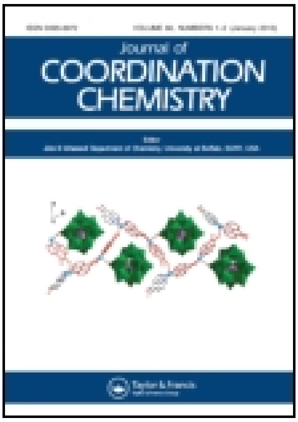

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Syntheses and structures of three Mn(II) coordination polymers assembled from a dithiocarboxylic acid and N-donor ligands

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Syntheses and structures of three Mn(II) coordination polymers assembled from a dithiocarboxylic acid and N-donor ligands

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Three new complexes, $\{[Mn(dtb)(bpe)\cdot 2H_2O]\cdot H_2O\}_n$ (**1**), $\{[Mn(dtb)(bpa)\cdot 2H_2O]\cdot H_2O\}_n$ (**2**), and $\{[Mn(dtb)(phen)]\}_n$ (**3**) [H_2dtb = 5,5′-dithiobis(2-nitrobenzoic acid), bpe = 1,2-bis(4-pyridyl)ethene, bpa = 1,2-bi(4-pyridyl)ethane, phen = 1,10-phenanthroline], have been synthesized under hydrothermal conditions with $Mn(OAc)_2\cdot 4H_2O$, dtb, and different *N*-donor ligands. X-ray structure analyses of **1** and **2** reveal analogous structures with 1D helical chains and 2D 4^4 chiral layers. The structure of **3** shows a 1D chain which is outwardly decorated with phen ligands. These neutral polymeric complexes exhibit structural diversity due to the different coordination modes of the flexible dtb ligand and the N-donor ligands. The thermogravimetric analyses and X-ray powder diffractions of **1–3** are also presented.

Keywords: Coordination polymer; Disulfide ligand; Co-ligand; Hydrothermal reaction

1. Introduction

The flourishing research into crystal engineering and metal-organic frameworks (MOFs) has furnished a favorable junction for the esthetics of crystalline architectures and the potential applications of MOFs. The ultimate research goal is synthesis of targeted materials with tailored structures and physicochemical properties [1–3]. It has been observed that the type, flexibility, and geometry of the ligands used to construct MOFs play crucial roles in the designed synthesis of coordination networks [4]. Among various organic ligands, polycarboxylates have been extensively used as multifunctional tectons, due to their ability to extend structures through both covalent bonding and supramolecular interactions (H-bonding and aromatic stacking) [5–7]. However, in contrast to rigid carboxylates, coordination networks constructed from flexible carboxylates are relatively underdeveloped [8]. It is difficult to predict either the composition or the network topology constructed

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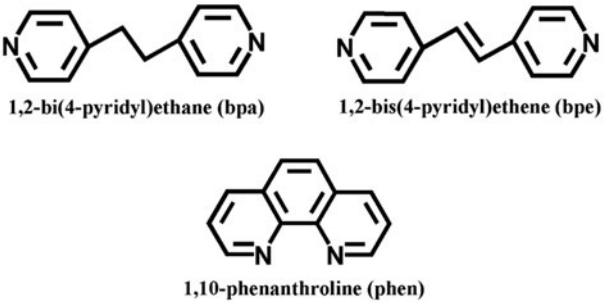
*Corresponding author. Email: hgxy@sust.edu.cn from a flexible carboxylate due to the conformational freedom of the linker during the assembly process. However, the conformational freedom and coordination functionality of flexible ligands might generate some unprecedented coordination frameworks [7c]. In this regard, flexible disulfide derivatives bearing –S–S– spacers have attracted interest because they can afford richer structural information than rigid ligands [9]. For this report, we focused our attention on utilization of a relatively unexplored, flexible disulfide derivative of a carboxylate, 5,5′-dithiobis(2-nitrobenzoic acid) (H_2dtb) [10]. This ligand has drawn our attention for the following reasons: (1) Different configurations can be generated by free rotation of the phenyl rings around the flexible –S–S– bridging group [11]. (2) H_2dtb can act as a hydrogen bond acceptor and donor depending on the degree of deprotonation. (3) H_2dtb contains multiple coordinating moieties, that is, the sulfur and nitro, which could afford interesting structures with tunable dimensionality [12a]. (4) The C–S–S–C torsion angles in aromatic carboxylates vary between 20° and 90°. The resulting axial chirality can potentially generate *M*- and *P*-enantiomeric helices and the formation of helical coordination polymers [12b].

