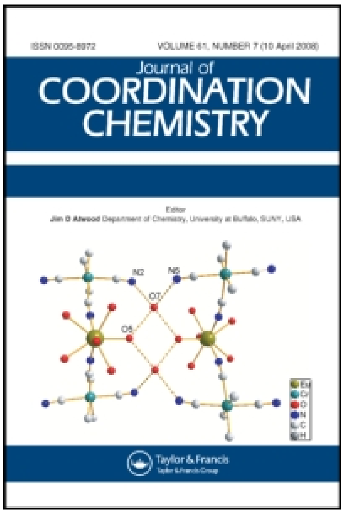

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Synthesis and crystal structures of pH-dependent Mn(II) coordination polymers with 3-pyrid-3-ylbenzoic acid

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Two pyridinecarboxylato-bridged coordination polymers $[Mn(pbc)_2]_n$ (**1**) and $[Mn(pbc)_2(H_2O)_2]_n$ (**2**) (Hpbc = 3-pyrid-3-ylbenzoic acid) have been synthesized by the hydrothermal method and characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. X-ray diffraction analysis reveals that pbc^- adopts two coordination modes: μ_2-N, O, O and μ_3-N, O, O in **1** and as diconnectors linking two Mn(II) centers through μ_2-N, O in **2**. Compound **1** is a dinuclear $Mn_2(pbc)_2$ metallocycle. Compound **2** is a double-stranded chain running along *a*.

Keywords: Coordination polymer; Mn(II); Hydrothermal method

1. Introduction

Interest in polymeric coordination networks is rapidly expanding for potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and molecular sensing and also for intriguing topologies [1–7]. Frameworks of coordination polymers are constructed by connectors and linkers. Transition metal ions are excellent connectors due to their versatility in coordination number and geometry. Suitable linkers must have a variety of linking sites. A common strategy to construct these polymeric transition metal complexes is to select suitable multidentate ligands to integrate metal ions to a desired framework. Multidentate ligands with suitable spacers between the linking groups are good choices to get infinite architectures. Hydrogen bonds are also frequently used in crystal engineering to form frameworks [8–11]. Pyridine-carboxylates have been used in many synthetic systems, resulting in a great variety of new complexes.

As a part of our work toward rational design of functional coordination frameworks, we present the synthesis and characterization of two coordination polymers $[Mn(pbc)_2]_n$ (**1**) and $[Mn(pbc)_2(H_2O)_2]_n$ (**2**) assembled from Mn(II) and 3-pyrid-3ylbenzoic acid.

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2. Experimental

2.1. *Materials and methods*

Reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pellets from 400 to 4000 cm^{-1}.

2.2. *Synthesis of* $[Mn(pbc)_2]_n$ *(1)*

A mixture of Hpbc (1 mmol, 0.199 g), $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol), and distilled water (12 mL) with the pH adjusted to *ca* 6.5 was heated in a 20 mL stainless-steel reactor with a Teflon liner at 160°C for 120 h and cooled to room temperature at 2°C h^{-1}. Colorless block crystals were obtained in 40% yield (based on Mn). Anal. Calcd (%) for $C_{24}H_{16}MnN_2O_4$: C, 63.87; H, 3.57; N, 6.21. Found (%): C, 63.52; H, 3.49; N, 6.17. IR (KBr cm^{-1}): 1640s; 1612s; 1480s; 651m; 426m.

2.3. *Synthesis of* $[Mn(pbc)_2(H_2O)_2]_n$ *(2)*

A mixture of Hpbc (0.199 g, 1 mmol), $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol), and distilled water (18 mL) with the pH adjusted to *ca* 8.0 was heated in a 25 mL stainless-steel reactor with a Teflon liner at 160°C for 120 h, followed by slow cooling to room temperature. Colorless block crystals of the complex were formed. Yield 62% (based on Mn). Anal. Calcd (%) for $C_{24}H_{20}MnN_2O_6$: C, 59.15; H, 4.14; N, 5.75. Found (%): C, 58.04; H, 4.26; N, 6.02. IR (KBr cm^{-1}): 3430br; 1610s; 1401s; 1335m; 637m; 408m.

2.4. *Single-crystal X-ray diffraction*

Single-crystal X-ray diffraction measurements for **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) and unit cell dimensions were obtained with least-squares refinements. The program SAINT [12] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [13]. All nonhydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares with anisotropic thermal parameters for nonhydrogen atoms on F^2. The hydrogens were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in table 1. Selected bond lengths and angles for **1** and **2** are listed in table 2.

