Supporting Information

Effects of two different solvents on the syntheses, structural diversity, magnetic property of six Mn^{2+} complexes derived from 3,3'-((5-carboxy-1,3-phenylene)bis(oxy))dibenzate and variable N-donor ligands

Dongdong Yang,‡[*a, b] Xiaxia Liu,‡[a] Liping Lu,[*a] and Miaoli Zhu[*a, c]

[a] Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People' s Republic of China.

[b] Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China.

[c] Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province; Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China.

Corresponding Author
*E-mail: luliping@sxu.edu.cn
*E-mail: miaoli@sxu.edu.cn

Contents

S1. Tries of synthesis and crystal growth conditions

S1.1 Ratio of solvents

S1.1.1 Complex 1. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (25.40 mg, 0.15 mmol), DMF (8.0 mL) and NaOH (0.80 mg, 0.02 mmol), then the mixture was sealed into Teflon-lined stainless steel container and heated at 120ºC for 72 h. The white powder were collected by filtration, and simulated and experimental PXRD patterns of complex **1**(Fig. S2a).

S1.1.2.1 Complex 2. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (25.40 mg, 0.15 mmol), 1,4-bib (31.5 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol) and DMF/H_2O (7mL, 3:4V/V) was placed in a 15 mL Teflon-lined stainless steel vessel, heated to 120ºC for 72 h, followed by slow cooling to room temperature. Colorless block-shaped crystals were collected by filtration, washed with H_2O several times, and dried in air (yield 60%, based on H_3cpboda).

S1.1.2.2 Complex 2. With the same $_{\text{synthetic}}$ method as above, except that DMF/H_2O (7mL, 3:4V/V) were replaced by DMF/H_2O (7mL, 1:6V/V). Colorless block-like crystals of **2** were obtained in 50% yield (based on H_3cpboda). The resulting colorless block-like crystals of **2** were isolated by washing with H_2O, and dried in air.

S1.1.3.1 Complex 3. H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (25.40 mg, 0.15 mmol), phen (29.70 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol), DMF(3ml) and H_2O (4ml) was placed in a 15 mL Teflon-lined stainless steel vessel, heated to 120ºC for 72 h. Giving colorless block crystals of **3**. Yield of 63% (based on H_3cpboda).

S1.1.3.2 Complex 3. With the same synthetic method as above, except that DMF/H_2O (7mL, 3:4V/V) were replaced by DMF/H_2O (7mL, 1:6V/V). Colorless block-like crystals of **3** were obtained in 42% yield (based on H_3cpboda). The resulting colorless block-like crystals of **3** were isolated by washing with H_2O, and dried in air.

S1.2 Reacting temperature

S1.2.1 Complex 2. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (25.40 mg, 0.15 mmol), 1,4-bib (31.5 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol), DMF(5ml) and H_2O (2ml), then the mixture was sealed into Teflon-lined stainless steel container and heated at 140ºC and 160ºC for 72 h, respectively. Colorless block-like crystals of **2** were obtained in 58% yield in 140ºC and 53% yield in 160ºC, respectively. (based on H_3cpboda).

S1.2.2 Complex 3. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (25.40 mg, 0.15 mmol), phen (29.70 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol), DMF(5ml) and H_2O (2ml), then the mixture was sealed into Teflon-lined stainless steel container and heated at 140ºC and 160ºC for 72 h, respectively. Colorless block-like crystals of **3** were obtained in 58% yield in 140ºC and 44% yield in 160ºC, respectively. (based on H_3cpboda).

S1.3 Dosage of metal ion

S1.3.1 Complex 1. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (42.32 mg, 0.25 mmol), NaOH (0.80 mg, 0.02 mmol) and DMF/H_2O (8mL, 5:3V/V) was placed in a 15 mL Teflon-lined stainless steel vessel, heated to 120ºC for 72 h, Colorless block-shaped crystals were collected by filtration, washed with H_2O and dried in air, yield 48% (based on H_3cpboda).

S1.3.2.1 Complex 2. A mixture of H_3cpboda (39.50 mg, 0.1 mmol), $MnSO_4 \cdot H_2O$ (8.46 mg, 0.05 mmol), 1,4-bib (31.5 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol) and DMF/H_2O (7 mL, 5:2 V/V) was placed in a 15 mL of Teflon-lined stainless steel vessel, heated to 120ºC for 72 h, Colorless block-shaped crystals were collected by filtration, washed with H_2O several times, and dried in air (yield 15%, based on H_3cpboda).