The ability to introduce secondary organic ligands into a reaction system offers prospects for improving applicable properties of metal-organic supramolecular frameworks. However, due to the presence of many subtle interactions and limitations in self-assembly process, as well as difficulty in predicting the resulting products, the formation of extended solids based on mixed bridging ligands is still at a primitive stage and remains a challenge to chemists [13,14]. Introduction of N-donor ligands into a system with dtb may generate new structures and allow fine-tuning of the structures of these metal-organic compounds. Employing this strategy, we have prepared three new Mn(II) coordination polymers with dtb and three N-donor ligands (bpe, bpa, phen) (Scheme 1). The crystal structures of these compounds, along with investigation on the effect of coordination modes of dtb dianions and neutral N-donor ligands on the ultimate framework, will be discussed. TG analysis and PXRD of **1–3** are provided.

2. Experimental

2.1. *Materials and measurements*

The reagents were used directly from commercial suppliers without purification. Elemental analyses (C, H, N) were determined with a PerkinElmer model 240C instrument. Infrared spectra on KBr pellets were recorded on a Bruker Equinox-55 spectrometer from 4000 to



Scheme 1. Structures of the three N-donor ligands used in this work.

400 cm^{-1}. Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The X-ray powder diffraction patterns were recorded with a Pigaku D/Max 3III diffractometer. Thermal analyses were determined with a Netzsch STA 449C microanalyzer under flowing N_2 at a heating rate of 10 °C/min.

2.2. *Preparation of {[Mn(dtb)(bpe)·2H$_2$O]·H$_2$O}$_n$ (1)*

Compound **1** was obtained by reaction of $Mn(OAc)_2 \cdot 4H_2O$ (0.025 g, 0.1 mmol), H_2dtb (0.039 g, 0.1 mmol), bpe (0.018 g, 0.1 mmol), ethanol (2.0 mL), and distilled water (15.0 mL) under hydrothermal conditions. The pH of the reaction solution was adjusted to 7 with 1 M NaOH; it was heated to 130 °C for 6 days and then cooled to room temperature at 5 °C h^{-1}. Colorless crystals of **1** (0.021 g, 55% yield) were collected. Anal. Calcd. for $C_{26}H_{22}MnN_4O_{11}S_2$: C, 45.55; H, 3.23; N, 8.17. Found: C, 46.04; H, 3.61; N, 8.36%. IR (KBr, cm^{-1}): 3458(w), 3238(w), 3082(w), 1646(s), 1561(s), 1519(s), 1339(s), 1149(w), 1099(w), 1035(w), 931(w), 875(w), 842(m), 760(w), 736(m), 656(w).

2.3. *Preparation of {[Mn(dtb)(bpa)·2H$_2$O]·H$_2$O}$_n$ (2)*

Compound **2** was synthesized analogously to **1** except that bpe was replaced by bpa. Colorless block X-ray-quality crystals (0.026 g, 60% yield) were obtained. Anal. Calcd for $C_{26}H_{24}MnN_4O_{11}S_2$: C, 45.42; H, 3.51; N, 8.15. Found: C, 45.54; H, 3.74; N, 8.71. IR (KBr, cm^{-1}): 3441(w), 3244(w), 3050(w), 1626(s), 1563(s), 1512(s), 1401(s), 1366(s), 1146(w), 1098(w), 1048(w), 880(w), 845(m), 790(w), 760(m), 728(m).

2.4. *Preparation of {[Mn(dtb)(phen)]}$_n$ (3)*

Compound **3** was synthesized analogously to **1** except that bpe was replaced by phen. Colorless block X-ray-quality crystals (0.022 g, 56% yield) were obtained. Anal. Calcd for $C_{26}H_{14}MnN_4O_8S_2$: C, 49.61; H, 2.24; N, 8.90. Found: C, 49.04; H, 2.74; N, 8.71. IR (KBr, cm^{-1}): 3561(w), 3461(w), 3078(w), 2959(w), 1624(s), 1564(s), 1518(s), 1430(s), 1360(s), 1323(s), 1230(w), 1152(w), 1069(w), 1035(w), 848(m), 813(w), 767(w), 738(m), 650(m).

2.5. *Crystallographic data collection and structure determination*

Single-crystal X-ray diffraction analyses of **1–3** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by using the ϕ/ω scan technique at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [15a] and refined using the full-matrix least-squares method on *F*2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [15]. The crystallographic data for **1–3** are listed in table 1 and selected bond lengths and angles are listed in table S1. Hydrogen-bonding parameters for **1** and **2** are listed in table S2.

Table 1. Crystal data and structure refinement parameters for **1–3**[a].

