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Syntheses, structures and magnetic properties of four coordination polymers based on nitrobenzene dicarboxylate and various N-donor coligands



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ABSTRACT

Four new coordination polymers $\{[\text{Ni}(\text{4-Nbdc})(\text{bpa})(\text{H}_2\text{O})]\}_n$ (**1**), $\{[\text{Co}(\text{4-Nbdc})(\text{bpp})(\text{H}_2\text{O})]\}_n$ (**2**), $\{[\text{Ni}(\text{4-Nbdc})(\text{bpp})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Mn}_2(\text{3-Nbdc})_2(\text{bib})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**4**) (4-Nbdc = 4-nitrobenzene-1,2-dicarboxylate, 3-Nbdc = 3-nitrobenzene-1,2-dicarboxylate, bpa = 1,2-bis(4-pyridyl)ethane, bpp = 1,3-bis(4-pyridyl)propane, and bib = 1,4-bis(1-imidazolyl)benzene), were synthesized by hydrothermal reactions, and characterized by single-crystal X-ray diffractions, elemental analysis, FT-IR, PXRD, TGA and magnetic analysis. Complexes **1** and **2** display quasi-trapezoidal chain and brick-wall layer, and both of them contain metal–carboxylate binuclear units. Complexes **3** and **4** exhibit three-dimensional frameworks with the (6⁶) **dia** topology and (4⁴.6¹⁰.8)(4⁴.6²) **psc** topology, and both of them contain metal–carboxylate chains. The carboxyl groups with *syn-anti* coordination mode mediate effectively the weak ferromagnetic coupling interaction within Ni(II)–carboxylate binuclear in **1** ($J = 1.27 \text{ cm}^{-1}$) and Ni(II)–carboxylate chain in **3** ($J = 1.44 \text{ cm}^{-1}$), respectively, and the carboxyl groups with *anti-anti* coordination mode leads to the classic antiferromagnetic coupling interaction within Mn(II)–carboxylate chain in **4** ($J = -0.77 \text{ cm}^{-1}$).

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1. Introduction

Interest in coordination polymers is rapidly increasing not only owing to their versatile intriguing architectures and topologies but also for their potential applications in a variety of areas, including catalysis [1–3], gas storage/separations [4–6], fluorescent sensing [7–9], nonlinear optics [10,11], electronic [12,13], and magnetic devices *etc* [14,15]. The mixed-ligands strategy by the judicious choice of various organic linkers, for example, the combination of benzene–carboxylates and N-donor ligands, has been proven to be high-efficient for the construction of novel coordination polymers. Recently, the subtle control over the structures and functional properties of coordination polymers can be implemented by using various functionalized benzene–carboxylates, for example, nitrobenzene-1,2-dicarboxylic acid (NbdcH₂) [16–21], in light of the electronic and steric effects of the substituent groups [22]. The linear dipyrindyl-typed ligands, such as 1,2-bis(4-pyridyl)ethane (bpa) and 1,3-bis(4-pyridyl)propane (bpp), are among ideal N-donor ligands [23–27],

though the biimidazolyl-typed ligands such as 1,4-bis(1-imidazolyl)benzene (bib) has rarely been concerned.

In the past two decades, the coordination polymeric magnetism has been experiencing much success in creating a number of new magnetic materials, which provides an effective approach to design these magnetic systems when magnetic metal ions are assembled into coordination polymers by employing suitable ligands. In the mixed-ligands system, the short bridging groups (oxygen, hydroxyl, halogen, cyano, and azido) [28–39] and even the carboxyl groups with various coordination modes (*syn-syn*, *syn-anti*, *anti-anti*) [40–43] mediate effectively near-neighbor magnetic interactions, which can also be assisted by the secondary magnetic interactions through N-donor coligands in such materials. Most of them show ferromagnetic interactions [14,28,42], or ferrimagnetic [33,34,44–47], and antiferromagnetic interactions [26,30,43].

