)–O(4)	1.237(4)		
	N(6)–O(2)	1.236(4)		
Complex **2**	Mn(1)–N(1)	2.327(6)	N(1)–Mn(1)–N(1)$^{\#1}$	180.0
	Mn(1)–N(3)	2.350(5)	N(1)$^{\#1}$–Mn(1)–N(3)$^{\#1}$	84.2(2)
	Mn(1)–N(1)$^{\#1}$	2.327(6)	N(1)–Mn(1)–Cl(1)	92.90(13)
	Mn(1)–Cl(1)	2.502(2)	N(3)–Mn(1)–Cl(1)	92.06(13)
	Mn(1)–N(3)$^{\#1}$	2.350(5)	N(3)$^{\#1}$–Mn(1)–Cl(1)$^{\#1}$	92.06(13)
	Mn(1)–Cl(1)$^{\#1}$	2.502(2)	N(1)–Mn(1)–N(3)$^{\#1}$	95.8(2)
	N(1)–C(1)	1.327(8)	N(1)–Mn(1)–N(3)	84.2(2)
	N(1)–C(2)	1.389(8)	N(1)$^{\#1}$–Mn(1)–Cl(1)	87.10(13)
	N(2)–C(1)	1.359(8)	N(1)–Mn(1)–Cl(1)$^{\#1}$	87.10(13)
	N(2)–C(8)	1.464(8)	N(3)–Mn(1)–Cl(1)$^{\#1}$	87.94(13)
	N(3)–C(21)	1.315(8)	N(1)$^{\#1}$–Mn(1)–N(3)	95.8(2)
	N(3)–C(15)	1.396(8)	N(3)$^{\#1}$–Mn(1)–N(3)	180.0
	N(4)–C(21)	1.335(8)	N(3)$^{\#1}$–Mn(1)–Cl(1)	87.94(1)
	N(4)–C(20)	1.383(8)	N(1)$^{\#1}$–Mn(1)–Cl(1)$^{\#1}$	92.90(1)
	N(4)–C(22)	1.469(8)	Cl(1)–Mn(1)–Cl(1)$^{\#1}$	180.0

TABLE III Selected IR data for Complexes **1** and **2**

Compound	$\nu_{Ar\text{–}H}$	$\nu_{C=N}$, $\nu_{C=C}$	ν_{NO_3}
Bbmb	3085 w, 3067 m, 3031 w	1610 m, 1488 s	
[Cu(NO$_3$)$_2$(bbmb)]$_n$	3108 m, 3074 w, 3033 w	1615 m, 1518 s	1463 m, 1384 s, 1291 s
[MnCl$_2$(bbmb)$_2$]$_m$	3143 w, 3095 m, 3053 w	1614 m, 1498 s	

Thermoanalyses

TG-DTA of bbmb and its complexes was carried out in air. There is an endothermic peak at 196°C in the DTA curve of bbmb, but without corresponding weight loss on the TG curve. This is the melting point. The bbmb ligand loses weight quickly from 288 to 566°C with two moderate exothermic peaks at 400 and 420°C and a strong one at 524°C in the DTA curve. TG-DTA curves of the complexes are completely different from those of bbmb. Complex **1** has two strong exothermic peaks at 268 and 316°C and three moderate exothermic peaks at 296, 240 and 432°C in the DTA curve. Complex **1** has a total weight loss of 87.1% from 266 to 600°C on the TG curve. The residue is thus Cu_2O. In the DTA curve of Complex **2**, there is one weak endothermic peak at 376°C and a moderate one at 590°C. Complex **2** keeps losing weight from 244 to 700°C, leaving a residue of MnO_2.

Description of Crystal Structures

The crystal structure of Polymer **1** is depicted in Fig. 1. Each Cu(II) atom is in a slightly distorted tetrahedral environment, coordinating to two nitrogen atoms from