S1.3.2.2 With the same synthetic method as above, except that $MnSO_4 \cdot H_2O$ (8.46 mg, 0.05 mmol) were replaced by $MnSO_4 \cdot H_2O$ (42.32 mg, 0.25 mmol). Colorless block-like crystals of **2** were obtained in 70% yield (based on H_3cpboda). The resulting colorless block-like crystals of **2** were isolated by washing with H_2O, and dried in air.

S1.3.3.1 Complex 3. A mixture of H_3cpboda (8.46 mg, 0.05 mmol), $MnSO_4 \cdot H_2O$ (16.93 mg, 0.1 mmol), phen (29.70 mg, 0.15 mmol), NaOH (0.80 mg, 0.02 mmol) and DMF/H_2O (7 mL, 5:2 V/V) was placed in a 15 mL of Teflon-lined stainless steel vessel, heated to 120ºC for 72 h, Colorless block-shaped crystals were collected by filtration, washed with H_2O several times, and dried in air (yield 23%, based on H_3cpboda).

S1.3.3.2 With the same synthetic method as above, except that $MnSO_4 \cdot H_2O$ (8.46 mg, 0.05 mmol) were replaced by $MnSO_4 \cdot H_2O$ (42.32 mg, 0.25 mmol). Colorless block-like crystals of **3** were obtained in 62% yield (based on H_3cpboda). The resulting colorless block-like crystals of **3** were isolated by washing with H_2O, and dried in air.

S2. The FT-IR spectra of H_3cpboda and 1-6

The FT-IR spectra of H_3cpboda and **1-6** are given in Fig. S1. In the spectra, the peaks at 3600-3400 cm^{-1}, attributed to the O-H stretching vibrations of water molecules.[S1] The strong bands from 1691 to 1376 cm^{-1} correspond to the COO^- symmetric stretching vibrations.[S2] The absorption peaks located at about 1200 cm^{-1} can be attributed to the C-O-C vibration of the ligand. Furthermore, the peaks at 840-650 cm^{-1} were assigned to the bending frequencies of O-C=O groups.[S3]

