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基于半刚性双(噻唑基苯并咪唑)和不同羧酸的五个一维配合物的合成和表征

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摘要:通过水热或溶剂热合成的方法制备了 5 个一维配合物$\{[Zn(btbb)_{0.5}(m\text{-phda})]\cdot 0.5H_2O\}_n$ (**1**),$\{[Cd_2(btbb)(adtda)_2(H_2O)]\cdot H_2O\}_n$ (**2**),$[Mn_2(btbb)(tbi)_2]_n$ (**3**),$\{[Cd(btbb)_{0.5}(3\text{-Nitro-}o\text{-bdc})(H_2O)]\cdot H_2O\}_n$ (**4**)和$[Cd_2(btbb)(tbi)_2]_n$ (**5**)(btbb=1,4-双(2-(4-噻唑基)苯并咪唑-1-基甲基)苯,m-H_2phda=间苯二甲酸,H_2adtda=1,3-金刚烷二羧酸,H_2tbi=5-叔丁基间苯二甲酸,3-Nitro-o-H_2bdc=3-硝基-1,2-苯二甲酸)。配合物 **1** 是一个包含 22 元环的一维链。配合物 **2** 是一个包含 8 元环的一维链,并且氮配体在这个一维链中仅仅起到装饰作用。配合物 **3** 是一个一维双链结构。配合物 **4** 是一个包含 14 元环的一维链。配合物 **5** 是一个阶梯状的一维双链结构。

关键词:配合物;半刚性配体;羧酸;晶体结构
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Syntheses, Characterization and Crystal Structures of Five 1D Complexes Based on Semi-rigid Bis(thiazolylbenzimidazole) and Different Types of Carboxylic Acid Linkers

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Abstract: Five coordination complexes, formulated as $\{[Zn(btbb)_{0.5}(m\text{-phda})]\cdot 0.5H_2O\}_n$ (**1**), $\{[Cd_2(btbb)(adtda)_2(H_2O)]\cdot H_2O\}_n$ (**2**), $[Mn_2(btbb)(tbi)_2]_n$ (**3**), $\{[Cd(btbb)_{0.5}(3\text{-Nitro-}o\text{-bdc})(H_2O)]\cdot H_2O\}_n$ (**4**) and $[Cd_2(btbb)(tbi)_2]_n$ (**5**) (btbb=1,4-bis(2-(4-thiazolyl)benzimidazole-1-ylmethyl)benzene, m-H_2phda=m-phenylenediacetic acid, H_2adtda=1,3-adamantanedicarboxylic acid, H_2tbi=5-tert-butylisophthalic acid, 3-Nitro-o-H_2bdc=3-Nitro-1,2-benzenedicarboxylic acid), have been obtained by hydro(solv)thermal reactions and structurally characterized. Complex **1** exhibits a 1D chain structure containing 22-membered rings. Complex **2** features a 1D chain structure having an 8-membered rings

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and btbb serves only as an ornament here. Complex **3** is a 1D double chain structure. Complex **4** possesses a 1D chain structure containing 14-membered rings. Complex **5** shows a 1D double chain taking on stair-step. CCDC: 1883643, **1**; 1883644, **2**; 1883645, **3**; 1883646, **4**; 1883647, **5**.

Keywords: complex; semi-rigid ligand; carboxylate; crystal structure

The design and construction of multifarious complexes has been a hot topic for all researchers owing to their intriguing structural motifs and potential applications in optics, magnetism, recognition, *etc* [1-8]. Although the assembly of complexes is affected by varied factors, we haven't stopped exploring them. In consideration of the superiority of the "mixed-ligand" synthetic strategies[9-12], which can lead to numerous graceful structures, we choose 1,4-bis(2-(4-thiazolyl) benzimidazole-1-ylmethyl)benzene (btbb) as the semi-rigid N-donor ligand and different multidentate O-donor carboxylates, *m*-phenylenediacetic acid (*m*-H_2phda), 1, 3-adamantanedicarboxylic acid (H_2adtda), 5-*tert*-butylisophthalic acid (H_2tbi), 3-Nitro-1,2-benzenedicarboxylic acid (3-Nitro-*o*-H_2bdc) as auxiliary ligands in the synthesis of metal-organic coordination polymer materials. Five diverse structural complexes, $\{[Zn(btbb)_{0.5}(m\text{-phda})]\cdot 0.5H_2O\}_n$ (**1**), $\{[Cd_2(btbb)(adtda)_2(H_2O)]\cdot H_2O\}_n$ (**2**), $[Mn_2(btbb)(tbi)_2]_n$ (**3**), $\{[Cd(btbb)_{0.5}(3\text{-Nitro-o-bdc})(H_2O)]\cdot H_2O\}_n$ (**4**) and $[Cd_2(btbb)(tbi)_2]_n$ (**5**) were prepared. The structures of **1**~**5** have been determined by single-crystal X-ray diffraction analyses and further characterized by infrared spectra, elemental analyses.

1 Experimental

1.1 Materials and methods

All reagents and solvents were commercially available without any further purification, except for ligand btbb, which was synthesized in accordance with the literature[13]. The data of FT-IR spectra were recorded on a FTIR-7600 spectrophotometer with KBr pellets in a scale of 400~4 000 cm^{-1}. Elemental analyses of C, H and N were performed introducing a FLASH EA 1112 analyzer.

