Two different three-dimensional microporous framework structures in $[Mn_2(H_2O)_4\{W(CN)_8\}\cdot 4H_2O]_n$ and $[Mn_2(H_2O)_4\{W(CN)_8\}(OH)\cdot 2H_2O]_n$

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Two novel cyano-bridged heterobimetallic coordination polymers, $[Mn_2(H_2O)_4\{W(CN)_8\}\cdot 4H_2O]_n$ (**1**) and $[Mn_2(H_2O)_4\{W(CN)_8\}(OH)\cdot 2H_2O]_n$ (**2**), have been synthesized from $[W(CN)_8]^{n-}$ ($n = 4, 5$) building blocks and structurally characterized, where all the CN groups of $[W(CN)_8]^{n-}$ are involved in bridging. Both polymers display different open microporous frameworks of the 3D polygonal type exhibiting zeolite-like properties. The 3D framework of **2** is unprecedented. The study of the magnetic properties showed that both polymers exhibit weakly antiferromagnetic interactions between the adjacent Mn ions through the diamagnetic NC–W^{IV}–CN spacer for **1** and between W^{V} and Mn ions for **2**.

Introduction

The design and synthesis of microporous materials mimicking zeolites is drawing a great deal of attention due to the applications of these materials as catalysts, adsorbents and ion exchanges, *etc.*[1] Successful examples of these materials are cyano-bridged inorganic coordination polymers prepared by assembling cyanometallate anions [*e.g.*, $M(CN)_2^{2-}$ (M = Au, Ag), $Ni(CN)_4^{2-}$, $M(CN)_6^{3-}$ (M = Fe, Cr), *etc.*] and transition metal complex building blocks. Cyano groups are used because they possess the ability to link various central atoms for the construction of multidimensional porous frameworks.[2–9] In the past decade, much attention has been paid to the control of the hierarchically structured pore. Since the pore properties, including pore surface chemistry and textural properties such as pore size distribution, pore size and shape, are mainly dependent on the pore structure, while the pore structure and texture are highly influenced by both host and guest molecules, the design and synthesis of microporous materials with hierarchically structural pores is a long-term challenge. Currently, octacyanometallates, $M(CN)_8^{n-}$ (M = Mo, W; $n = 3, 4$), which are good building blocks, are widely used to develop a wide range of architectures that exhibit various structures with interesting magnetic properties.[10–15] However, cyano-bridged inorganic coordination polymers based on octacyanometallates (M = Mo, W), to our best knowledge, have been not reported as porous materials in the literatures so far, despite the fact that the building blocks show various geometrical structures (*e.g.*, square antiprism, dodecahedron, bicapped trigonal prism, *etc.*).[16,17] Here we report the crystal structures, pore properties and magnetic properties of two cyano-bridged inorganic coordination polymers prepared from the $W(CN)_8^{n-}$ ($n = 3, 4$) and $Mn(H_2O)^{2+}$ building blocks.

Experimental

Measurements

Elemental analyses were carried out using a Perkin–Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} region. Thermogravimetric analyses were carried out using an NETZSCH TG 209 analyzer. X-Ray diffraction patterns were recorded on a DMAX device using diffracted beam, graphite-monochromated Cu Kα radiation ($\lambda = 1.5406$ Å). Magnetization measurements were carried out in the temperature range of 78–300 K on an LDJ-9600 vibrating-sample magnetometer in an applied magnetic field of 5000 G. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility.

Preparations

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handed in small quantities with care.

$K_4[W(CN)_8]\cdot 2H_2O$ and $K_3[W(CN)_8]\cdot H_2O$ were synthesized according to the methods in the literature.[18,19] Other reagents were commercially available and used as received.