Complexes	**1**	**2**	**3**
Empirical formula	$C_{26}H_{22}MnN_4O_{11}S_2$	$C_{26}H_{24}MnN_4O_{11}S_2$	$C_{26}H_{14}MnN_4O_8S_2$
Formula mass	685.54	687.55	629.47
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P−1*	*P−1*	*C2/c*
a [Å]	9.916(2)	9.982(2)	27.075(5)
b [Å]	11.906(3)	11.990(3)	11.716(2)
c [Å]	13.431(3)	13.427(3)	20.668(6)
α [°]	67.168(4)	67.228(4)	90.00
β [°]	71.504(4)	71.334(4)	128.131(2)
γ [°]	81.029(5)	80.291(4)	90.00
V [Å^3]	1385.0(5)	1402.0(5)	5157(2)
Z	2	2	8
$D_{Calcd.}$ [g cm^{-3}]	1.644	1.629	1.627
μ [mm^{-1}]	0.698	0.690	0.734
F [0 0 0]	702	706	2568.0
θ [°]	1.71−25.19	1.71−25.20	1.98–25.10
Reflections	7083/4880	6612/4891	12,749/4582
R_{int}	0.0372	0.0259	0.0601
GOF on F^2	1.000	1.039	0.983
Data/parameters	4880/397	4891/397	4582/370
Final $R^{[a]}$ indices (all data)	$R_1 = 0.1090$	$R_1 = 0.0931$	$R_1 = 0.0795$
	$wR_2 = 0.1672$	$wR_2 = 0.2335$	$wR_2 = 0.1012$

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

3. Result and discussion

3.1. *Crystal structure*

3.1.1. {[Mn(dtb)(bpe)·2H$_2$O]·H$_2$O}$_n$ (1). Single-crystal X-ray diffraction analysis showed that **1** crystallized in the *P-1* space group. The asymmetric unit consists of one Mn(II), one dtb, one bpe, two coordinated waters, and one lattice water, as shown in figure 1a. Each Mn (II) is coordinated in the equatorial plane by four O, one from each of two dtb ligands and two waters, and two N from two bridging bpe ligands, in axial positions, to furnish an octahedral geometry. The Mn–O and Mn–N bond distances are 2.142(4)–2.254(4) and 2.268(5)–2.291(4) Å, respectively, in agreement with those reported for other Mn(II) complexes [16].

The carboxylate of dtb coordinates to Mn(II) with a bridging bis(monodentate) mode to produce chiral, 1D helical chains (Mn^{2+}–dtb^{2-}–Mn^{2+})$_n$, due to the twist of the dtb ligand.

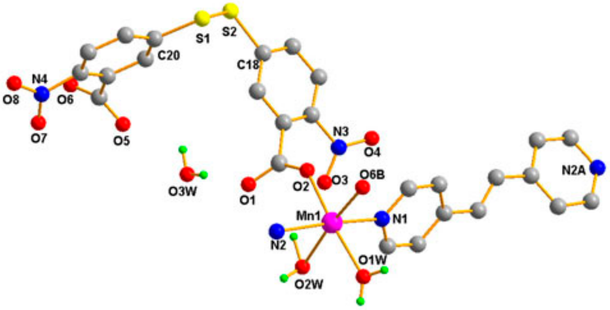


Figure 1a. Local coordination environment of the Mn(II) ion in **1**.

Both enantiomers of the chiral chains are present (figure 1b), affording the overall achiral structure. The bpe ligands link these 1D chains to generate 2D 4^4 chiral layers (figure 1c). Furthermore, the 2D layers are offset to each other, with the linkers of one layer placed between the grids of the adjacent layer (figure 1d). There is also hydrogen bonding between the 2D sheets, involving $-COO^-$ of dtb and coordinated and lattice water to form a 3D supramolecular network (O···O 2.688–3.029 Å) (figures 1e and S1).

3.1.2. {[Mn(dtb)(bpa)·2H$_2$O]·H$_2$O}$_n$ (2).

When bpa was used instead of bpe, **2** was formed. The single-crystal X-ray diffraction analysis revealed that **1** and **2** have the same Mn(II) coordination environment and same coordination mode of dtb (figure S2). Analogous 1D helical chains and 2D 4^4 chiral layers (figures S3 and S4) are also formed. Comparison of the C–C–C–C torsion angles and the dihedral angles of the two phenyl rings in bpe and bpa, and the S–S bond length, the C–S–S–C torsion angle, and the dihedral angle of the two phenyl rings in the dtb ligand (tables S3 and S4) showed that the configurations of bpe, bpa, and dtb are similar in **1** and **2**. As in **1**, the hydrogen-bonding interactions between coordinated waters and $-COO^-$ of dtb link the 2D layer to form a supramolecular network (O···O 2.697–3.262 Å) (figure S5).

3.1.3. {[Mn(dtb)(phen)]}$_n$ (3).