1.2 Synthesis of $\{[Zn(btbb)_{0.5}(m\text{-phda})]\cdot 0.5H_2O\}_n$ (1)

A mixture of $Zn(Ac)_2\cdot 2H_2O$ (0.2 mmol), btbb (0.1 mmol), *m*-H_2phda (0.1 mmol), NaOH (0.2 mmol) and H_2O (10 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 180 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **1** were obtained with a yield of 10% (based on Zn). Anal. Calcd. for $C_{24}H_{20}ZnN_3O_5S$ (%): C, 54.60; H, 3.81; N, 7.95. Found(%): C, 54.63; H, 3.79; N, 7.98. IR (KBr, cm^{-1}): 3 421(s), 2 988(vw), 1 615(s), 1 481(w), 1 448(w), 1 395(m), 1 364(m), 1 314(vw), 1 272(vw), 1 174(w), 1 079(w), 1 001(w), 937(m), 887(w), 828(w), 784(w), 750(w), 622(w).

1.3 Synthesis of $\{[Cd_2(btbb)(adtda)_2(H_2O)]\cdot H_2O\}_n$ (2)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol), btbb (0.1 mmol), *p*-H_2adtda (0.05 mmol), EtOH (5 mL) and H_2O (5 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 170 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **2** were obtained with a yield of 15% (based on Cd). Anal. Calcd. for $C_{52}H_{52}Cd_2N_6O_{10}S_2$ (%): C, 51.61; H, 4.33; N, 6.94. Found(%): C, 51.59; H, 4.30; N, 6.97. IR (KBr, cm^{-1}): 3 440(s), 2 908 (m), 2 946(m), 1 616(w), 1 562(s), 1 479(w), 1 448(s), 1 386 (s), 1 307(s), 1 241(w), 1 124(w), 1 041(w), 931(m), 889 (m), 823(m), 744(s), 713(m), 622(w).

1.4 Synthesis of $[Mn_2(btbb)(tbi)_2]_n$ (3)

A mixture of $MnCl_2\cdot 4H_2O$ (0.1 mmol), btbb (0.05 mmol), H_2tbi (0.05 mmol), CH_3CN (4 mL) and H_2O (6 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 160 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **3** were obtained with a yield of 13% (based on Mn). Anal. Calcd. for $C_{52}H_{44}Mn_2N_6O_8S_2$(%): C, 59.20; H, 4.20; N, 7.96. Found(%): C, 59.23; H, 4.22;

N, 7.92. IR (KBr, cm^{-1}): 3 409(m), 3 091(m), 2 962(s), 2 865(w), 1 604(s), 1 554(s), 1 436(s), 1 371(s), 1 307 (s), 1 268(s), 1 108(s), 1 014(m), 923(s), 850(s), 819 (s), 725(s).

1.5 Synthesis of $\{[Cd(btbb)_{0.5}(3\text{-Nitro-}o\text{-bdc})(H_2O)]\cdot H_2O\}_n$ (4)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol), btbb (0.05 mmol), 3-Nitro-*o*-H_2bdc (0.05 mmol), EtOH (7 mL) and H_2O (3 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 120 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **4** were obtained with a yield of 16% (based on Cd). Anal. Calcd. for $C_{22}H_{17}CdN_4O_8S$(%): C, 43.32; H, 2.80; N, 9.18. Found (%): C, 43.27; H, 2.81; N, 9.22. IR (KBr, cm^{-1}): 3 397 (m), 3 139(w), 3 099(w), 3 048(w), 1 581(s), 1 527(s), 1 459(s), 1 394 (s), 1 349(s), 1 261(w), 1 162(m), 1 014(m), 935(s), 892(s), 831(s), 752(s), 717(s).

1.6 Synthesis of $[Cd_2(btbb)(tbi)_2]_n$ (5)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.05 mmol), btbb (0.05 mmol), H_2tbi (0.05 mmol), EtOH (7 mL) and H_2O (3 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 120 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **5** were obtained with a yield of 20% (based on Cd). Anal. Calcd. for $C_{52}H_{44}Cd_2N_6O_8S_2$(%): C, 53.38; H, 3.79; N, 7.18. Found(%): C, 53.35; H, 3.80; N, 7.16. IR (KBr, cm^{-1}): 3 432(m), 3 112(w), 2 958(w), 1 604(m), 1 550(s), 1 425(s), 1 386(s), 1 311(w), 1 116 (vw), 927(s), 854(vw), 767(s), 725(m).

1.7 Crystal structural determination

The data of **1~5** were collected on a Rigaku Saturn 724 CCD diffractomer (Mo $K\alpha$, λ=0.071 073 nm) at temperature of 293(2) K. Absorption corrections were applied by using multi-scan program. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELX-97 crystallographic software package[14]. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for **1~5** are summarized in Table 1. Selected bond lengths and bond angles for **1~5** are listed in Table 2, respectively.

CCDC: 1883643, **1**; 1883644, **2**; 1883645, **3**; 1883646, **4**; 1883647, **5**.

Table 1 Crystal data and structure refinement details for complexes 1~5

Complex	1	2	3	4	5
Formula	$C_{24}H_{20}ZnN_3O_5S$	$C_{52}H_{52}Cd_2N_6O_{10}S_2$	$C_{52}H_{44}Mn_2N_6O_8S_2$	$C_{22}H_{17}CdN_4O_8S$	$C_{52}H_{44}Cd_2N_6O_8S_2$
Formula weight	527.86	1 207.90	1 054.93	608.85	1 169.85
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / nm	0.862 78(17)	1.987 7(4)	1.024 2(2)	1.332 6(3)	1.033 8(2)
b / nm	1.075 7(2)	2.118 5(4)	2.218 5(4)	1.094 7(2)	2.222 5(4)
c / nm	1.322 9(3)	1.164 0(2)	2.027 8(4)	1.575 4(3)	2.015 0(4)
α / (°)	72.83(3)				
β / (°)	84.65(3)	93.39(3)	96.39(3)	100.31(3)	95.79(3)
γ / (°)	73.83(3)				
V / nm^3	1.126 5(4)	4.892 7(17)	4.578 9(16)	2.261 1(8)	4.605 7(16)
Z	2	4	4	4	4
D_c / (g·cm^{-3})	1.556	1.640	1.530	1.789	1.687
μ / mm^{-1}	1.225	1.022	0.708	1.117	1.079
F(000)	542	2 448	2 176	1 216	2 360
θ range / (°)	1.61~27.90	1.41~25.50	1.37~25.50	1.55~27.89	1.98~25.00
GOF	1.041	1.036	1.027	1.036	1.037