$[Mn_2(H_2O)_4\{W(CN)_8\}\cdot 4H_2O]_n$(1). The yellow crystals of **1** were obtained by adding 15 ml of an aqueous solution of $Mn(ClO_4)_2\cdot 6H_2O$ (36.2 mg, 0.2 mmol) and 15 ml of an aqueous solution of $K_4[W(CN)_8]\cdot 2H_2O$ (58.4 mg, 0.1 mmol) into the two shoulders of an H-shaped tube with 5 ml isopropyl alcohol. Anal. found: C, 14.57; H, 2.74; N, 17.23%; calcd for $C_8H_{16}Mn_2N_8O_8W$: C, 14.86; H, 2.47; N, 17.33%. IR (KBr, cm^{-1}): 2161 (ν_{CN}).

$[Mn_2(H_2O)_4\{W(CN)_8\}(OH)\cdot 2H_2O]_n$ (2). The yellow crystals of **2** were obtained with the same synthetic procedure as for **1** with $K_3[W(CN)_8]\cdot H_2O$ (52.7 mg) instead of $K_4[W(CN)_8]\cdot 2H_2O$. Anal. found: C, 15.55; H, 2.34; N, 17.26%; calcd for $C_8H_{13}Mn_2N_8O_7W$: C, 15.31; H, 2.07; N, 17.86%. IR (KBr, cm^{-1}): 2154 (ν_{CN}).

X-Ray crystallography

Determination of the unit cell and data collection were performed on a Bruker Smart 1000 area detector using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97[20a]) and refined by full-matrix least-squares procedures on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97[20b]). Selected crystal data collection and refinement parameters are given in Table 1.†

Table 1 Summary of crystallographic data for complexes **1**and **2**

	1	2
Formula	$C_8H_{16}Mn_2N_8O_8W$	$C_8H_{13}Mn_2N_8O_7W$
FW	646.02	626.99
Crystal system	Tetragonal	Monoclinic
Space group	$I4/m$	$P2(1)/n$
μ(Mo Kα)/mm^{-1}	7.476	7.421
a/Å	11.915(4)	7.3159(10)
b/Å	11.915(4)	14.3390(17)
c/Å	13.252(9)	18.052(2)
α/°	90	90.00
β/°	90	91.067(7)
γ/°	90	90.00
U/Å^3	1881.1(16)	1893.3(4)
Z	4	4
Total reflections	5434	5944
Observed reflections	1025	3246
R_{int}	0.0427	0.0578
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0236	0.0462
$wR_2{}^b$ $[I > 2\sigma(I)]$	0.0487	0.0995

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

Results and discussion

Crystal structures

$[Mn_2(H_2O)_4\{W(CN)_8\}\cdot 4H_2O]_n$ (1). The atomic labeling scheme is shown in Fig. 1 and selected bond lengths and angles are listed in Table 2. The structure determination of **1** discloses an open microporous material of 3D polygonal type. In the polymer the coordination environment of the W(IV) ion surrounded by eight CN is close to a square antiprism. The W(1A)–C(1A) bond length is equal to 2.160(4) Å. The W–CN bond angle deviates slightly from 180° and is equal to 175.6(4)° (see Table 2). Each $[W(CN)_8]^{4-}$ links eight Mn(II) ions coordinated by means of four nitrile nitrogen atoms from four bridging $[W(CN)_8]^{4-}$ ligands in the equatorial plane and two oxygen atoms of H_2O molecules in axial positions in a distorted octahedron geometry. The Mn(1E)–N(1E) and Mn(1E)–N(1K) bond lengths are equal to 2.209(4) and 2.248 Å, respectively. The Mn(1E)–O(1E) and Mn(1E)–O(2E) bond lengths are equal to 2.153(6) and 2.206(6) Å, respectively. The bond angles N(1E)–Mn(1E)–N(2J) and O(1E)–Mn(1E)–O(2E) are 176.08(17) and 177.2(3)°, respectively. Each Mn atom is connected to four others by four equatorial NC–W–CN bridges, resulting in a two-dimensional network along the equatorial plane with a grid-shaped parallel quadrilateral mesh constituted of W–CN–Mn units (edge lengths of 5.406 and 5.471 Å, acute angle of roughly 84°). In the highly symmetrical 3D structure two perpendicular grids result in an open micropore framework of the 3D polygonal type with dimensions of about 11.92 × 13.61 Å^2 (Fig. 2). The non-coordinated water molecules occupy the crystalline channels as guest molecules and are connected with the coordinated water by hydrogen bonds with an O···O distance of 2.931 Å. The non-coordinated waters are also connected to each other by hydrogen bonds with an O···O distance 2.952 Å. The guest water molecules in the crystallite, from a topological point of view, have the ability to leave the host lattice. The results of the dehydration process and the X-ray powder diffraction pattern will be discussed in the following sections. The principle shortest distances between metallic sites are 5.406 Å for W···Mn, 6.063 Å for Mn···Mn and 6.586 Å for W···W.