Complex **3** was synthesized with phen. The asymmetric unit consists of one Mn(II), one dtb, and one phen, as shown in figure 2a. Mn(II) is coordinated by four O from four dtb ligands and two N from phen in an octahedral coordination geometry perturbed by the Jahn–Teller distortion. The Mn–N bond lengths are 2.295(3) Å and 2.387(3) Å, and the Mn–O bond lengths are 2.133(2)–2.242(2) Å. While the Mn(1)–N(1) bond length of 2.387 Å is longer than the other Mn-N bond distances in **1–3**, it is still within normal ranges [16f,g]. Each carboxylate of dtb bridges two Mn to give a paddle-wheel shaped unit with Mn···Mn distance of 3.641(8) Å, which is similar to the reported Mn-Mn distance in the dimanganese paddle-wheel SUB unit of the MOF Mn-5TIA-3 (5-tia = 5-triazole isophthalic acid) [17]. The Mn-Mn distance in **3** is longer than the Mn-Mn distance of 3.462 Å reported for [Mn(dpa)(2,2′-bipy)]$_n$ (dpa = 2,4′-diphenic acid) [18]. The bimetallic Mn(II) units are linked by dtb ligands to form a 1D chain, which lies in the *a*-plane (figure 2b). The exterior of the 1D chains are decorated with phen ligands. Different 1D chains are alternately stacked in the crystal, as shown in figure S6.

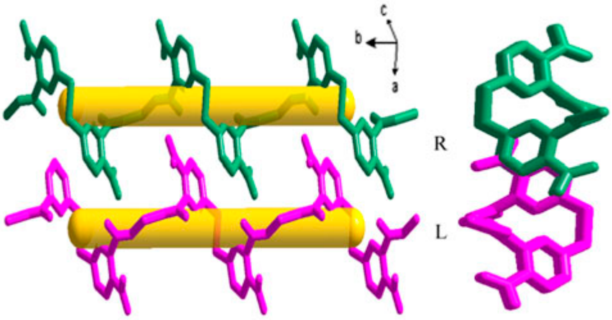


Figure 1b. Perspective views of the left-handed and right-handed helices of **1**.

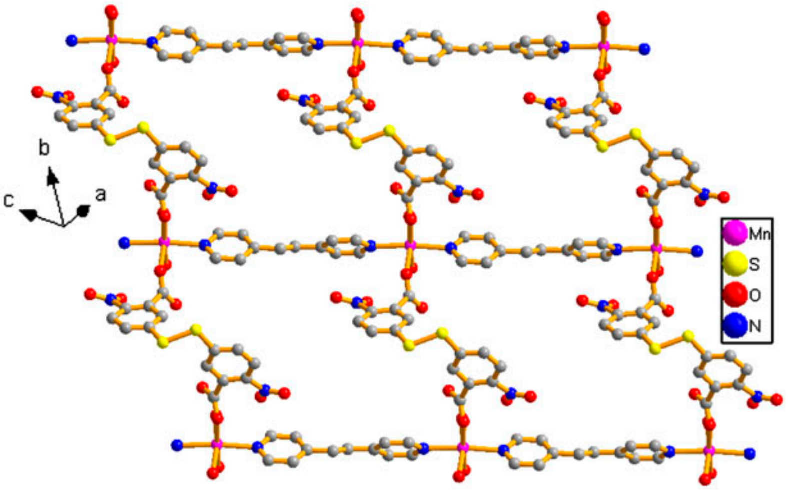


Figure 1c. The 2D chiral sheet of **1** connected by 1D helical chains and bpe ligands.

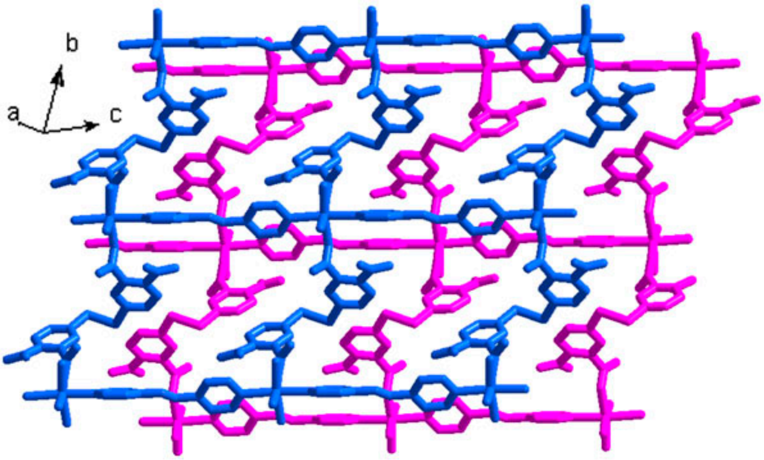


Figure 1d. Schematic representation of the offset arrangement of adjacent layers in **1**.