Continued Table 1

R_1 [$I>2\sigma(I)$][a]	0.065 0	0.074 8	0.087 8	0.078 7	0.097 3
wR_2 [$I>2\sigma(I)$][b]	0.147 9	0.176 7	0.224 1	0.168 3	0.169 0

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

Table 2　Selected bond lengths (nm) and bond angles (°) for 1~5

Complex **1**					
Zn(1)-O(1)	0.197 8(3)	Zn(1)-O(2)	0.243 2(3)	Zn(1)-O(4)#1	0.213 3(4)
Zn(1)-O(3)#1	0.233 6(6)	Zn(1)-N(2)	0.214 1(4)	Zn(1)-N(1)	0.205 3(3)
O(1)-Zn(1)-N(1)	138.48(15)	O(1)-Zn(1)-O(4)#1	114.26(17)	N(1)-Zn(1)-O(4)#1	94.52(14)
O(1)-Zn(1)-N(2)	100.37(15)	N(1)-Zn(1)-N(2)	77.73(12)	O(4)#1-Zn(1)-N(2)	132.77(16)
O(1)-Zn(1)-O(3)#1	97.36(18)	N(1)-Zn(1)-O(3)#1	123.88(16)	O(4)#1-Zn(1)-O(3)#1	56.71(16)
N(2)-Zn(1)-O(3)#1	89.06(15)	O(1)-Zn(1)-O(2)	57.06(12)	N(1)-Zn(1)-O(2)	91.85(12)
O(4)#1-Zn(1)-O(2)	96.79(16)	N(2)-Zn(1)-O(2)	129.59(14)	O(3)#1-Zn(1)-O(2)	134.10(16)
Complex **2**					
Cd(1)-O(8)#1	0.216 4(7)	Cd(1)-O(2)	0.224 4(5)	Cd(1)-O(3)	0.226 8(5)
Cd(2)-O(4)	0.226 8(6)	Cd(2)-O(5)	0.253 8(6)	Cd(1)-O(1)	0.258 3(5)
Cd(2)-O(7)#2	0.219 8(6)	Cd(2)-O(6)	0.221 3(6)	Cd(1)-N(1)	0.227 9(6)
Cd(2)-N(5)	0.232 4(6)	Cd(2)-N(4)	0.240 2(7)	Cd(1)-N(3)	0.243 7(6)
O(8)#1-Cd(1)-O(2)	104.9(3)	O(8)#1-Cd(1)-O(3)	111.9(3)	O(2)-Cd(1)-O(3)	95.70(19)
O(8)#1-Cd(1)-N(1)	87.8(3)	O(2)-Cd(1)-N(1)	105.4(2)	O(3)-Cd(1)-N(1)	146.48(19)
O(8)#1-Cd(1)-N(3)	89.9(3)	O(2)-Cd(1)-N(3)	164.40(19)	O(3)-Cd(1)-N(3)	82.97(19)
N(1)-Cd(1)-N(3)	69.7(2)	O(8)#1-Cd(1)-O(1)	155.3(3)	O(2)-Cd(1)-O(1)	53.10(16)
O(3)-Cd(1)-O(1)	83.91(19)	N(1)-Cd(1)-O(1)	88.20(19)	N(3)-Cd(1)-O(1)	111.37(18)
O(7)#2-Cd(2)-O(6)	116.9(3)	O(7)#2-Cd(2)-O(4)	86.5(3)	O(6)-Cd(2)-O(4)	91.6(3)
O(7)#2-Cd(2)-N(5)	107.4(3)	O(6)-Cd(2)-N(5)	131.1(3)	O(4)-Cd(2)-N(5)	111.4(2)
O(7)#2-Cd(2)-N(4)	90.3(3)	O(6)-Cd(2)-N(4)	89.6(3)	O(4)-Cd(2)-N(4)	176.8(2)
N(5)-Cd(2)-N(4)	69.9(2)	O(7)#2-Cd(2)-O(5)	139.0(3)	O(6)-Cd(2)-O(5)	78.9(2)
O(4)-Cd(2)-O(5)	54.01(19)	N(5)-Cd(2)-O(5)	81.19(19)	N(4)-Cd(2)-O(5)	129.2(2)
Complex **3**					
Mn(1)-O(3)	0.213 2(4)	Mn(1)-O(6)#1	0.217 6(4)	Mn(1)-O(2)	0.224 4(4)
Mn(2)-O(7)#1	0.244 9(4)	Mn(2)-O(4)	0.217 2(4)	Mn(1)-O(1)	0.234 4(4)
Mn(2)-O(5)#1	0.212 0(4)	Mn(2)-O(8)#1	0.214 1(4)	Mn(1)-N(1)	0.234 3(4)
Mn(2)-N(5)	0.224 5(5)	Mn(2)-N(4)	0.233 2(6)	Mn(1)-N(2)	0.225 4(5)
O(3)-Mn(1)-O(6)#1	99.19(15)	O(3)-Mn(1)-O(2)	105.51(16)	O(6)#1-Mn(1)-O(2)	89.71(15)
O(3)-Mn(1)-N(2)	150.13(17)	O(6)#1-Mn(1)-N(2)	87.97(17)	O(2)-Mn(1)-N(2)	103.47(17)
O(3)-Mn(1)-N(1)	84.83(16)	O(6)#1-Mn(1)-N(1)	132.10(16)	O(2)-Mn(1)-N(1)	135.48(15)
N(2)-Mn(1)-N(1)	69.37(17)	O(3)-Mn(1)-O(1)	90.41(15)	O(6)#1-Mn(1)-O(1)	146.30(16)
O(2)-Mn(1)-O(1)	56.59(14)	N(2)-Mn(1)-O(1)	99.60(16)	N(1)-Mn(1)-O(1)	80.66(15)
O(5)#1-Mn(2)-O(8)#1	106.90(17)	O(5)#1-Mn(2)-O(4)	102.29(15)	O(8)#1-Mn(2)-O(4)	92.06(15)
O(5)#1-Mn(2)-N(5)	152.22(17)	O(8)#1-Mn(2)-N(5)	99.64(18)	O(4)-Mn(2)-N(5)	84.52(17)
O(5)#1-Mn(2)-N(4)	82.89(17)	O(8)#1-Mn(2)-N(4)	142.84(17)	O(4)-Mn(2)-N(4)	121.45(16)
N(5)-Mn(2)-N(4)	70.87(19)	O(5)#1-Mn(2)-O(7)#1	89.07(14)	O(8)#1-Mn(2)-O(7)#1	56.73(14)
O(4)-Mn(2)-O(7)#1	148.78(14)	N(5)-Mn(2)-O(7)#1	98.92(16)	N(4)-Mn(2)-O(7)#1	88.50(16)