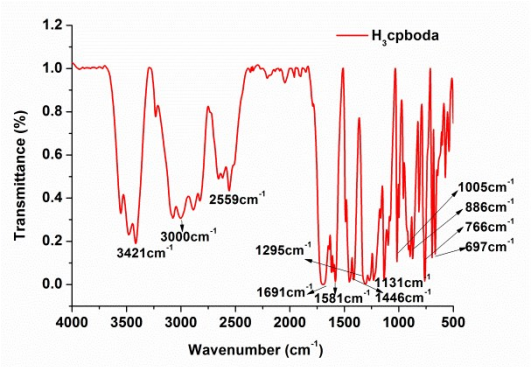


Fig. S1a

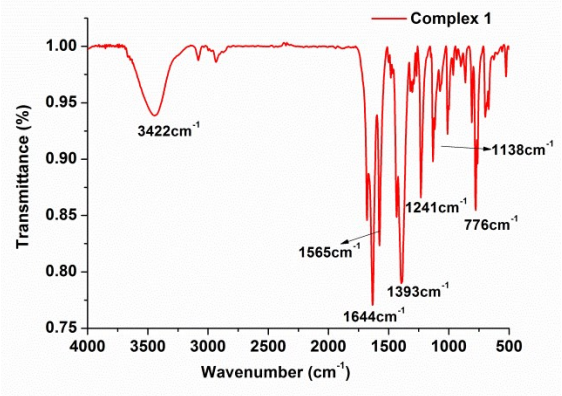


Fig. S1b

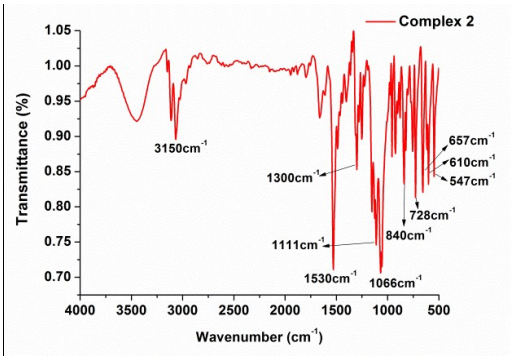


Fig. S1c

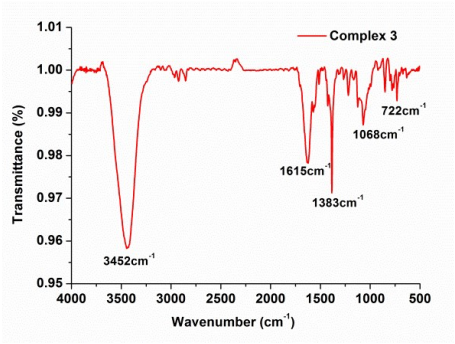


Fig. S1d

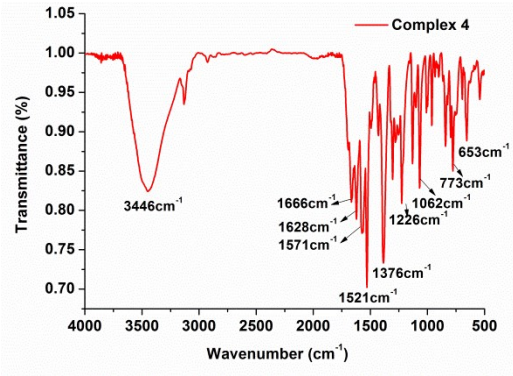


Fig. S1e

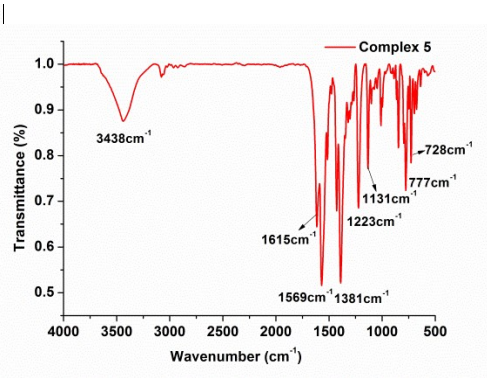


Fig. S1f

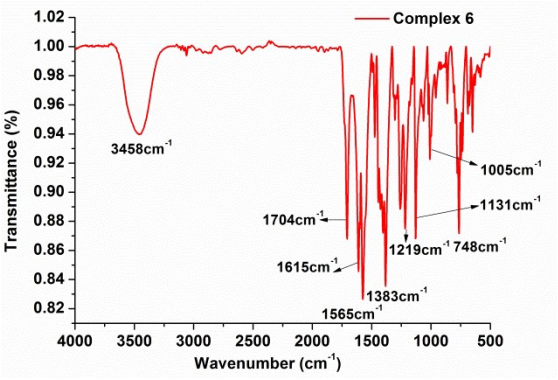
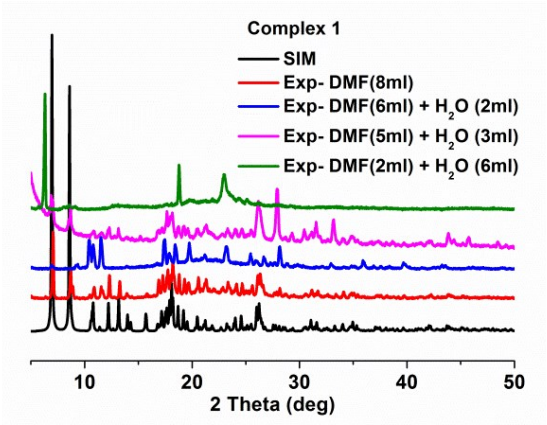
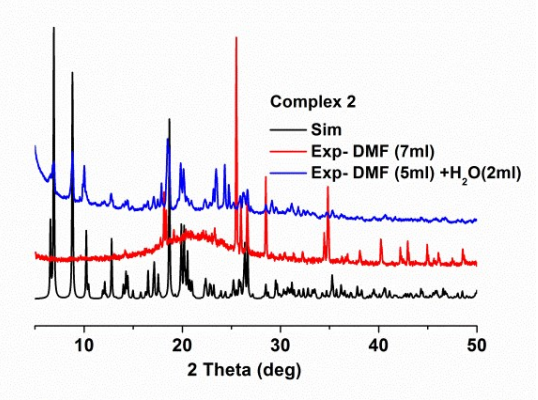


Fig. S1g

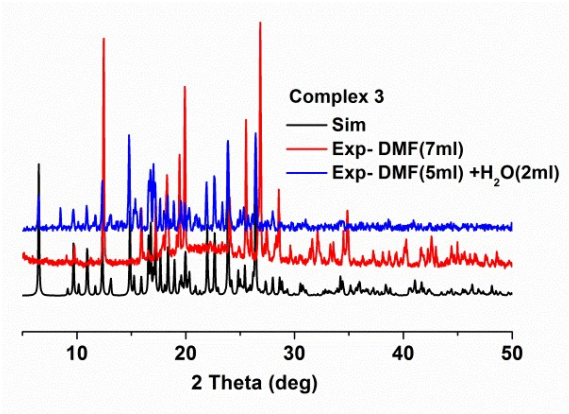
Fig. S1 The IR spectra of H_3cpboda ligand and complexes **1-6**