$[Mn_2(H_2O)_4\{W(CN)_8\}(OH)\cdot 2H_2O]_n$ (2). The atomic labeling scheme is shown in Fig. 3 and selected bond lengths and angles are listed in Table 3. The structure determination of **2** discloses a 3D polygonal-type open microporous framework, which is different from that of **1**. In the polymer the Mn/W ratio is 2, and the coordination environment of the W^{V} ion surrounded by eight CN is close to bicapped trigonal prism. The W(1A)–C(1A) and W(1A)–C(8A) bond lengths are equal to 2.143(13) and 2.208(14) Å, respectively. The W–CN bond angles deviate slightly from 180° and the W(1A)–C(1A)–N(1A), W(1A)–C(5A)–N(5A) bond angles are equal to 174.8(11)° and 179.9(13)°, respectively (see Table 3). $[W(CN)_8]^{3-}$ anions act as μ_8 bridging ligands and each $[W(CN)_8]^{3-}$ anion links eight different Mn(II) ions. There are two kinds of Mn(II) ions with different coordination environments in the polymer. The geometry of the central Mn(2A) is a slightly distorted octahedron with an N_4O_2donor set composed of four nitrile nitrogen atoms from four bridging $[W(CN)_8]^{4-}$ ligands in the equatorial plane and two oxygen atoms of H_2O molecules in axial positions. The Mn(1A) ion is also six-coordinated, with a distorted octahedron geometry, by means of four nitrile nitrogen atoms from four bridging $[W(CN)_8]^{4-}$ ligands and two oxygen atoms of H_2O molecules in a cis arrangement. The Mn(1A)–N(2A) and Mn(1A)–N(5E) bond lengths are equal to 2.228(11) and 2.222(10) Å, respectively. The Mn(1A)–O(1A) and Mn(1A)–O(2A) bond

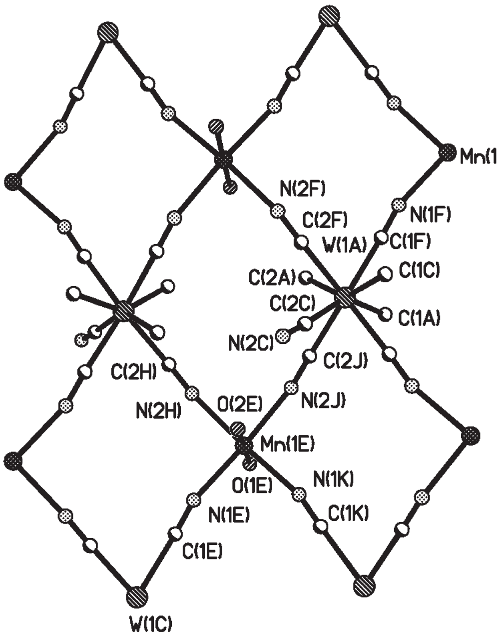

Fig. 1 The atom numbering scheme of **1**.

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† CCDC reference numbers 212 604 and 212 605 for **1** and **2**, respectively. See http://www.rsc.org/suppdata/nj/b3/b306755f/ for crystallographic data in .cif or other electronic format.