Continued Table 2

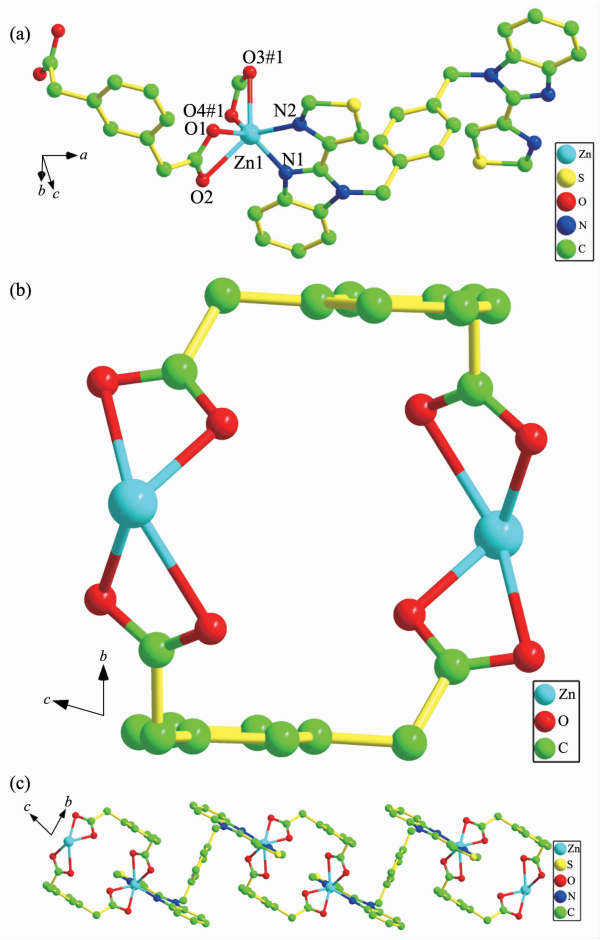
Complex **4**					
Cd(1)-O(1)	0.256 8(7)	Cd(1)-O(3)#1	0.245 6(5)	Cd(1)-O(2)	0.234 8(5)
Cd(1)-O(7)	0.237 1(6)	Cd(1)-O(4)#1	0.238 9(6)	Cd(1)-N(1)	0.234 5(6)
Cd(1)-N(2)	0.229 8(5)				
N(2)-Cd(1)-N(1)	72.2(2)	N(2)-Cd(1)-O(2)	128.60(18)	N(1)-Cd(1)-O(2)	98.0(2)
N(2)-Cd(1)-O(7)	99.84(19)	N(1)-Cd(1)-O(7)	170.8(2)	O(2)-Cd(1)-O(7)	83.30(19)
N(2)-Cd(1)-O(4)#1	94.42(18)	N(1)-Cd(1)-O(4)#1	107.4(2)	O(2)-Cd(1)-O(4)#1	135.36(18)
O(7)-Cd(1)-O(4)#1	77.3(2)	N(2)-Cd(1)-O(3)#1	141.95(18)	N(1)-Cd(1)-O(3)#1	95.8(2)
O(2)-Cd(1)-O(3)#1	88.12(17)	O(7)-Cd(1)-O(3)#1	93.4(2)	O(4)#1-Cd(1)-O(3)#1	53.91(18)
N(2)-Cd(1)-O(1)	76.71(19)	N(1)-Cd(1)-O(1)	87.8(3)	O(2)-Cd(1)-O(1)	52.19(18)
O(7)-Cd(1)-O(1)	85.7(3)	O(4)#1-Cd(1)-O(1)	159.3(2)	O(3)#1-Cd(1)-O(1)	140.19(19)
Complex **5**					
Cd(1)-O(3)	0.228 7(7)	Cd(1)-O(5)	0.228 7(7)	Cd(1)-O(1)#1	0.230 5(7)
Cd(2)-O(6)	0.229 5(7)	Cd(2)-O(8)#2	0.253 9(7)	Cd(1)-O(2)#1	0.248 4(7)
Cd(2)-O(7)#2	0.224 7(7)	Cd(2)-O(4)	0.226 3(8)	Cd(1)-N(1)	0.233 7(10)
Cd(2)-N(4)	0.231 1(11)	Cd(2)-N(6)	0.243 5(13)	Cd(1)-N(3)	0.240 9(9)
O(3)-Cd(1)-O(5)	101.4(3)	O(3)-Cd(1)-O(1)#1	87.5(3)	O(5)-Cd(1)-O(1)#1	106.2(3)
O(3)-Cd(1)-N(1)	89.0(3)	O(5)-Cd(1)-N(1)	148.6(3)	O(1)#1-Cd(1)-N(1)	103.8(3)
O(3)-Cd(1)-N(3)	137.1(3)	O(5)-Cd(1)-N(3)	85.1(3)	O(1)#1-Cd(1)-N(3)	131.8(3)
N(1)-Cd(1)-N(3)	67.8(3)	O(3)-Cd(1)-O(2)#1	141.5(3)	O(5)-Cd(1)-O(2)#1	89.6(3)
O(1)#1-Cd(1)-O(2)#1	54.0(3)	N(1)-Cd(1)-O(2)#1	100.6(3)	N(3)-Cd(1)-O(2)#1	80.1(3)
O(7)#2-Cd(2)-O(4)	107.6(3)	O(7)#2-Cd(2)-O(6)	90.8(3)	O(4)-Cd(2)-O(6)	101.5(3)
O(7)#2-Cd(2)-N(4)	101.6(4)	O(4)-Cd(2)-N(4)	149.6(4)	O(6)-Cd(2)-N(4)	86.0(3)
O(7)#2-Cd(2)-N(6)	141.5(3)	O(4)-Cd(2)-N(6)	83.3(4)	O(6)-Cd(2)-N(6)	123.9(3)
N(4)-Cd(2)-N(6)	68.5(4)	O(7)#2-Cd(2)-O(8)#2	54.5(3)	O(4)-Cd(2)-O(8)#2	90.6(3)
O(6)-Cd(2)-O(8)#2	145.3(3)	N(4)-Cd(2)-O(8)#2	99.8(3)	N(6)-Cd(2)-O(8)#2	89.5(3)