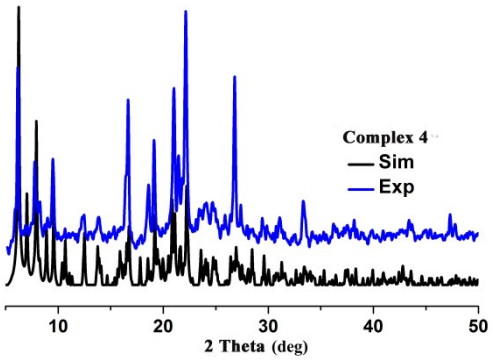
(a)



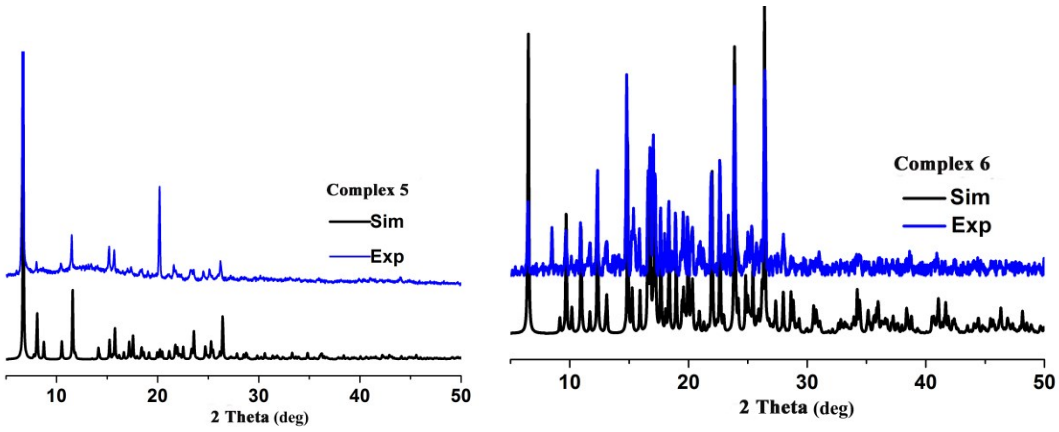
(b)



(c)



(d)



(e) (f)

Fig. S2 The PXRD of complexes **1-6**

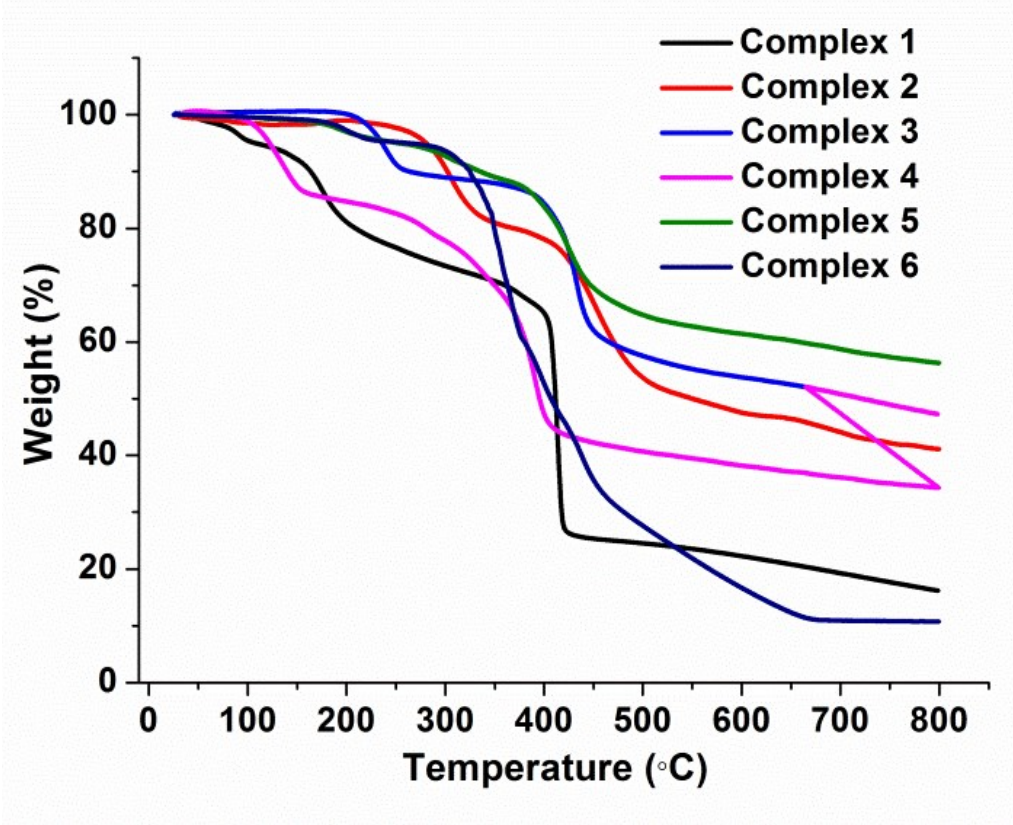


Fig. S3 The thermal curves of complexes **1a**-**4b**.