Table 1. Crystallographic data and structure refinements for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{16}MnN_2O_4$	$C_{24}H_{20}MnN_2O_6$
Formula weight	451.33	487.36
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.965(5)	9.581(5)
b	10.299(5)	9.457(5)
c	20.643(5)	11.848(5)
α	90.000(5)	90.000(5)
β	95.010(5)	97.961(5)
γ	90.000(5)	90.000(5)
Volume (Å^3), Z	1898.7(15), 4	1063.2(9), 2
Calculated density (g cm^{-3})	1.579	1.522
Absorption coefficient (mm^{-1})	0.732	0.666
$F(000)$	924	502
θ range for data collection (°)	1.98–28.47	
Limiting indices	$-11 \le h \le 11$; $-13 \le k \le 7$; $-23 \le l \le 27$	$-11 \le h \le 12$; $-12 \le k \le 11$; $-15 \le l \le 15$
Reflections collected	11994	6788
Unique	4601	2601
Goodness-of-fit on F^2	1.034	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0293$, $wR_2 = 0.0705$	$R_1 = 0.0328$, $wR_2 = 0.0862$
R indices (all data)	$R_1 = 0.0372$, $wR_2 = 0.0745$	$R_1 = 0.0444$, $wR_2 = 0.0944$
Largest difference peak and hole (e Å^{-3})	0.309 and −0.268	0.321 and −0.279

$wR^2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$. $w = 1/[\sigma^2(F^o)^2 + (AP)^2 + BP]$ with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound **1** $C_{24}H_{16}MnN_2O_4$			
Mn(1)–O(1)#1	2.126(13)	Mn(1)–O(2)	2.128(12)
Mn(1)–O(4)	2.194(13)	Mn(1)–N(1)#2	2.274
Mn(1)–N(2)#3	2.281(15)	Mn(1)–O(3)	2.433(16)
O(1)#1–Mn(1)–O(2)	103.34(5)	O(1)#1–Mn(1)–O(4)	92.24(5)
O(2)–Mn(1)–O(4)	160.60(5)	O(1)#1–Mn(1)–N(1)#1	88.63(5)
O(2)–Mn(1)–N(1)#2	82.28(5)	O(4)–Mn(1)–N(1)#2	86.68(6)
O(1)#1–Mn(1)–N(2)#3	105.40(5)	O(2)–Mn(1)–N(2)#3	86.89(5)
O(4)–Mn(1)–N(2)#3	100.19(6)	N(1)–Mn(1)–N(2)#3	163.97(5)
O(1)#1–Mn(1)–O(3)	106.72(4)	O(4)–Mn(1)–O(3)	56.26(4)
N(1)#2–Mn(1)–O(3)	85.22(5)	N(2)#3–Mn(1)–O(3)	86.63(5)
Compound **2** $C_{24}H_{20}MnN_2O_6$			
Mn–O(2)#1	2.157(14)	Mn–N(1)#2	2.285(17)
Mn–O(1WA)#1	2.194(16)	Mn–N(1A)#3	2.285(17)
O(2)#1–Mn–O(2A)	180.00(4)	O(2)#1–Mn–N(1)#2	90.34(6)
O(2)#1–Mn–O(1WA)#1	91.41(6)	O(2)#1–Mn–N(1A)#3	89.66(6)
O(2)#1–Mn–O(1W)	88.60(6)	O(1W)–Mn–N(1)#2	88.71(6)
O(1W)–Mn–O(1WA)#1	180.00	O(1W)–Mn–N(1A)#3	91.29(6)

Symmetry code for compounds: (**1**) #1: $1-x$, $-y$, $-z$; #2: $-1/2+x$, $-1/2-y$, $-1/2+z$; #3: $-x$, $1-y$, $-z$; (**2**) #1: $-x$, $-y$, $1-z$; #2: $1-x$, $-y$, $1-z$; #3: $-1+x$, y, z.