Symmetry codes: #1: $-x$, $-y$, $-z+1$ for **1**; #1: $-x+1$, $-y+1$, $-z+1$; #2: $-x$, $-y+1$, $-z+1$ for **2**; #1: $x+1$, y, z for **3**; #1: $-x$, $-y+1$, $-z$ for **4**; #1: $x+1$, y, z; #2: $x-1$, y, z for **5**.

2 Results and discussion

2.1 Crystal structure of {[Zn(btbb)$_{0.5}$(*m*-phda)]·0.5H$_2$O}$_n$ (1)

For complex **1**, it consists of one crystallographically independent Zn(Ⅱ) ion, half a btbb ligand, one *m*-phda^{2-} ligand, and half a lattice water molecule. As illustrated in Fig.1a, Zn1(Ⅱ) ion is six-coordinated by four O atoms of carboxylate groups (O1, O2, O3#1, O4#1) provided by two different *m*-phda^{2-} ligands, and two nitrogen atoms (N1, N2) deriving from one btbb ligand to give a octahedral coordination geometry. The distances of Zn1-N1/N2 is 0.205 1(3)/0.213 4(3) nm, while the Zn1-O bond lengths range from 0.197 8(3) to 0.242 9(3) nm. Ligand btbb exhibit asymmetrical *trans*-conformation. $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angles of btbb is 143.613° and 143.614°, respectively. Ligand *m*-phda^{2-} adopts asymmetric *cis*-conformation, and the angles of two -CH$_2$- are 112.478° and 116.908°. In **1**, two carboxylic groups of the "V" shape ligand *m*-phda^{2-} take a chelating bidentate coordination modes. The m-phda^{2-} anions connect two adjacent Zn(Ⅱ) ions using its two carboxylate groups resulting in a 22-membered rings along *a*-axis (Fig.1b). The 22-membered rings are linked by btbb leading to a 1D chain along the *a*-axis (Fig.1c). The Zn…Zn distances across btbb ligands are 1.322 17 nm.

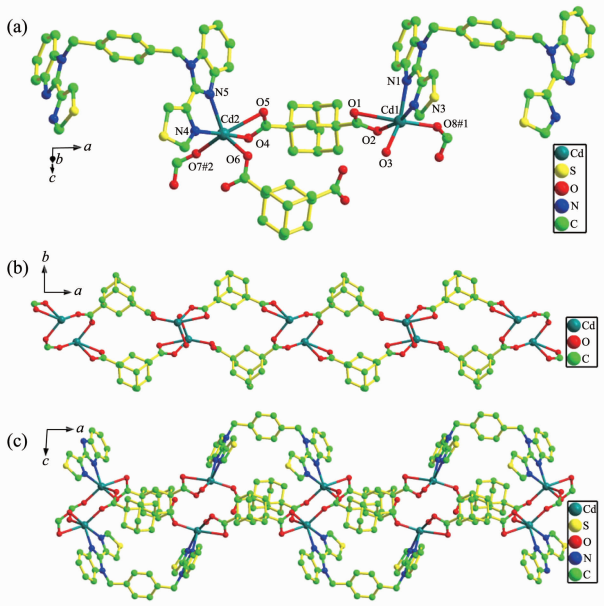


Hydrogen atoms are omitted for clarity; Symmetry codes: #1: $-x$, $-y$, $1-z$

Fig.1　(a) Coordination environments of Zn(Ⅱ) in complex **1**; (b) View of 22-membered rings constructed by two m-phda^{2-} ligands and two Zn(Ⅱ) ions along the *a*-axis; (c) 1D chain structure containing 22-membered rings along the *a*-axis