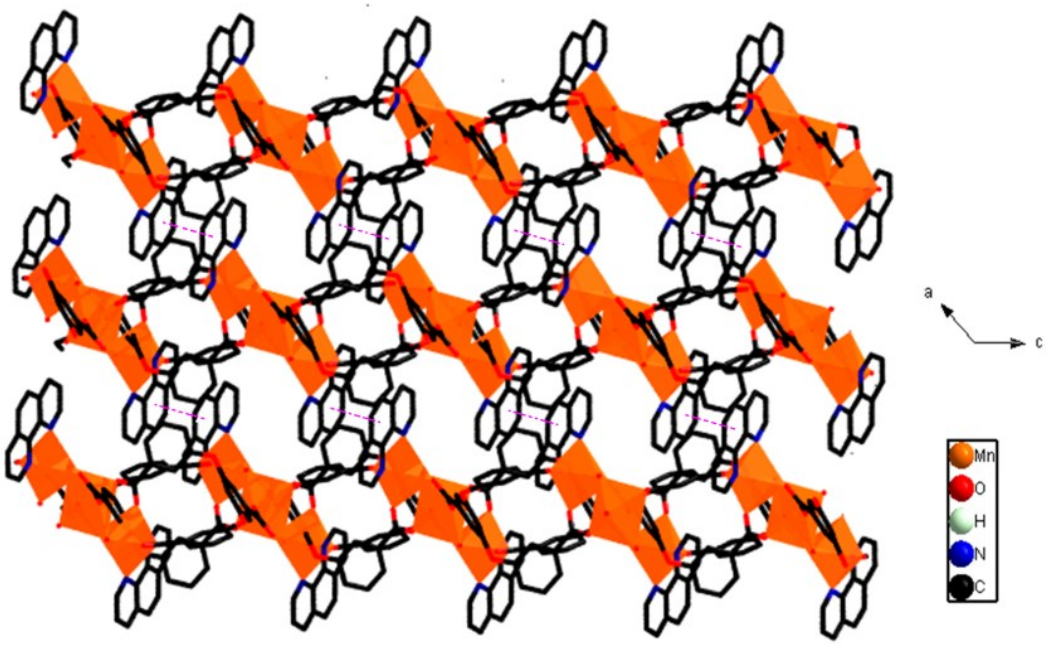


Fig. S4 A perspective view of the three-dimensional supramolecular structure to crystallographically equivalent nets *via* π···π interactions in **3**.

Table S1 Tries of synthesis and crystal growth conditions **1–5**

	Variable		Results
Related synthesis of complex **1**	Solvent ratio	DMF(8ml)	Crystal not for X-ray single diffracting
		DMF(6ml), H_2O (2 ml)	Precipitation
		DMF(4ml), H_2O (4 ml)	Solution
		DMF(2ml), H_2O (6 ml)	Precipitation
	Temperature(ºC)	120 ºC	Crystals of complex **1**
		140 ºC	Solution
		160 ºC	Solution
	Dosage of metal ion	$MnSO_4·H_2O$ (8.46 mg, 0.05 mmol)	Solution
		$MnSO_4·H_2O$ (25.40 mg, 0.15 mmol)	Crystals of complex **1**
		$MnSO_4·H_2$	Crystals of complex **1**

		O (42.32 mg, 0.25 mmol)	
	Different solvent	EtOH(5ml, H_2O (3 ml)	Precipitation
		EtOH(2ml, H_2O (6 ml)	Precipitation

Related synthesis of complex **2**	Variable		Results
	Solvent ratio	DMF(7ml)	Precipitation
		DMF(3ml), H_2O (4 ml)	Crystals of complex **2**
		DMF(1ml), H_2O (6 ml)	
	Temperature(ºC)	120 ºC	Crystals of complex **2**
		140 ºC	
		160 ºC	
	Dosage of metal ion	$MnSO_4·H_2O$ (8.46 mg, 0.05 mmol)	Crystals of complex **2**
		$MnSO_4·H_2O$ (25.40 mg, 0.15 mmol)	
		$MnSO_4·H_2O$ (42.32 mg, 0.25 mmol)	
	Different solvents	EtOH(2ml, H_2O (5 ml)	Crystals of complex **4**
		EtOH(5ml, H_2O (2 ml)	Precipitation