3. Results and discussion

3.1. *Description of the structure of 1*

Polymer **1** crystallizes in monoclinic system space group $P2_1/n$. Each Mn(II) is coordinated by four oxygens (Mn–O = 2.126–2.433 Å) and two nitrogens (Mn(1)–N(1) = 2.274(15) Å and Mn(1)–N(2) = 2.274(15) Å). The Mn–O and Mn–N bond lengths agree well with results for related complexes [14–16], and bond angles of O(N)–Mn–O(N) are from 56.24(4) to 163.97(5)°. Oxygens form the equatorial plane (the equation of plane is $7.846x + 2.756y + 6.709z = 10.629$, the maximal and the mean deviation are 0.4222 Å and 0.2111 Å, respectively), and nitrogens occupy axial sites (figure 1). In **1**, pbc$^-$ has two coordination modes, a diconnector linking two Mn(II) centers through a N and O_{COO}^{-} (μ_2-N, O, O shown in scheme 1(a)) and a triconnector linking three Mn(II) centers (μ_3-N, O, O shown in scheme 1(b)). One carboxylate is bidentate chelate and the other O_{COO}^{-} is bis-monodentate *syn-anti* bridging constructing a dinuclear octahedral [$Mn_2C_2O_4$] SBU, with nonbonding Mn···Mn distance of 4.544 Å. The SBUs are further interconnected through different pbc$^-$ ligands, generating a 3-D extended network composed of six-connected nodes (figure 2). The structure of **1**, $4^46^{10}8$ topology, can be described as comprising three intersecting (4,4) nets. The dihedral angles are 43.67° (μ_3-N, O, O) and 48.36° (μ_2-N, O, O) between pyridine and phenyl in pbc$^-$.

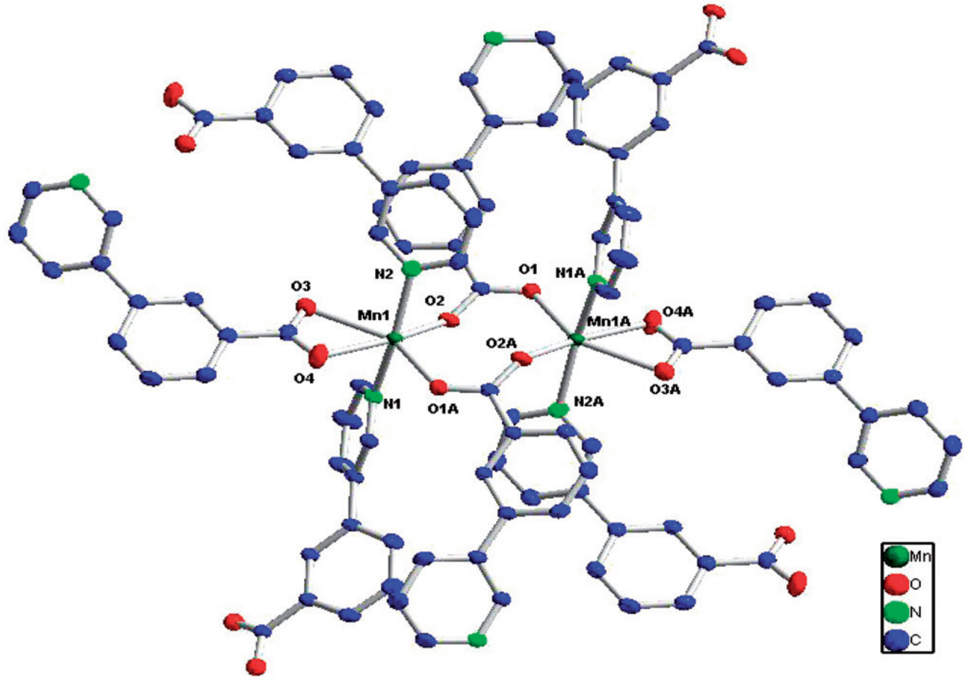
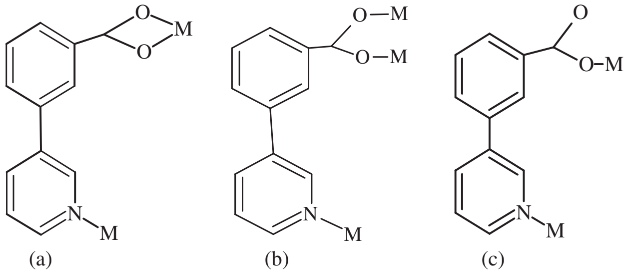


Figure 1. Coordination environment of Mn(I) with thermal ellipsoids drawn at 50% probability level. All hydrogens are omitted for clarity.