Table 2 Selected bond distances (Å) and bond angles (°) of complex **1**

W(1)–C(2)#1	2.160(4)	C(2)#1–W(1)–C(1)	139.07(17)
W(1)–C(2)	2.160(4)	C(2)–W(1)–C(1)	76.20(17)
W(1)–C(2)#2	2.160(4)	C(2)#2–W(1)–C(1)	80.51(17)
W(1)–C(2)#3	2.160(4)	C(2)#3–W(1)–C(1)	146.00(17)
W(1)–C(1)#2	2.160(5)	C(1)#2–W(1)–C(1)	72.81(12)
W(1)–C(1)#1	2.160(5)	C(1)#1–W(1)–C(1)	72.81(12)
W(1)–C(1)	2.160(5)	C(2)#1–W(1)–C(1)#3	80.51(17)
W(1)–C(1)#3	2.160(5)	C(2)–W(1)–C(1)#3	146.00(17)
C(1)–N(1)	1.138(6)	C(2)#2–W(1)–C(1)#3	139.07(17)
N(1)–Mn(1)	2.209(4)	C(2)#3–W(1)–C(1)#3	76.20(17)
C(2)–N(2)	1.150(6)	C(1)#2–W(1)–C(1)#3	72.81(12)
N(2)–Mn(1)#4	2.248(4)	C(1)#1–W(1)–C(1)#3	72.81(12)
Mn(1)–O(1)	2.153(6)	C(1)–W(1)–C(1)#3	114.1(2)
Mn(1)–O(2)	2.206(6)	N(1)–C(1)–W(1)	175.6(4)
Mn(1)–N(1)#5	2.209(4)	C(1)–N(1)–Mn(1)	165.8(4)
Mn(1)–N(2)#6	2.248(4)	N(2)–C(2)–W(1)	176.3(4)
Mn(1)–N(2)#4	2.248(4)	C(2)–N(2)–Mn(1)#4	154.7(4)
C(2)#1–W(1)–C(2)	72.84(11)	O(1)–Mn(1)–O(2)	177.2(3)
C(2)#1–W(1)–C(2)#2	114.2(2)	O(1)–Mn(1)–N(1)	86.22(19)
C(2)–W(1)–C(2)#2	72.84(11)	O(2)–Mn(1)–N(1)	91.80(16)
C(2)#1–W(1)–C(2)#3	72.84(11)	O(1)–Mn(1)–N(1)#5	86.22(19)
C(2)–W(1)–C(2)#3	114.2(2)	O(2)–Mn(1)–N(1)#5	91.80(16)
C(2)#2–W(1)–C(2)#3	72.84(11)	N(1)–Mn(1)–N(1)#5	90.6(2)
C(2)#1–W(1)–C(1)#2	146.00(17)	O(1)–Mn(1)–N(2)#6	96.15(19)
C(2)–W(1)–C(1)#2	139.07(17)	O(2)–Mn(1)–N(2)#6	85.94(16)
C(2)#2–W(1)–C(1)#2	76.20(17)	N(1)–Mn(1)–N(2)#6	176.08(17)
C(2)#3–W(1)–C(1)#2	80.51(17)	N(1)#5–Mn(1)–N(2)#6	92.65(15)
C(2)#1–W(1)–C(1)#1	76.20(17)	O(1)–Mn(1)–N(2)#4	96.15(19)
C(2)–W(1)–C(1)#1	80.51(17)	O(2)–Mn(1)–N(2)#4	85.94(16)
C(2)#2–W(1)–C(1)#1	146.00(17)	N(1)–Mn(1)–N(2)#4	92.65(15)
C(2)#3–W(1)–C(1)#1	139.07(17)	N(1)#5–Mn(1)–N(2)#4	176.08(17)
C(1)#2–W(1)–C(1)#1	114.1(2)	N(2)#6–Mn(1)–N(2)#4	84.0(2)