3.2. *Comparison of the structures*

The flexible –S–S– bridging group plays an important role in free rotation of the two phenyl rings of dtb. In **1** and **2**, the carboxylate groups of dtb show the same coordination mode. Furthermore, the dtb ligands and the *N*-donor ligands (bpe, bpa) in **1** and **2** have similar configurations, resulting in similar structures. This is surprising given that bpa has extra rotational freedom as compared to bpe. The V-shaped configuration of dtb is good for formation of helices because of its twist conformation with a C–S–S–C torsion angle of ca. 90° and axial chirality that can potentially generate *M*- and *P*-helical enantiomers, as described in the relevant chiral crystal engineering literature [10,14]. When rod-like co-ligands (bpe and bpa) were selected as auxiliary ligands, it was found that these could extend the metal–dtb 1D chains connected by Mn(II) and dtb ligands to produce 2D sheets

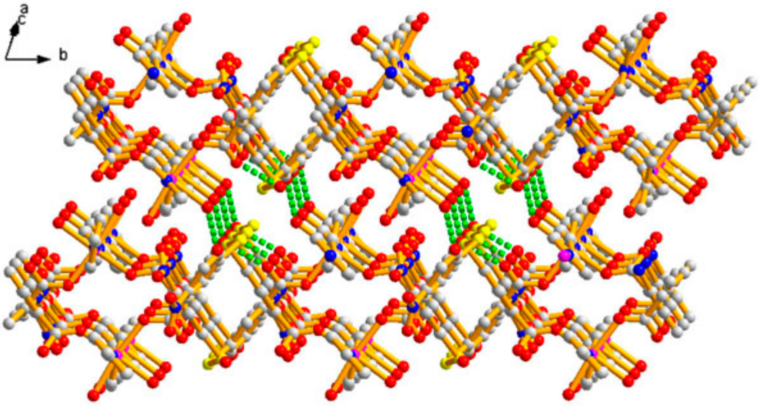


Figure 1e. The 3D supramolecular network of **1** formed through hydrogen bonding.

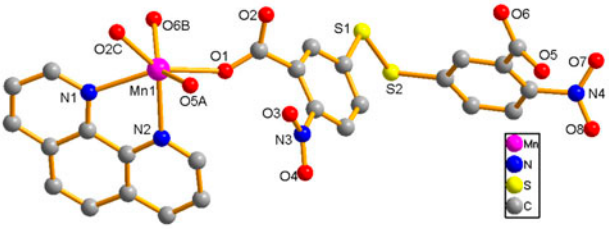


Figure 2a. Local coordination environment of the Mn(II) ion in **3**.

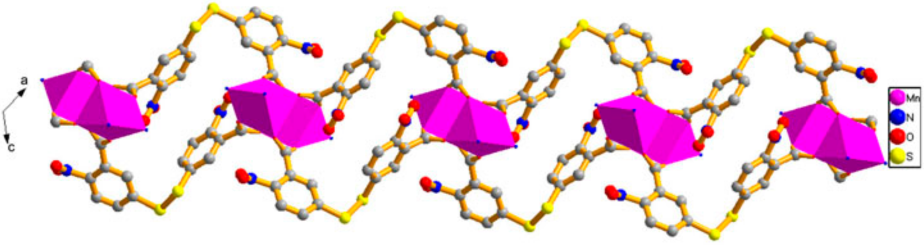


Figure 2b. The 1D chain of **3** connected by the bimetallic Mn(II) units and dtb ligands.

in **1** and **2** [14a]. When the chelating N-donor (phen) was employed as the starting reactant, a simple 1D chain polymer was obtained. This implies that the steric hindrance and chelation of these terminal ligands can constrain the prolongation of the framework and result in formation of lower dimensionality. Although the above-mentioned factors work together to affect the structures of compounds, it is difficult to control and separate them, because all the variable factors cannot be accurately forecast. Therefore, comprehensive research is required, and the goal of rational design of coordination polymers is a long-term challenge [14].

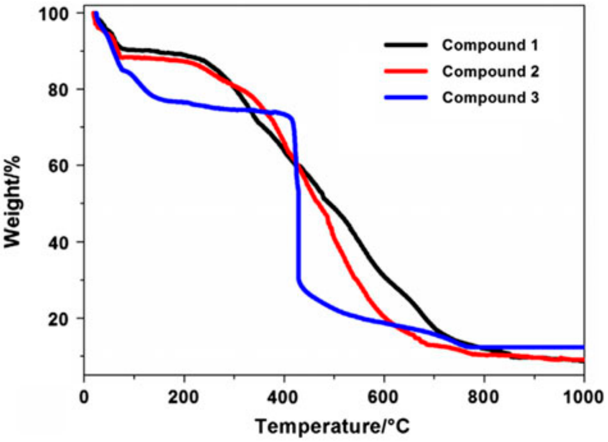


Figure 3. TGA curves of **1–3**.