	Variable		Results
	Solvent ratio	DMF(7ml)	Precipitation
		DMF(3ml), H_2O (4 ml)	Crystals of complex **3**
		DMF(1ml), H_2O (6 ml)	

Related synthesis of complex **3**			
	Temperature(℃)	120 ℃	Crystals of complex **3**
		140 ℃	
		160 ℃	
	Dosage of metal ion	$MnSO_4·H_2O$ (8.46 mg, 0.05 mmol)	Crystals of complex **3**
		$MnSO_4·H_2O$ (25.40 mg, 0.15 mmol)	
		$MnSO_4·H_2O$ (42.32 mg, 0.25 mmol)	
	Different solvents	EtOH(2ml, H_2O (5 ml)	Crystals of complex **5**
		EtOH(5ml, H_2O (2 ml)	Precipitation

Tables S2. Selected bond lengths (Å) and angles (°) for complexes 1-6.

Complex 1

Mn1—O6^{i}	2.127 (2)	Mn2—O1	2.127 (3)
Mn1—O6	2.127 (2)	Mn2—O11	2.153 (3)
Mn1—O2	2.148 (2)	Mn2—O5	2.155 (2)
Mn1—O2^{i}	2.148 (2)	Mn2—O7	2.184 (2)
Mn1—O9^{i}	2.272 (2)	Mn2—O10	2.212 (2)
Mn1—O9	2.272 (2)	Mn2—O9	2.251 (2)
O6^{i}—Mn1—O6	180.0	O2—Mn1—O2^{i}	180.00 (6)
O6^{i}—Mn1—O2	88.68 (9)	O6^{i}—Mn1—O9^{i}	92.21 (8)
O6—Mn1—O2	91.31 (9)	O6—Mn1—O9^{i}	87.79 (8)
O6^{i}—Mn1—O2^{i}	91.32 (9)	O2—Mn1—O9^{i}	89.49 (9)
O6—Mn1—O2^{i}	88.69 (9)	O2^{i}—Mn1—O9^{i}	90.51 (9)
O6^{i}—Mn1—O9	87.79 (8)	O1—Mn2—O5	94.48 (10)
O6—Mn1—O9	92.21 (8)	O11—Mn2—O5	87.73 (10)
O2—Mn1—O9	90.51 (9)	O1—Mn2—O7	84.79 (11)
O2^{i}—Mn1—O9	89.49 (9)	O11—Mn2—O7	93.73 (10)

O9^{i}—Mn1—O9	180.0	O5—Mn2—O7	178.34 (10)
O1—Mn2—O11	88.20 (10)	O1—Mn2—O10	169.19 (10)
O11—Mn2—O10	86.38 (10)	O11—Mn2—O9	177.14 (9)
O5—Mn2—O10	94.65 (10)	O5—Mn2—O9	90.99 (9)
O7—Mn2—O10	86.23 (10)	O7—Mn2—O9	87.58 (9)
O1—Mn2—O9	94.45 (9)	O10—Mn2—O9	91.18 (8)

Symmetry codes: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*, *z*-1/2; (iii) *x*, -*y*, *z*+1/2.

Complex 2

Mn1—O3^{i}	2.089 (3)	Mn1—O9	2.338 (3)
Mn1—O2^{i}	2.109 (3)	Mn2—O4^{iii}	2.119 (3)
Mn1—O8	2.115 (3)	Mn2—O1^{i}	2.138 (3)
Mn1—O11^{ii}	2.235 (3)	Mn2—O10	2.216 (3)
Mn1—O10	2.284 (3)	Mn2—O9^{iv}	2.233 (3)
Mn2—O11^{ii}	2.270 (3)	Mn2—N1	2.235 (4)
O3^{i}—Mn1—O2^{i}	88.47 (14)	O8—Mn1—O10	87.16 (11)
O3^{i}—Mn1—O8	97.94 (14)	O11^{ii}—Mn1—O10	74.51 (10)
O2^{i}—Mn1—O8	98.28 (13)	O3^{i}—Mn1—O9	86.85 (13)
O3^{i}—Mn1—O11^{ii}	101.13 (13)	O2^{i}—Mn1—O9	174.84 (13)
O2^{i}—Mn1—O11^{ii}	92.08 (12)	O8—Mn1—O9	84.53 (11)
O8—Mn1—O11^{ii}	158.51 (12)	O11^{ii}—Mn1—O9	86.70 (10)
O3^{i}—Mn1—O10	173.79 (14)	O10—Mn1—O9	97.21 (11)
O2^{i}—Mn1—O10	87.29 (12)	O4^{iii}—Mn2—O1^{i}	170.32 (14)
O4^{iii}—Mn2—O10	93.84 (13)	O10—Mn2—N1	172.97 (13)
O1^{i}—Mn2—O10	90.74 (12)	O9^{iv}—Mn2—N1	95.24 (13)
O4^{iii}—Mn2—O9^{iv}	96.77 (12)	O4^{iii}—Mn2—O11^{ii}	86.12 (12)
O1^{i}—Mn2—O9^{iv}	91.66 (12)	O1^{i}—Mn2—O11^{ii}	86.83 (12)
O10—Mn2—O9^{iv}	90.94 (11)	O10—Mn2—O11^{ii}	75.17 (11)
O4^{iii}—Mn2—N1	88.74 (14)	O9^{iv}—Mn2—O11^{ii}	166.00 (10)
O1^{i}—Mn2—N1	85.76 (13)	N1—Mn2—O11^{ii}	98.52 (13)