Symmetry operators: #1 $-y+1, x-1$, z; #2 $y+1, -x+1, z$; #3 $-x+2, -y, z$; #4 $-x+3/2, -y+1/2, -z+1/2$; #5 $x, y, -z+1$; #6 $-x+3/2, -y+1/2, z+1/2$

lengths are equal to 2.253(8) and 2.265(10) Å, respectively. The bond angles N(7A)–Mn(1A)–N(2A) and O(1A)–Mn(1A)–O(2A) are 160.5(4)° and 87.5(4)°, respectively. The Mn(2A)–N(1A) and Mn(2A)–N(3D) bond lengths are equal to 2.185(10) and 2.205(10) Å, respectively. Each Mn(II) ion is connected to four others by four NC–W–CN bridges, resulting in an open micropore framework of the 3D polygonal type (Fig. 4). The size of the open micropore is around 11.98 × 13.32 Å^2 The non-coordinated water molecules and OH$^-$ groups occupy the crystalline channels as guest molecules and are connected with the coordinated water by hydrogen bonds with the shortest O···O distance being 2.612 Å. The non-coordinated water molecules are also connected to each other by hydrogen bonds with an O···O distance of 2.933 Å. The guest molecules in the crystallite, from a topological point of view, have the ability to leave the host lattice. The results of the dehydration process and the X-ray powder diffraction pattern will be discussed in the following sections. The main shortest distances between metallic sites are 5.444 Å for W···Mn, 5.791 Å for Mn···Mn, and 7.316 Å for W···W.

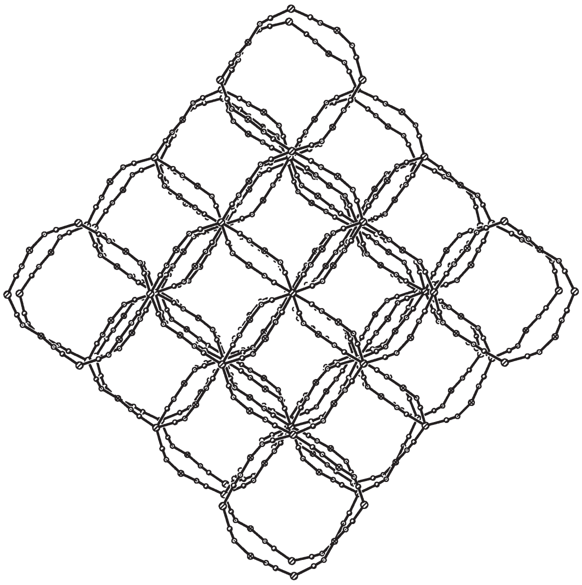

Fig. 2 The 3D polygonal-type open microporous framework of **1**. All water molecules are omitted for clarity.

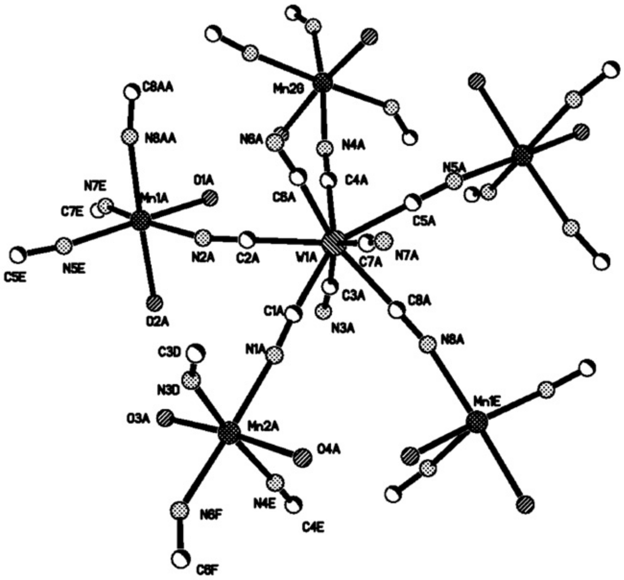

Fig. 3 The atom numbering scheme of **2**.