2.2　Crystal structure of {[Cd_2(btbb)(adtda)$_2$(H_2O)]·H_2O}$_n$ (2)

Single crystal X-ray diffraction analysis reveals that **2** crystallizes in monoclinic space group $P2_1/c$. The asymmetric unit of **2** consists of two Cd(Ⅱ) ions, one btbb ligand, two adtda^{2-} anions, one coordinated water molecule and one lattice water molecule. As shown in Fig.2a, the Cd1(Ⅱ) ion adopts a distorted octahedral geometry via coordinating with four oxygen atoms (O1, O2, O8#1) from two adtda^{2-} anions, one oxygen atom (O3) from one coordinated water molecule and two nitrogen atoms (N1 and N3) from one btbb ligand. The Cd1-O bond distances vary from 0.216 4(7) to 0.258 3(5) nm, while the Cd1-N1/N3 bond length is 0.227 9(6)/0.243 7(6) nm, separately. While the octahedral coordination geometry of the central Cd2(Ⅱ) ion is completed by two N atoms (N4 and N5) of one btbb ligand, and four O atoms (O4, O5, O6, O7#2) of three adtda^{2-} anions. The Cd2-O bond distances vary from 0.219 8(6) to 0.253 8(6) nm, while the Cd2-N4/N5 bond length is 0.240 2(7)/0.232 4(6) nm. The btbb ligand adopts asymmetric *trans*-conformation with two different $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angles of 71.150° and 93.156°. The ligand adtda^{2-} takes two different coordination modes. The first type (adtda^{2-}-Ⅰ) is that one carboxylate group of adtda^{2-} ligand is in a bridging bidentate mode, and the other adopts a monodentate mode, whereas the two carboxylate groups of the second type (adtda^{2-}-Ⅱ) both adopt chelating bidentate modes. The adtda^{2-}-Ⅰ and adtda^{2-}-Ⅱ anions link Cd(Ⅱ) ions to produce a one-dimensional (1D) chain structure having a dinuclear units [$Cd_2(OCO)_2$] with a Cd⋯Cd separation of 0.424 84 nm (Fig.2b). Interestingly, 1D Cd(Ⅱ)/adtda^{2-} chain is further embellished by btbb giving rise to a more complex and beautiful 1D chain



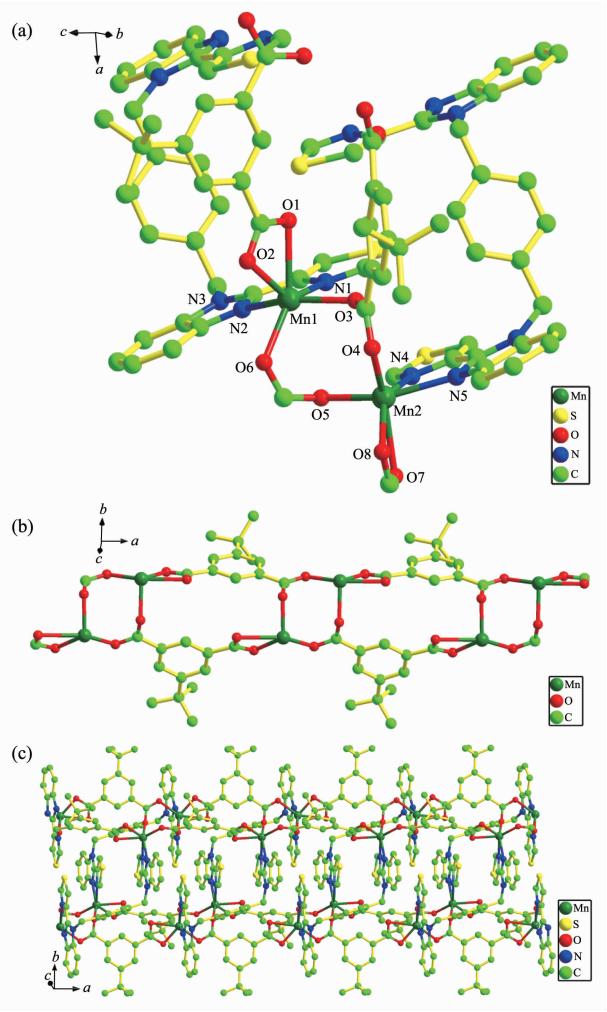
Hydrogen atoms are omitted for clarity; Symmetry codes: #1: $-x+1$, $-y+1$, $-z+1$; #2: $-x$, $-y+1$, $-z+1$

Fig.2　(a) Perspective view of the coordination environment of Cd(Ⅱ) ion in **2**; (b) 1D chain constructed by Cd(Ⅱ) ions and adtda^{2-} anions having a 8-membered rings; (c) 1D chain embellished by btbb

structure, and the Cd ··· Cd separation across btbb bridge is 1.013 00 nm (Fig.2c).