3.3. *PXRD patterns and thermal stability analyses*

The PXRD patterns of **1–3** and their comparison to simulated patterns from the single-crystal data reveal that all compounds are single-phase pure (figure S7).

To study the thermal stabilities of these complexes, thermal gravimetric analysis (TGA) of **1–3** was carried out under N_2 (figure 3). The TGA curves of **1** and **2** are similar, thus only the thermal stability of **1** is discussed. For **1**, the first step in the temperature range 27–182 °C corresponds to the loss of free and coordinated water (obsd 8.31%, Calcd 7.89%). The second step occurs between 200 and 870 °C, corresponding to loss of bpe and dtb. The remaining weight of 12.01% is consistent with that for MnO (Calcd 10.35%). The TG curve of **3** shows that it undergoes loss of phen below 390 °C (obsd 73.04%, Calcd 71.37%), followed by a rapid decomposition of the remaining substance which is finally finished at 850 °C. The final residue of 12.11 wt% corresponds to MnO (Calcd 11.27%).

4. Conclusion

Reactions of dtb and N-donors with a Mn(II) salt afford three transition-metal polymeric frameworks. Compounds **1** and **2** reveal similar 1D helical chains and 2D 4^4 chiral layers. Compound **3** shows a 1D chain which is outwardly decorated with phen ligands. These neutral polymeric complexes exhibit structural and dimensional diversity due to the different coordination modes of the flexible dtb ligand and the effect of the N-donor ligands. Particularly, the steric hindrance and chelating effects of a terminal ligand (phen) can constrain the prolongation of the framework and result in the formation of polymers with lower dimensionality. Simultaneously, the V-shaped configuration of dtb is good for construction of helical structures. Further investigations on similar systems involving dtb will be pursued in future work.

Supplementary material

Tables of bond distances and angles, hydrogen-bonding interactions, and torsion angles for **1–3**; structural representations of **2** and **3**; experimental and simulated PXRD data for **1–3**.

Crystallographic data for **1–3** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC: 898301–898303). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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References

[1] (a) J.Q. Liu, Y.N. Zhang, Y.Y. Wang, J.C. Jin, E.K. Lermontova, Q.Z. Shi. *Dalton Trans*., 5365 (2009); (b) O. M. Yaghi, J.L.C. Rowsell. *J. Am. Chem. Soc*., **128**, 1304 (2006); (c) X. Zhao, B. Xiao, A.J. Fletcher, K.M. Thomas, D. Bradshaw, M.J. Rosseinsky. Science, **306**, 1012 (2004); (d) N.L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi. Science, **300**, 1127 (2003); (e) Y.W. Li, R.T. Yang. J. Am. Chem. Soc., **128**, 726 (2006).

[2] (a) Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T.C. Kobayashi. *Angew. Chem., Int. Ed*., **44**, 920 (2005); (b) S. Horike, R. Matsuda, D. Tanaka, M. Mizuno, K. Endo, S. Kitagawa. *J. Am. Chem. Soc*., **128**, 4222 (2006); (c) M. Dinca, A.F. Yu, J.R. Long. *J. Am. Chem. Soc*., **128**, 8904 (2006); (d) Y.N. Zhang, X. Hai, Y.T. Li, L. Cui, Y.Y. Wang. *J. Coord. Chem*., **65**, 2724 (2012).

[3] (a) A.C. Sudik, A.R. Millward, N.W. Ockwig, A.P. Cote, J. Kim, O.M. Yaghi. *J. Am. Chem. Soc*., **127**, 7110 (2005); (b) X.S. Wang, S. Ma, D. Sun, S. Parkin, H.C. Zhou. *J. Am. Chem. Soc*., **128**, 16474 (2006); (c) S. Sun, D. Ma, M. Ambrogio, J.A. Fillinger, S. Parkin, H.C. Zhou. *J. Am. Chem. Soc*., **129**, 1858 (2007).

[4] (a) X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Bu, M. Shionoya, F. Brisse, J. Ribas. *Angew. Chem., Int. Ed*., **40**, 3201 (2001); (b) D.N. Dybtsev, H. Chun, K. Kim. *Angew. Chem., Int. Ed*., **43**, 5033 (2004); (c) X.L.Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu. *Angew. Chem., Int. Ed*., **43**, 5036 (2004); (d) L.F. Ma, L.Y. Wang, X.K. Huo, Y.Y. Wang, Y.T. Fan, J.G. Wang, S.H. Chen. *Cryst. Growth Des*., **8**, 620 (2008).