Thermogravimetric studies and X-ray powder diffraction

The thermogravimetric analyses of crystalline samples of **1** and **2** show weight losses of 10.76% and 5.56%, respectively, at 70 °C, corresponding to the loss of the guest water occupying the channels. Upon heating to 180 °C, the remaining compound releases the coordinated water molecules with a weight loss of 10.98% and 11.28%, respectively. The remaining compounds are heated to 250 °C (**1**) or 280 °C (**2**) without any additional weight decrease, indicating a robust open framework. To examine the porous properties of the materials the synthesized crystal samples were heated at 100 °C for 24 h in order to remove the guest water molecules. It is worth noting that upon reintroducing water into the pores over a period of 2 h, the XRD patterns of the regenerated solids exhibit peak positions and intensities fully coincident to those observed for the original solids (see Fig. 5), which indicates that this process is reversible, that the structures can be envisaged as inclusion compounds, and that removal of the H-bond network does not lead to destruction of the structures. These results show that polymers **1** and **2** exhibit sieving properties resembling those of zeolites.

Magnetic properties

At room temperature the μ_{eff}values are 7.75 B.M. and 7.81 B.M. for **1** and **2**, respectively, which are lower than the expected spin-only values (8.36 B.M. per Mn_2 for **1**, 8.48 B.M per Mn_2W for **2**). Upon cooling to 77 K, the μ_{eff} values decrease slowly to 7.58 B.M. and 7.54B.M. for **1** and **2**, respectively, suggesting weak antiferromagnetic interactions between adjacent Mn(II) ions through diamagnetic NC–W$^{\text{IV}}$–CN spacer for **1** and between W$^{\text{V}}$ and Mn ions for **2**.