Symmetry codes: (i) -*x*, -*y*+1, -*z*+2; (ii) -*x*, *y*+1/2, -*z*+3/2; (iii) *x*, -*y*+1/2, *z*-1/2; (iv) -*x*, *y*-1/2, -*z*+3/2

Complex 3

Mn1—O4	2.101 (3)	Mn2—O1	2.106 (3)
Mn1—O2	2.123 (3)	Mn2—O1^{i}	2.106 (3)
Mn1—O5	2.162 (3)	Mn2—O3^{i}	2.161 (3)
Mn1—O9	2.249 (2)	Mn2—O3	2.161 (3)
Mn1—N1	2.256 (3)	Mn2—O9^{i}	2.296 (2)
Mn1—N2	2.280 (3)	Mn2—O9	2.296 (2)
O4—Mn1—O2	92.97 (11)	O2—Mn1—O9	91.11 (9)
O4—Mn1—O5	85.30 (11)	O5—Mn1—O9	84.36 (9)
O2—Mn1—O5	174.93 (10)	O4—Mn1—N1	91.02 (11)
O4—Mn1—O9	96.54 (10)	O2—Mn1—N1	89.75 (11)
O5—Mn1—N1	95.04 (11)	O1^{i}—Mn2—O3^{i}	90.47 (11)
O9—Mn1—N1	172.34 (10)	O1—Mn2—O3	90.47 (11)
O4—Mn1—N2	163.50 (11)	O1^{i}—Mn2—O3	89.53 (11)
O2—Mn1—N2	92.72 (10)	O3^{i}—Mn2—O3	180.00 (14)
O5—Mn1—N2	90.23 (10)	O1—Mn2—O9^{i}	87.44 (10)
O9—Mn1—N2	98.82 (10)	O1^{i}—Mn2—O9^{i}	92.56 (10)
N1—Mn1—N2	73.54 (11)	O3^{i}—Mn2—O9^{i}	98.87 (9)
O1—Mn2—O1^{i}	180.0	O3—Mn2—O9^{i}	81.13 (9)
O1—Mn2—O3^{i}	89.53 (11)	O1—Mn2—O9	92.56 (10)
O3^{i}—Mn2—O9	81.13 (9)	O9^{i}—Mn2—O9	180.00 (14)
O3—Mn2—O9	98.87 (9)		

Symmetry codes: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*+1, *z*-1/2

Complex 4

Mn1—O6^{i}	2.142 (2)	Mn1—N1	2.244 (3)
Mn1—O5	2.151 (2)	Mn1—N5	2.254 (3)
Mn1—N4	2.231 (3)	Mn1—O9	2.314 (2)
O6^{i}—Mn1—O5	110.85 (9)	N4—Mn1—N1	178.69 (11)
O6^{i}—Mn1—N4	89.37 (10)	O6^{i}—Mn1—N5	163.70 (9)
O5—Mn1—N4	92.24 (10)	O5—Mn1—N5	85.21 (10)
O6^{i}—Mn1—N1	89.68 (9)	N4—Mn1—N5	92.89 (11)
O5—Mn1—N1	87.25 (10)	N1—Mn1—N5	88.27 (10)

O6^{i}—Mn1—O9	82.49 (8)	N1—Mn1—O9	90.75 (9)
O5—Mn1—O9	166.48 (8)	N5—Mn1—O9	81.37 (9)
N4—Mn1—O9	90.03 (10)		