2.3 Crystal structure of $[Mn_2(btbb)(tbi)_2]_n$ (3)

The asymmetric unit of complex **3** contains two Mn(Ⅱ) ions, one btbb ligand and two tbi^{2-} ligands in the monoclinic space group $P2_1/c$. As shown in Fig.3a, the Mn1 center is six-coordinated by four oxygen atoms (O1, O2, O3 and O6) belonging to three separated tbi^{2-} ligands as well as two nitrogen atoms (N1 and N2) from one btbb ligand to generate a distorted octahedral coordination geometry. The Mn1-O bond distances lie in a range of 0.213 2(4)~0.234 4(4) nm, and Mn1-N1/N2 bond distances are 0.234 3(4)/0.225 4(5) nm, respectively. The Mn2 center also adopts a distorted octahedral coordination environment, which is provided by two nitrogen atoms (N4, N5) from one separate btbb and four oxygen atoms (O4, O5, O7, O8) from three tbi^{2-}. The Mn2-O bond distances lie in a range of 0.212 0(4)~0.244 9(4) nm, and Mn2-N4/N5 bond distances are 0.233 2(6)/0.224 5(5) nm. As shown in Fig.3b, both carboxylate groups of rigid tbi^{2-} anions adopt the mono-bidentate-bridging coordination fashion and chelating bidentate mode, separately, linking Mn(Ⅱ) ions to a 1D chain, which contains a dual-core unit $[Mn_2(OCO)_2]$ with the Mn···Mn distance of 0.413 54 nm. The ligand btbb adopts asymmetric *trans*-conformation with two different $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angles of 44.822° and 78.136°, and it connects two adjacent 1D Mn(Ⅱ)/tbi^{2-} chain by sharing the Mn(Ⅱ) ions resulting in a 1D double chain (Fig.3c).

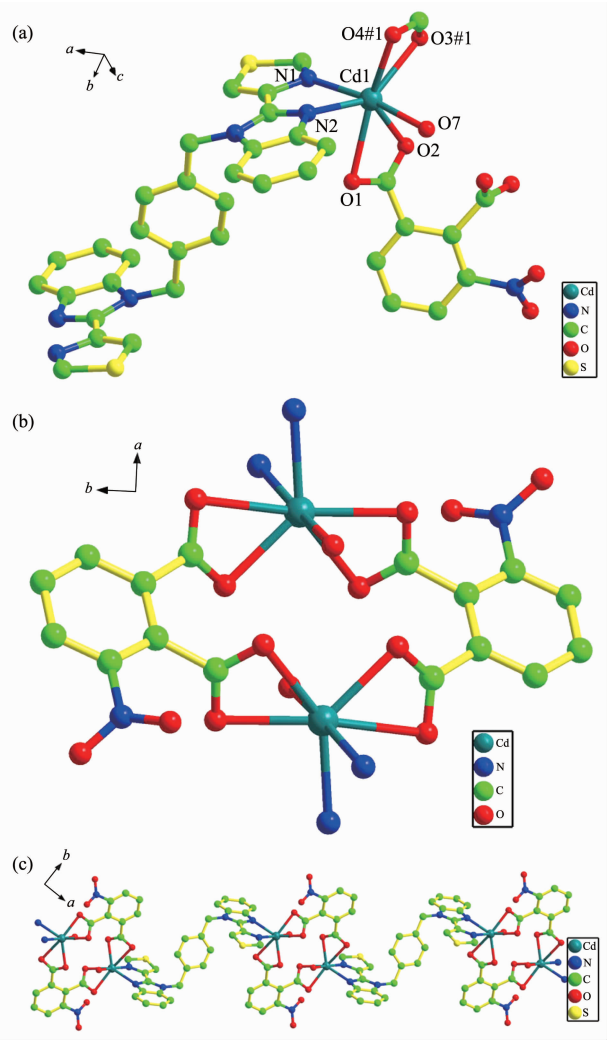


Hydrogen atoms are omitted for clarity

Fig.3 (a) Coordination environments of Mn(Ⅱ) in complex **3**; (b) View of 1D Mn(Ⅱ)/tbi^{2-} chain; (c) 1D double chain structure of **3**

2.4 Crystal structure of $\{[Cd(btbb)_{0.5}(3\text{-Nitro-}o\text{-bdc})(H_2O)]\cdot H_2O\}_n$ (4)

Structural analysis indicates that complex **4** is a 1D chain structure and crystallizes in the monoclinic $P2_1/c$ space group. The asymmetric unit of **4** is composed of one crystallographically independent Cd(Ⅱ) ion, half a btbb ligand, and one 3-Nitro-*o*-bdc^{2-} ligand, a coordination water molecule and a free water molecule. As shown in Fig.4a, the Cd(Ⅱ) ion adopts a seven-coordinated environment, which is provided by two nitrogen atoms (N1, N2) from one btbb ligand, four oxygen atoms (O1, O2, O3#1, O4#1) from two 3-Nitro-*o*-bdc^{2-} anions and one oxygen atom (O7) from a coordination water molecule. The Cd-O distances are in a range of 0.234 8(5)~0.256 8(7) nm, while the Cd-N1/N2 bond length are 0.234 5(6)/2.298(5) nm, separately. The ligand btbb shows the symmetric *trans*-conformation with the $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angle of 162.223°. The carboxylic groups of each 3-Nitro-*o*-bdc^{2-} anion both adopt chelating bidentate coordination modes. By this way, two 3-Nitro-*o*-bdc^{2-} anions bridge two adjacent Cd(Ⅱ) ions to form a 14-membered ring along *c*-axis (Fig.4b). Interestingly, the neighboring 14-membered rings are connected by the *trans*-conformational btbb ligands generating the 1D chain of **4** (Fig.4c), with a Cd···Cd distance of 1.334 02 nm.