3.2. *Description of the structure of 2*

The local coordination geometry of **2** with atom-numbering scheme is shown in figure 3. The Mn1 is octahedral with the equatorial positions occupied by two carboxyl oxygens (Mn(1)–O(2) = 2.157(14) Å and Mn(1)–O(2A) = 2.157(14) Å) and two waters (Mn(1)–O1W = 2.194(16) Å and Mn(1)–O(1WA) = 2.194(16) 2.098(2) Å); the axial positions are occupied by two $N_{pyridinyl}$ (Mn(1)–N(1) = 2.285(17) Å and Mn(1)–N(1A) = 2.285(17) Å) with N–Ni–N angle of 180°. In **2**, all pbc^- ligands are diconnectors linking two Mn(II) centers in μ_2-N, O (scheme 1c) which form a zigzag 1-D chain viewed along the *c*-axis (figure 4). The dihedral angle between pyridine ring and phenyl ring is 73.34°. Two pbc^- ligands connect two Mn(II) to achieve an 18-member $Mn_2(pbc)_2$ metalacyclic ring (Mn–Mn separation of 9.581 Å).

Crystal packing analysis of **2** shows the formation of independent interchain (O–H···O) as well as intrachain (O–H···O) hydrogen bonds (figure 5) between $Mn_2(pbc)_2$ metalacycles. During the formation of the interchain O–H···O hydrogen bond, the O–H of coordinated water of one chain is linked through uncoordinated



Scheme 1. The coordination modes of pbc^-.

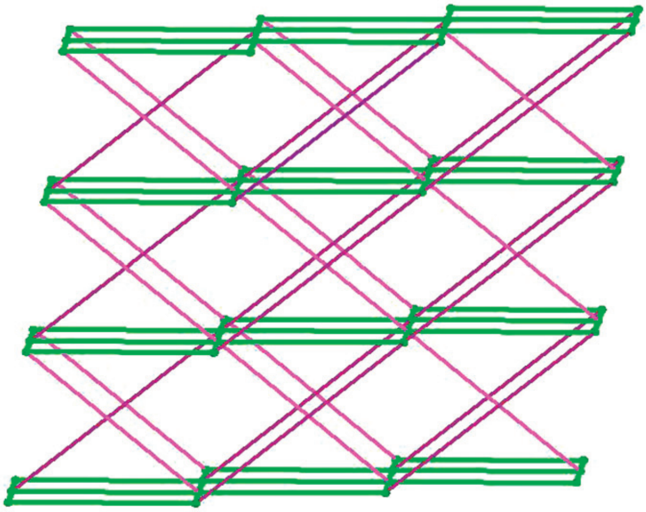


Figure 2. Topological representation of the structure of **1** leading to a $4^4 6^{10} 8$ topology.

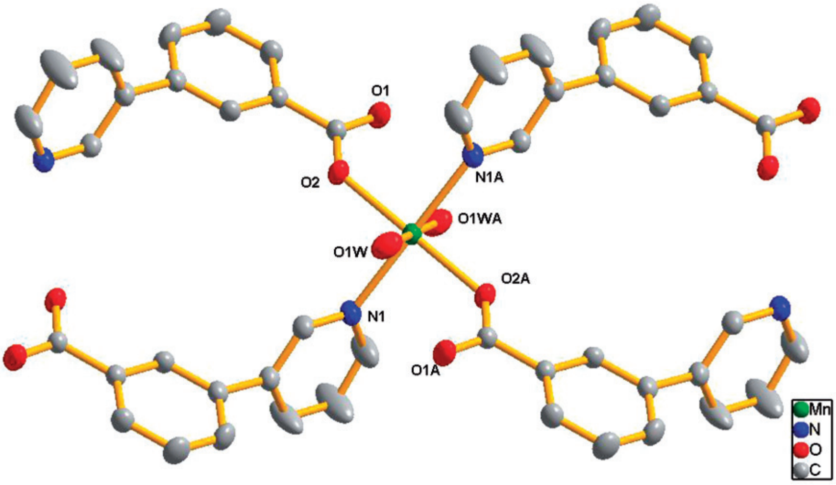


Figure 3. The coordination environment of Mn(II) in **2** with thermal ellipsoids drawn at 50% probability level and all hydrogens omitted for clarity.

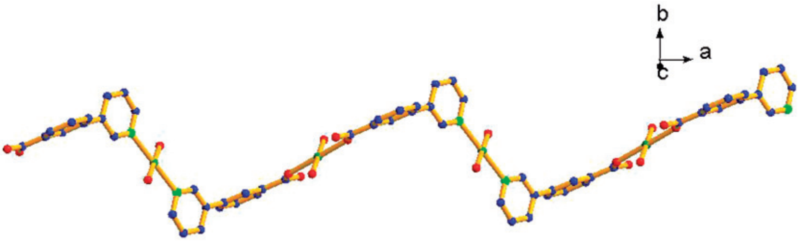


Figure 4. View of the 1-D zigzag chain along the *c*-axis.