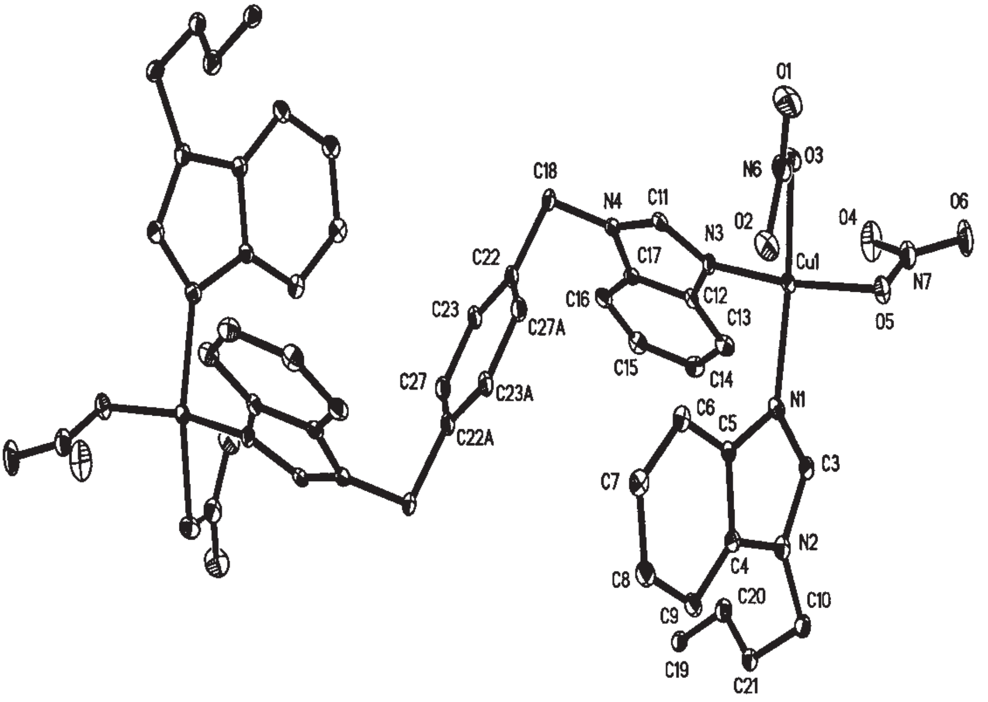


FIGURE 1 Crystal structure of Polymer **1**.

two different bbmb ligands and two oxygen atoms from two NO_3 groups. The N–Cu–O bond angles range from 92 to 163.62°, the O–Cu–O bond angle is 86.87° and the N–Cu–N bond angle is 92.31°. This distortion leads to a difference between the two Cu–N bondlengths (1.946(3) Å and 1.960(3) Å), with the two Cu–O bondlengths [1.980(3) Å and 2.015(3) Å]. Of bbmb in this polymer, the three rings (two benzimidazole rings and one benzene) are not coplanar. The dihedral angle between the coordinated benzimidazole and benzene is 93.9°, indicating the two planes are almost perpendicular. The two benzimidazole ring planes in bbmb are parallel. The two coordinated nitrogen atoms in the benzimidazole rings of bridging bbmb are trans to the central benzene plane. This feature and the preference of Cu(II) for tetrahedral coordination geometry are probably causes of the formation of a zigzag polymeric structure (Fig. 2).

The coordination geometry of Polymer **2** is shown in Fig. 3. The coordination environment of Mn(II) is a distorted octahedron. Mn(II) is situated at a center of symmetry, coordinated by four nitrogen atoms from four bridging bbmb groups and two chloride atoms, Mn(1)–Cl(1) is 2.502(2) Å, Mn(1)–N(1) is 2.327(6) Å and Mn(1)–N(3) is 2.350(5) Å. Mn1–N1 is shorter than Mn(1)–N(3). Bond angles N(1)–Mn(1)–N(1)$^{\#1}$, N(3)–Mn(1)–N(3)$^{\#1}$, and C(11)–Mn(1)–C(11)$^{\#1}$ are 180°. In this coordination mode, each Mn(II) ion is linked by bbmb ligands forming a two-dimensional rhombohedral grid network. Each rhombohedral grid is formed from four bbmb ligands with four Mn(II) ions at the vertices giving $(Mn(II)L)_4$ (L = bbmb) 52-membered metallocyclic rings. The diagonal-to-diagonal distances of the grid are 13.334 × 16.503 Å and dimensions are 10.608 × 10.608 Å. When the conformation of coordinated bbmb is considered, the rings are much like the projection of dumbbells packed waist-to-tail

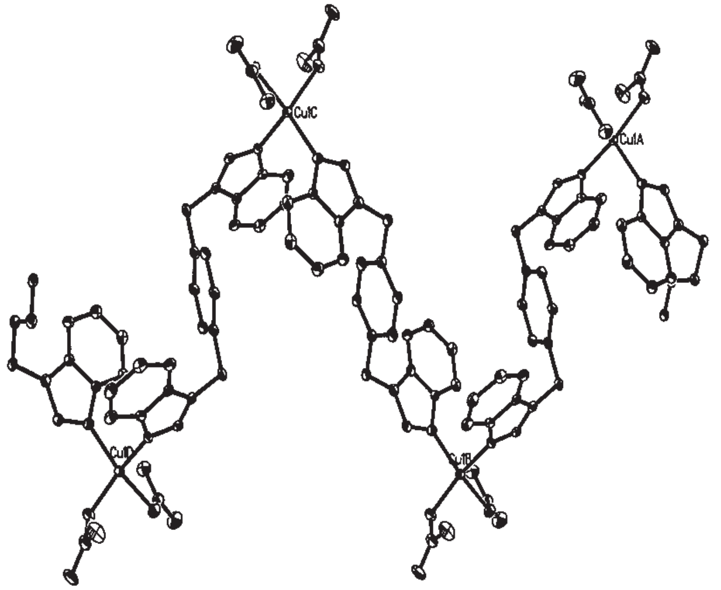


FIGURE 2 The dimensional zigzag chain in Polymer **1**.