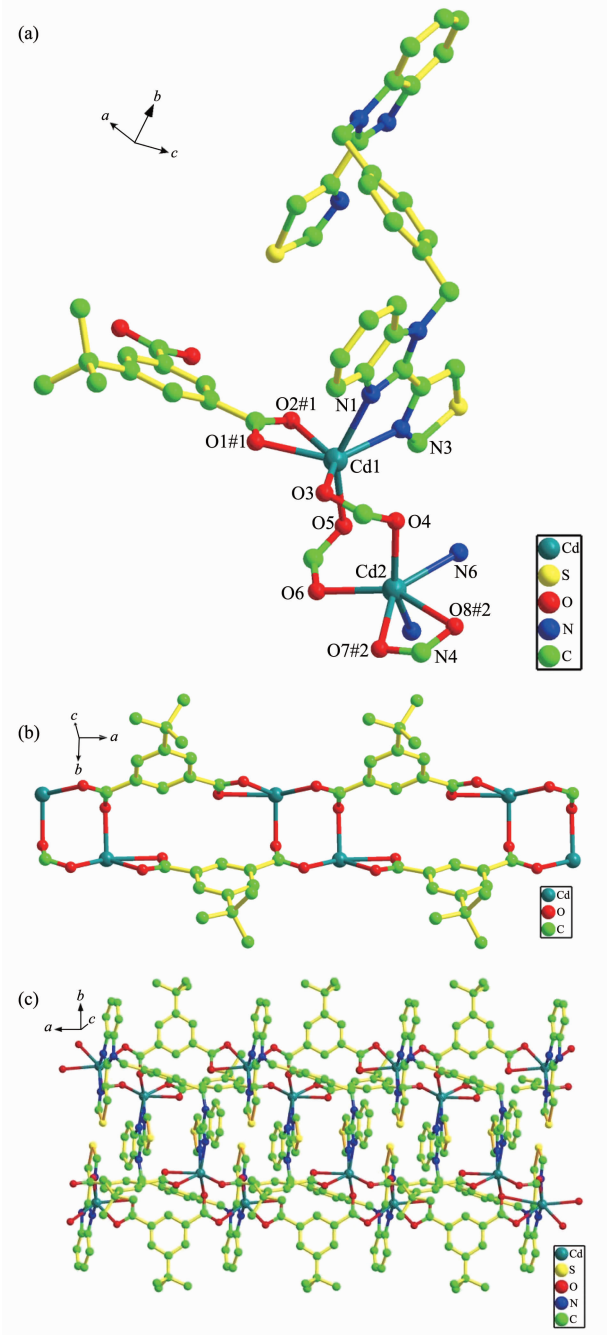


Hydrogen atoms are omitted for clarity; Symmetry codes: #1: $-x$, $1-y$, $-z$

Fig.4　(a) Coordination environments of Cd(Ⅱ) in complex **4**; (b) View of 14-membered rings constructed by two 3-Nitro-*o*-bdc^{2-} anions and two Cd(Ⅱ) ions along the *c*-axis; (c) 1D chain structure containing 14-membered rings along the *c*-axis

2.5　Crystal structure of $[Cd_2(btbb)(tbi)_2]_n$ (5)

Single crystal X-ray diffraction analysis shows that **5** crystallizes in the space group $P2_1/c$. As shown in Fig.5a, Cd1(Ⅱ) ion adopts a distorted octahedral coordination environment, defined by four oxygen atoms (O1#1, O2#1, O3, O5) deriving from three different tbi^{2-} anions and two nitrogen atoms (N1, N3) originating from one btbb ligand. The distances of Cd1-N1/N3 are 0.233 7(10)/0.240 9(9) nm, while the Cd1-O bond lengths range from 0.228 7(7) to 0.248 4(7) nm. It can be clearly seen that the Cd2(Ⅱ) ion also sits in a distorted octahedral coordination geometry defined by four oxygen atoms (O4, O6, O7#2, O8#2) from three different tbi^{2-} anions and two nitrogen atoms (N4, N6) from one btbb ligand. The distances of Cd2-N4/N6 are 0.231 1(11)/0.243 5(13) nm, while the Cd2-O bond



Hydrogen atoms are omitted for clarity; Symmetry codes: #1: $x+1$, y, z; #2: $x-1$, y, z

Fig.5　(a) Perspective view of the coordination environment of Cd(Ⅱ) ion in **5**; (b) 1D chain constructed by Cd(Ⅱ) ions and tbi^{2-} anions; (c) 1D double chain of **5**

lengths range from 0.224 7(7) to 0.253 9(7) nm. Interestingly, there are one kind of independent tbi^{2-}, in which one carboxylate group adopts a bisdentate chelated coordination mode and the other adopts a bridging bidentate mode. The tbi^{2-} anions connect two Cd(Ⅱ) ions resulting in a $Cd_2(OCO)_2$, and Cd…Cd distance is 0.403 32 nm. The dual-core $Cd_2(OCO)_2$ units are further linked and extended by tbi^{2-} anions leading to the production of a 1D Cd(Ⅱ)/tbi^{2-} chain (Fig.5b). While the btbb ligand adopts asymmetric *trans*-conformation with two different $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angles of 78.334° and 43.989°, and the bridged Cd…Cd distances along μ-btbb are 1.099 83 nm. Finally, the Cd1(Ⅱ) ion and Cd2(Ⅱ) ion are connected by btbb to afford a 1D double chain taking on stair-step (Fig.5c).

3 Conclusions

In short, the synergistic effect of the btbb and various carboxylates to react with Zn(Ⅱ)/Cd(Ⅱ)/Mn(Ⅱ) ions gains five different complexes. Complexes **1~5** exhibit captivating structural motifs.

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