Table 3 Selected bond distances (Å) and bond angles (°) of complex **2**

W(1)–C(6)	2.133(12)	N(8)#1–Mn(1)–O(1)	90.5(4)
W(1)–C(1)	2.143(13)	N(7)#2–Mn(1)–O(1)	79.0(4)
W(1)–C(3)	2.153(12)	N(5)#3–Mn(1)–O(1)	172.9(4)
W(1)–C(4)	2.169(11)	N(2)–Mn(1)–O(1)	82.5(4)
W(1)–C(5)	2.160(12)	N(8)#1–Mn(1)–O(2)	177.8(4)
W(1)–C(7)	2.192(11)	N(7)#2–Mn(1)–O(2)	87.7(4)
W(1)–C(2)	2.208(13)	N(5)#3–Mn(1)–O(2)	89.7(4)
W(1)–C(8)	2.208(14)	N(2)–Mn(1)–O(2)	85.2(4)
Mn(1)–N(8)#1	2.219(12)	O(1)–Mn(1)–O(2)	87.5(4)
Mn(1)–N(7)#2	2.219(10)	N(1)–Mn(2)–N(3)#4	87.0(4)
Mn(1)–N(5)#3	2.222(10)	N(1)–Mn(2)–N(6)#5	174.6(4)
Mn(1)–N(2)	2.228(11)	N(3)#4–Mn(2)–N(6)#5	87.8(4)
Mn(1)–O(1)	2.253(8)	N(1)–Mn(2)–O(4)	91.2(4)
Mn(1)–O(2)	2.265(10)	N(3)#4–Mn(2)–O(4)	86.7(4)
Mn(2)–N(1)	2.185(10)	N(6)#5–Mn(2)–O(4)	87.2(4)
Mn(2)–N(3)#4	2.205(10)	N(1)–Mn(2)–O(3)	90.5(4)
Mn(2)–N(6)#5	2.215(10)	N(3)#4–Mn(2)–O(3)	101.0(4)
Mn(2)–O(4)	2.231(9)	N(6)#5–Mn(2)–O(3)	91.8(3)
Mn(2)–O(3)	2.236(8)	O(4)–Mn(2)–O(3)	172.2(4)
Mn(2)–N(4)#6	2.241(10)	N(1)–Mn(2)–N(4)#6	91.1(4)
C(1)–N(1)	1.148(15)	N(3)#4–Mn(2)–N(4)#6	172.8(4)
C(2)–N(2)	1.148(14)	N(6)#5–Mn(2)–N(4)#6	94.0(4)
C(3)–N(3)	1.171(14)	O(4)–Mn(2)–N(4)#6	86.4(4)
N(3)–Mn(2)#7	2.205(10)	O(3)–Mn(2)–N(4)#6	85.9(4)
C(4)–N(4)	1.150(14)	N(1)–C(1)–W(1)	174.8(11)
N(4)–Mn(2)#1	2.241(10)	C(1)–N(1)–Mn(2)	174.5(11)
C(5)–N(5)	1.151(14)	N(2)–C(2)–W(1)	177.9(9)
N(5)–Mn(1)#8	2.222(10)	C(2)–N(2)–Mn(1)	155.1(9)
C(6)–N(6)	1.167(15)	N(3)–C(3)–W(1)	173.4(10)
N(6)–Mn(2)#9	2.215(10)	C(3)–N(3)–Mn(2)#7	150.8(10)
C(7)–N(7)	1.144(14)	N(4)–C(4)–W(1)	179.6(12)
N(7)–Mn(1)#10	2.219(10)	C(4)–N(4)–Mn(2)#1	172.8(10)
C(8)–N(8)	1.121(16)	N(5)–C(5)–W(1)	179.9(13)
N(8)–Mn(1)#6	2.219(12)	C(5)–N(5)–Mn(1)#8	155.1(9)
C(6)–W(1)–C(1)	99.2(4)	N(6)–C(6)–W(1)	174.2(10)
C(6)–W(1)–C(3)	145.4(4)	C(6)–N(6)–Mn(2)#9	147.4(9)
C(1)–W(1)–C(3)	86.7(4)	N(7)–C(7)–W(1)	176.8(11)
C(6)–W(1)–C(4)	79.4(4)	C(7)–N(7)–Mn(1)#10	159.2(11)
C(1)–W(1)–C(4)	145.6(4)	N(8)–C(8)–W(1)	178.0(11)
C(3)–W(1)–C(4)	77.0(4)	C(8)–N(8)–Mn(1)#6	165.7(10)
C(6)–W(1)–C(5)	94.8(4)	C(7)–W(1)–C(2)	124.0(4)
C(1)–W(1)–C(5)	143.9(5)	C(6)–W(1)–C(8)	142.8(4)
C(3)–W(1)–C(5)	100.3(4)	C(1)–W(1)–C(8)	74.3(4)
C(4)–W(1)–C(5)	69.7(4)	C(3)–W(1)–C(8)	71.7(4)
C(6)–W(1)–C(7)	68.1(4)	C(4)–W(1)–C(8)	126.5(4)
C(1)–W(1)–C(7)	76.0(4)	C(5)–W(1)–C(8)	74.5(4)
C(3)–W(1)–C(7)	145.4(5)	C(7)–W(1)–C(8)	74.8(4)
C(4)–W(1)–C(7)	132.0(4)	C(2)–W(1)–C(8)	134.1(5)
C(5)–W(1)–C(7)	78.7(4)	N(8)#1–Mn(1)–N(7)#2	92.8(4)
C(6)–W(1)–C(2)	73.3(4)	N(8)#1–Mn(1)–N(5)#3	92.4(4)
C(1)–W(1)–C(2)	71.7(4)	N(7)#2–Mn(1)–N(5)#3	94.4(4)
C(3)–W(1)–C(2)	76.3(4)	N(8)#1–Mn(1)–N(2)	93.6(4)
C(4)–W(1)–C(2)	75.1(4)	N(7)#2–Mn(1)–N(2)	160.5(4)
C(5)–W(1)–C(2)	144.3(4)	N(5)#3–Mn(1)–N(2)	103.8(4)