[5] (a) L. Pan, H. Liu, X. Lei, X. Huang, D.H. Olson, N.J. Turro, J. Li. *Angew. Chem., Int. Ed*., **42**, 542 (2003); (b) S.K. Ghosh, R. Joan, P.K. Bharadwaj. *Cryst. Growth Des*., **5**, 623 (2005); (c) T.K. Maji, M. Ohba, S. Kitagawa. *Inorg. Chem*., **44**, 9225 (2005); (d) H.A. Habib, J. Sanchiz, C. Janiak. *Dalton Trans*., 4877 (2008); (e) J.F. Ma, J. Yang, G.L. Zheng, L. Li, J.F. Liu. *Inorg. Chem*., **42**, 7531 (2003); (f) L. Wang, M. Yang, G.H. Li, Z. Shi, S.H. Feng. *Inorg. Chem*., **45**, 2474 (2006); (g) J.G. Lin, S.Q. Zang, Z.F. Tian, Y.Z. Li, Y.Y. Xu, H.Z. Zhu, Q.J. Meng. *CrystEngComm*, **9**, 915 (2007).

[6] (a) W.G. Lu, J.Z. Gu, L. Jiang, M.Y. Tan, T.B. Lu. *Cryst. Growth Des*., **8**, 192 (2008); (b) H. Chun, H. Jung. *Inorg. Chem*., **48**, 417 (2009); (c) M. Du, X.J. Jiang, X.J. Zhao. *Inorg. Chem*., **46**, 3984 (2007); (d) X.D. Guo, G.S. Zhu, F.X. Sun, Z.Y. Li, X.J. Zhao, X.T. Li, H.C. Wang, S.L. Qiu. *Inorg. Chem*., **45**, 2581 (2006); (e) G.B. Che, C.B. Liu, B. Liu, Q.W. Wang, Z.L. Xu. *CrystEngComm*, **10**, 184 (2008); (f) D.R. Xiao, E.B. Wang, H.Y. An, Y.G. Li, Z.M. Su, C.Y. Sun. *Chem. Eur. J*., **12**, 6528 (2006); (g) C.B. Ma, C.N. Chen, Q.T. Liu, F. Chen, D.Z. Liao, L.C. Li, L.H. Sun. *Eur. J. Inorg. Chem*., **16**, 3316 (2004); (h) S.C. Manna, E. Zangrando, J. Ribas, N.R. Chaudhuri. *Eur. J. Inorg. Chem*., **9**, 1400 (2008).

[7] (a) H.K. Chae, D.Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi. *Nature*, **427**, 523 (2004); (b) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003); (c) G.Q. Kong, C.D. Wu. *Cryst. Growth Des*., **10**, 4590 (2010).

[8] (a) Y.B. Dong, Y.Y. Jiang, J. Li, J.P. Ma, F.L. Liu, B. Tang, R.Q. Huang, S.R. Batten. *J. Am. Chem. Soc*., **129**, 4520 (2007); (b) A.K. Bar, R. Chakrabarty, P.S. Mukherjee. *Inorg. Chem*., **48**, 10880 (2009); (c) Z.H. Zhang, Y. Song, T.A. Okamura, Y. Hasegawa, W.Y. Sun, N. Ueyama. *Inorg. Chem*., **45**, 2896 (2006); (d) X. G. Liu, L.Y. Wang, X. Zhu, B.L. Li, Y. Zhang. *Cryst. Growth Des*., **9**, 3997 (2009); (e) S.N. Wang, R. Sun, X.S. Wang, Y.Z. Li, Y. Pan, J. Bai, M. Scheer, X.Z. You. *CrystEngComm*, **9**, 1051 (2007).

[9] (a) L.F. Ma, L.Y. Wang, M. Du. *CrystEngComm*, **11**, 2593 (2009); (b) J.H. Luo, M.C. Hong, R.H. Wang, D. Q. Yuan, R. Cao, L. Han, Y.Q. Xu, Z.Z. Lin. *Eur. J. Inorg. Chem*., 3623 (2003); (c) X.Y. Yu, M. Maekawa, T. Morita, H.C. Chang, S. Kitagawa, G.X. Jin. *Bull. Chem. Soc. Jpn*., **75**, 267 (2002); (d) A.J. Blake, N.R. Brooks, N.R. Champness, M. Crew, D.H. Gregory, P. Hubberstey, M. Schroder, A. Deveson, D. Fenske, L.

R. Hanton. *Chem. Commun*., 1432 (2001); (e) F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang. *J. Am. Chem. Soc*., **123**, 7740 (2001); (f) M. Kondo, M. Shimamura, S. Noro, Y. Kimura, K. Uemura, S. Kitagawa. *J. Solid State Chem*., **152**, 113 (2000); (g) R. Horikoshi, T. Mochida, M. Kurihara, M. Mikuriya. *Cryst. Growth Des*., **5**, 243 (2005).