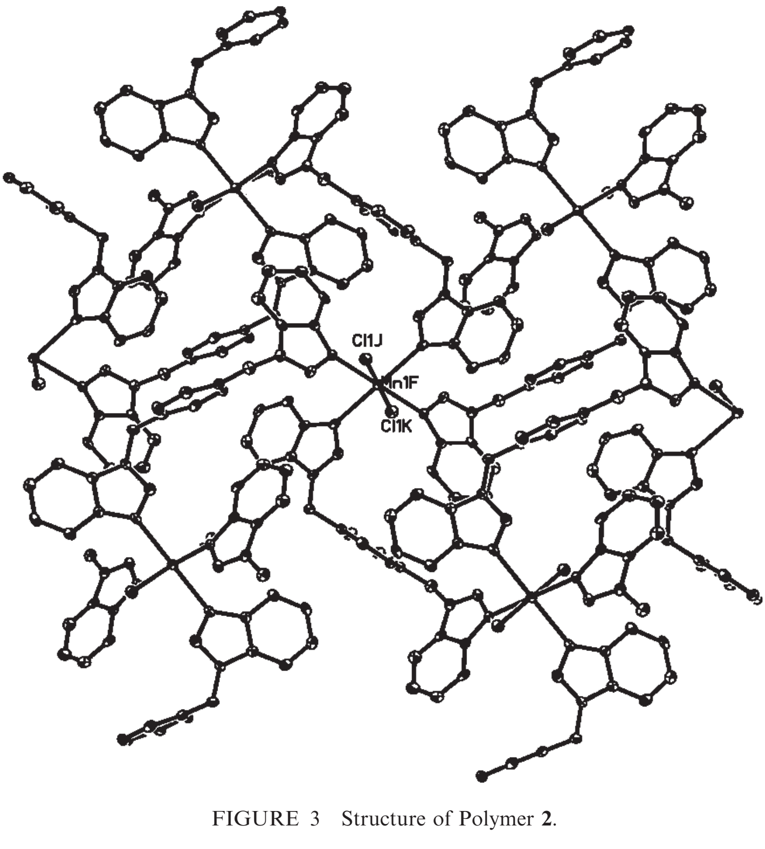
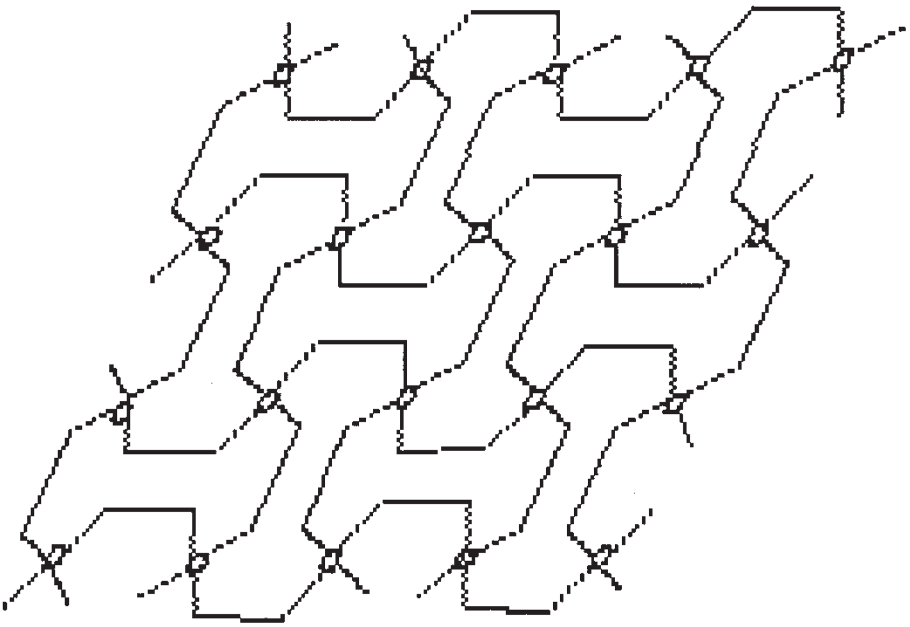


FIGURE 3 Structure of Polymer **2**.



SCHEME 1

(Scheme 1). The two benzene rings at the waist are parallel, and the distance is 2.8751 Å, indicating a significant π–π interaction between the two planes. The two benzimidazole rings at one side of the benzene rings are also nearly parallel with a dihedral angle of 17.2° and the distance between the two planes is $1.82 \sim 2.98$ Å. Thus π-π interaction between the two planes can be considered to exist. Compared with some similar reported Mn(II) polymers such as $[\mathrm{Mn(II)(hfac)_2(4,4\text{-}bpy)}]_n$ (a zigzag one-dimensional chain) [2], $\mathrm{Mn(II)[(bix)_3(NO_3)_2]}_n \cdot 4\mathrm{H_2O}$ (a *quasi*-two-dimensional network structure) [9], and $[\mathrm{Mn(II)(bimb)_3}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$ (an infinite one-dimensional chain containing a poly-metallocage) [12], the two-dimensional rhombohedral grid structure of Polymer **2** is completely new.

The solid-state structure of Polymer **2** exhibits a layered packing mode. The shortest distance between adjacent layers is 6.715 Å, much longer than the π-π interactions.

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