Symmetry operators: #1 $-x+1/2, y+1/2, -z+3/2$; #2 $x+1/2, -y+3/2, z-1/2$; #3 $x-1/2, -y+3/2, z-1/2$; #4 $x-1, y, z$; #5 $-x-1/2, y-1/2, -z+3/2$; #6 $-x+1/2, y-1/2, -z+3/2$; #7 $x+1, y, z$; #8 $x+1/2, -y+3/2, z+1/2$; #9 $-x-1/2, y+1/2, -z+3/2$; #10 $x-1/2, -y+3/2, z+1/2$

Conclusion

Two novel cyano-bridged heterobimetallic coordination polymers, $[Mn_2(H_2O)_4\{W(CN)_8\}\cdot 4H_2O]_n$(**1**) and $[Mn_2(H_2O)_4\{W(CN)_8\}(OH)\cdot 2H_2O]_n$ (**2**), have been synthesized from $[W(CN)_8]^{n-}$ ($n = 4, 5$) building blocks and structurally characterized. Both polymers display open microporous frameworks of the 3D polygonal type that exhibit zeolite-like properties. The 3D framework of **2** is unprecedented. The overall behavior of polymers **1** and **2** corresponds to weak antiferromagnetically coupled systems.

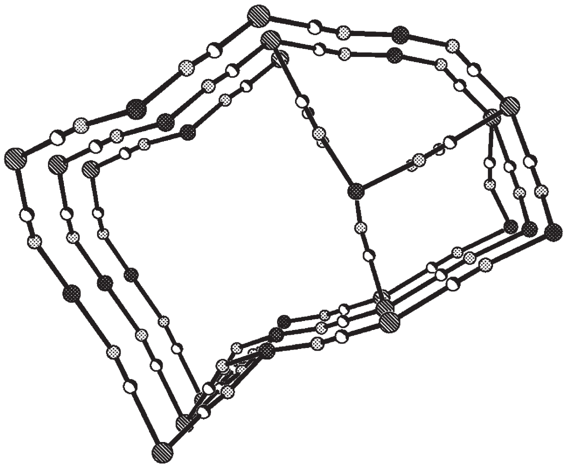

Fig. 4 The 3D polygonal-type open microporous framework of **2**. All water molecules are omitted for clarity.

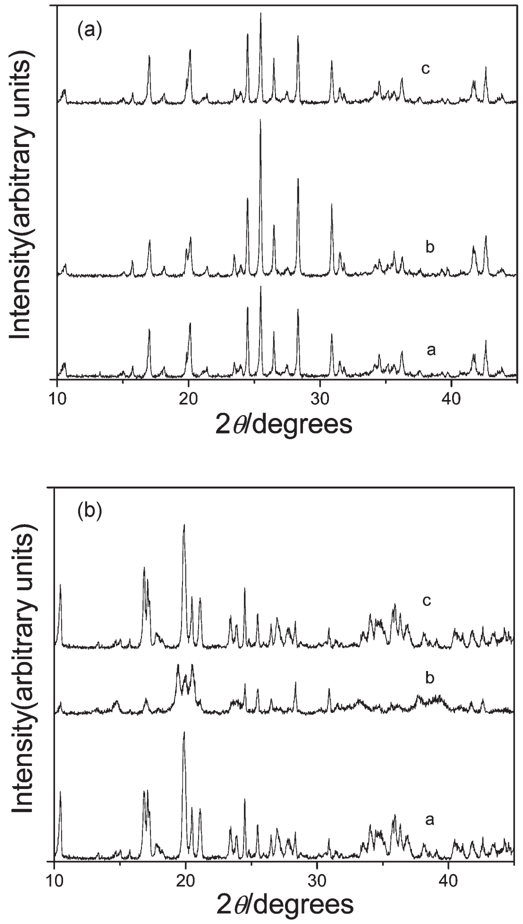

Fig. 5 The XRD patterns of (a) **1** and (b) **2**: (spectra a) as-synthesized material; (spectra b) dehydrated solid; (spectra c) regenerated solid.

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