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) *x*, *y*-1, *z*

Complex 5

Mn1—O2	2.1233 (14)	Mn1—N2	2.2531 (12)
Mn1—O8^{ii}	2.1530 (13)	Mn1—N1	2.2905 (15)
Mn1—O6^{iii}	2.1939 (11)	Mn1—O1	2.3123 (11)
Mn2—O9	2.0935 (16)	O1—Mn2^{ii}	2.2147 (11)
Mn2—O9^{i}	2.0935 (16)	Mn2—N3^{i}	2.236 (3)
Mn2—O1^{iv}	2.2148 (11)	Mn2—N3A^{i}	2.408 (3)
Mn2—O1^{v}	2.2148 (11)		
O2—Mn1—O8^{ii}	86.33 (5)	O6^{iii}—Mn1—N1	84.61 (5)
O2—Mn1—O6^{iii}	90.19 (5)	N2—Mn1—N1	73.05 (5)
O8^{ii}—Mn1—O6^{iii}	169.23 (4)	O2—Mn1—O1	89.61 (4)
O2—Mn1—N2	95.90 (5)	O8^{ii}—Mn1—O1	84.30 (5)
O8^{ii}—Mn1—N2	84.13 (5)	O6^{iii}—Mn1—O1	85.48 (4)
O6^{iii}—Mn1—N2	106.39 (4)	N2—Mn1—O1	166.84 (4)
O2—Mn1—N1	165.79 (4)	N1—Mn1—O1	103.11 (5)
O8^{ii}—Mn1—N1	101.04 (5)	Mn2^{ii}—O1—Mn1	123.48 (5)
O9—Mn2—O9^{i}	119.59 (8)	O9^{i}—Mn2—O1^{v}	86.62 (5)
O9—Mn2—O1^{iv}	86.62 (5)	O1^{iv}—Mn2—O1^{v}	165.63 (6)
O9^{i}—Mn2—O1^{iv}	86.17 (5)	O9—Mn2—N3	94.60 (8)
O9—Mn2—O1^{v}	86.17 (5)	O9^{i}—Mn2—N3	145.22 (8)
O1^{iv}—Mn2—N3	89.98 (7)	O1^{iv}—Mn2—N3^{i}	102.97 (14)
O1^{v}—Mn2—N3	102.97 (7)	O1^{v}—Mn2—N3^{i}	89.98 (13)
O9—Mn2—N3^{i}	145.22 (10)	N3—Mn2—N3^{i}	52.72 (15)
O9^{i}—Mn2—N3^{i}	94.60 (10)	O9—Mn2—N3A^{i}	162.78 (11)
O9^{i}—Mn2—N3A^{i}	76.50 (11)	O9^{i}—Mn2—N3A	162.78 (7)
O1^{iv}—Mn2—N3A^{i}	101.42 (13)	O1^{iv}—Mn2—N3A	88.93 (6)
O1^{v}—Mn2—N3A^{i}	88.93 (13)	O1^{v}—Mn2—N3A	101.42 (6)

O9—Mn2—N3A	76.50 (7)	N3A^{i}—Mn2—N3A	88.34 (15)

Symmetry codes: (i) -*x*+1, *y*, -*z*+1/2; (ii) *x*, *y*-1, *z*; (iii) -*x*+1, -*y*, -*z*; (iv) *x*, *y*+1, *z*; (v) -*x*+1, *y*+1, -*z*+1/2

Complex 6

Mn1—O8^{i}	2.053 (3)	Mn1—N1	2.226 (3)
Mn1—O9	2.127 (3)	Mn1—N2	2.249 (3)
Mn1—O1	2.192 (3)	Mn1—O2	2.518 (3)
O8^{i}—Mn1—O9	94.69 (11)	O8^{i}—Mn1—N2	168.90 (12)
O8^{i}—Mn1—O1	95.09 (11)	O9—Mn1—N2	85.63 (10)
O9—Mn1—O1	150.71 (10)	O1—Mn1—N2	89.90 (11)
O8^{i}—Mn1—N1	96.96 (11)	N1—Mn1—N2	72.62 (12)
O9—Mn1—N1	110.15 (11)	O8^{i}—Mn1—O2	105.91 (10)
O1—Mn1—N1	95.95 (11)	O9—Mn1—O2	95.84 (9)
O1—Mn1—O2	54.91 (9)	N2—Mn1—O2	85.06 (10)
N1—Mn1—O2	143.72 (10)	O1—C1—O2	121.8 (4)

Symmetry codes: (ii) -*x*+1, -*y*+2, -*z*; (iii) *x*+1, *y*, *z*; (iv) *x*, *y*-1, *z*; (v) *x*, *y*+1, *z*

References

S1 D. D. Yang, L. P. Lu and M. L. Zhu, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2019, **75**, 1580-1592.

S2 F. Su, L. Lu, S. Feng and M. Zhu, *CrystEngComm,* 2014, **16**, 7990 – 7999.

S3 D. D. Yang, L. P. Lu and M. L. Zhu, *CrystEngComm*, 2020, **22**, 5207 – 5217.