[10] (a) Z. Dong, Y.Y. Wang, R.T. Liu, J.Q. Liu, Q.Z. Shi. *Cryst. Growth Des*., **10**, 3311 (2010); (b) Z. Dong, W. H. Zhang, Y.Y. Wang. *Chin. Sci. Bull*., **54**, 4285 (2009); (c) S.Q. Zang, Y. Su, Y.Z. Li, Z.P. Ni, Q.J. Meng. *Inorg. Chem*., **45**, 174 (2006); (d) S.L. Li, Y.Q. Lan, J.F. Ma. *Cryst. Growth Des*., **47**, 1610 (2008); (e) D.R. Xiao, E.B. Wang, H.Y. *An. Cryst. Growth Des*., **7**, 506 (2007); (f) Q. Chu, G.X. Liu, Y.Q. Huang. Dalton Trans., 4302 (2007); (g) L.J. Wang. *Acta Cryst*., **E64**, o2051 (2008); (h) E. Shefter, T.I. Kalman. *J. Chem. Soc. D*, 1027 (1969).

[11] (a) R. Horikoshi, M. Mikuriya. *Cryst. Growth Des*., **5**, 223 (2005); (b) R. Horikoshi, T. Mochida. *Inorg Chem*., **40**, 2430 (2001).

[12] (a) C.Y. Niu, B.L. Wu, X.F. Zhang. H.W. Hong, Y.Y. Niu, Z.J. Li. Cryst. *Growth Des*., **8**, 1566 (2008); (b) H.L. Zhou, J.L. Lin, W. Xu, J. Zhang, Y.Q. Zheng. *J. Coord. Chem*., **64**, 2088 (2011).

[13] (a) L. Carlucci, G. Ciani, D.M. Proserpio, R. Silvia. *CrystEngComm*, **5**, 190 (2003); (b) Y.N. Zhang, X. Hai, Y.T. Li, L. Cui, Y.Y. Wang. *J. Coord. Chem*., **65**, 2724 (2012); (c) L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato. *CrystEngComm*, **4**, 121 (2002); (d) F.A.A. Paz, J. Klinowski. *Inorg. Chem*., **43**, 3882 (2004); (e) X. J. Luan, Y.Y. Wang, D.S. Li, P. Liu, H.M. Hu, Q.Z. Shi, S.M. Peng. *Angew. Chem., Int. Ed*., **44**, 3864 (2005).

[14] (a) Y.N. Zhang, Y.Y. Wang, L. Hou, P. Liu, J.Q. Liu, Q.Z. Shi. *CrystEngComm*, **12**, 3840 (2010); (b) Y.N. Zhang, Y.Y. Wang, L.Y. Wu, L.Y. Pang, Q.Z. Shi. *Cryst. Growth Des*., **11**, 1531 (2011).

[15] (a) G.M. Sheldrick. *Acta Crystallogr., Sect. A*, **46**, 467 (1990); (b) G.M. Sheldrick, *SHELXS*, University of Göttingen, Germany (1997); (c) W. Madison, Bruker *APEX2* Software, Bruker AXS Inc.V2.0-1, USA (2005); (d) G.M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1997); (e) G.M. Sheldrick, *SHELXL, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).

[16] (a) X.H. Chang, J.H. Qin, J.F. Ma. *Cryst. Growth Des*., **12**, 4649 (2012); (b) L. Zhang, X.L. Wu, A.Q. Wang, F. Qin, D.W. Meng, X.Y. Liu. *J. Coord. Chem*., **65**, 1518 (2012); (c) Y.F. Deng, Z.H. Zhou. *J. Coord. Chem*., **62**, 778 (2009); (d) J.P. Zou, S.C. Dai, W.T. Guan, H.B. Yang, Y.F. Feng, X.B. Luo. *J. Coord. Chem*., **65**, 2877 (2012); (e) X. Feng, Y.Y. Wang, Y.C. Hu, S.P. Chen, W.J. Zhao, X.W. Yang. *J. Coord. Chem*., **65**, 2692 (2012); (f) M. Leopoldini, N. Russo, M. Toscano. *Chem. Eur. J*., **15**, 8026 (2009); (g) K. Meyer, J. Bendix, N. Metzler-Nolte, T. Weyhermuller, K. Wieghardt. *J. Am. Chem., Soc*., **120**, 7260 (1998).

[17] T. Panda, P. Pradip, R. Banerjee. *Chem. Commun*., **47**, 7674 (2011).

[18] F. Guo, B.Y. Zhu, Y.L. Song, X.L. Zhang. *J. Coord. Chem*., **63**, 1304 (2010).