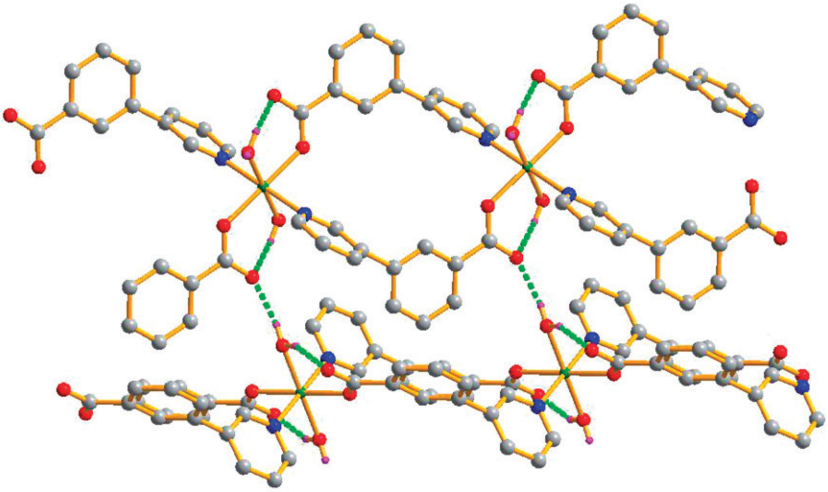


Figure 5. Crystal packing of **2**; hydrogens, except those involved in hydrogen bonding, are omitted for clarity.

oxygen of the adjacent chain at a D···A distance of 2.766 Å and an O–H–O angle of 173° (symmetry code: x, $1/2-y$, $-1/2+z$). The intrachain hydrogen bond is formed between O–H group of coordinated water and an uncoordinated carboxylate oxygen at a D···A distance of 2.727 Å and an O–H–O angle of 150° (symmetry code: $-x$, $1-y$, $-z$).

4. Conclusion

Two inorganic–organic compounds were isolated at different pH values. At higher pH value, Mn^{2+} ions are mononuclear octahedral. With decrease in pH, binuclear manganese clusters condensed to new subunits. The work, to some extent, provides an example of reasonable design and controllable assembly of inorganic–organic hybrid materials.

Supplementary material

Crystallographic information of the two compounds has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 710872 and 706294. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] B.O. Patrick, C.L. Stevens, A. Storr, R.C. Thompson. *Polyhedron*, **24**, 2242 (2005).
[2] Y.H. Wen, J.K. Cheng, Y.L. Feng, J. Zhang, Z.L. Li, Y.G. Yao. *Inorg. Chim. Acta*, **358**, 3347 (2005).
[3] X.L. Wang, C. Qin, E.B. Wang, L. Xu. *J. Mol. Struct.*, **749**, 45 (2005).
[4] S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003).
[5] M. Dinca, A.F. Yu, J.R. Long. *J. Am. Chem. Soc.*, **128**, 17153 (2006).
[6] J. Heo, Y.M. Jeon, C.A. Mirkin. *J. Am. Chem. Soc.*, **129**, 7712 (2007).
[7] F. Guo, W. Yu, X.L. Zhang. *Chin. J. Struct. Chem.*, **27**, 1123 (2008).
[8] J. Lewiński, J. Zachara, I. Justyniak, M. Dranka. *Coord. Chem. Rev.*, **249**, 1185 (2005).
[9] H.J. Chen, J. Zhang, W.L. Feng, M. Fu. *Inorg. Chem. Commun.*, **9**, 300 (2006).
[10] T.L. Hu, R.Q. Zou, J.R. Li, X.H. Bu. *J. Chem. Soc., Dalton Trans.*, 1302 (2008).
[11] J.F. Song, Y. Chen, Z.G. Li, R.S. Zhou, X.Y. Xu, J.Q. Xu. *J. Mol. Struct.*, **842**, 125 (2007).
[12] Bruker AXS. *SAINT Software Reference Manual*, Madison, WI (1998).
[13] G.M. Sheldrick. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[14] W.G. Lu, J.Z. Gu, L. Jiang, M.Y. Tan, T.B. Lu. *Cryst. Growth Des.*, **8**, 7192 (2008).
[15] S.M. Humphrey, T.J.P. Angliss, M. Aransay, D. Cave, L.A. Gerrard, G.F. Weldon, P.T. Wood. *Z. Anorg. Allg. Chem.*, **633**, 2342 (2007).
[16] X.W. Wang, Y.R. Dong, Y.Q. Zheng, J.Z. Chen. *Cryst. Growth Des.*, **7**, 613 (2007).