In fact, previous experimental and theoretical studies of carboxylato-bridged transition metal complexes have shown that the value of the exchange coupling between metal ions through bridging carboxylate (J) is strongly dependent on the bridging mode of the carboxylate (*syn-syn*, *anti-anti*, and *syn-anti*) and the type of M–O–C–O–M pathway involved (equatorial–equatorial or equatorial–apical) [43,48]. Herein, we prepared four new coordination polymers by the mixed-ligands strategy in the presence of

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nitrobenzene-1,2-dicarboxylic acids and various N-donor coligands, namely, $\{[\text{Ni}(4\text{-Nbdc})(\text{bpa})(\text{H}_2\text{O})]\}_n$ (**1**), $\{[\text{Co}(4\text{-Nbdc})(\text{bpp})(\text{H}_2\text{O})]\}_n$ (**2**), $\{[\text{Ni}(4\text{-Nbdc})(\text{bpp})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Mn}_2(3\text{-Nbdc})_2(\text{bib})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**4**). The magnetic susceptibility measurements indicate the occurrence of ferromagnetic interactions within Ni(II)–carboxylate binuclear in **1** and Ni(II)–carboxylate chain in **3**, both of them adopt nonplanar *syn-anti* carboxylato-bridged mode (equatorial–equatorial pathway), and classic antiferromagnetic coupling interaction within Mn(II)–carboxylate chain in **4** adopting the *anti-anti* carboxylato-bridged mode.

2. Experimental

2.1. Materials and physical measurements

All chemicals for synthesis were of reagent grade and used as received without further purification. Elemental analyses for C, H and N were carried out using a Flash 2000 organic elemental analyzer. Infrared spectra ($4000\text{--}600\text{ cm}^{-1}$) were recorded on powdered samples using a NICOLET 6700 FT-IR spectrometer. The thermogravimetric analyses (TGA) were performed on a SII EXStar 6000 TG/DTA6300 analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ up to $900\text{ }^\circ\text{C}$ under N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns were taken on a Bruker D8-ADVANCE X ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). Variable temperature magnetic susceptibilities were measured by using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Synthesis of $\{[\text{Ni}(4\text{-Nbdc})(\text{bpa})(\text{H}_2\text{O})]\}_n$ (**1**)

A mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.025 g, 0.10 mmol), 4-NbdcH₂ (0.021 g, 0.10 mmol), bpa (0.018 g, 0.10 mmol), KOH (0.006 g, 0.10 mmol), and H₂O (7 mL) was placed in a 23 mL Teflon-lined autoclave, the vessel was heated to $120\text{ }^\circ\text{C}$ for 4 days, and then cooled to room temperature. Green block crystals were obtained. Elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_7\text{Ni}$: C 51.02%, H 3.61%, N 8.91%. Found: C 51.10%, H 3.65%, N 8.94%. Selected IR (KBr, cm^{-1}): 3114(w), 1615(s), 1557(s), 1517(s), 1475(w), 1408(s), 1361(m), 1336

(s), 1236(w), 1158(w), 1067(w), 1020(w), 921(w), 842(m), 826(s), 812(s), 753(m), 729(s), 708(s), 667(w).

2.3. Synthesis of $\{[\text{Co}(4\text{-Nbdc})(\text{bpp})(\text{H}_2\text{O})]\}_n$ (**2**)

A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.049 g, 0.20 mmol), 4-NbdcH₂ (0.042 g, 0.20 mmol), bpp (0.020 g, 0.10 mmol), KOH (0.006 g, 0.10 mmol), and H₂O (7 mL) was placed in a 23 mL Teflon-lined autoclave, the vessel was heated to $120\text{ }^\circ\text{C}$ for 4 days, and then cooled to room temperature. Purple block crystals were obtained. Elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_7\text{Co}$: C 51.96%, H 3.92%, N 8.74%. Found: C 52.08%, H 3.95%, N 8.68%. Selected IR (KBr, cm^{-1}): 3078(w), 1611(s), 1571(s), 1450(m), 1412(m), 1388(m), 1332(s), 1231(w), 1156(w), 1064(m), 1017(w), 920(w), 849(w), 827(s), 792(m), 752(m), 726(m), 663(m).

2.4. Synthesis of $\{[\text{Ni}(4\text{-Nbdc})(\text{bpp})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**3**)

A mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.049 g, 0.20 mmol), 4-NbdcH₂ (0.042 g, 0.20 mmol), bpp (0.020 g, 0.10 mmol), KOH (0.012 g, 0.20 mmol), and H₂O (7 mL) was placed in a 23 mL Teflon-lined autoclave. The vessel was heated to $120\text{ }^\circ\text{C}$ for 4 days, and then cooled to room temperature. Green block crystals were obtained. Elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_8\text{Ni}$: C 50.21%, H 4.17%, N 8.35%. Found: C 50.23%, H 4.21%, N 8.37%. Selected IR (KBr, cm^{-1}): 3080(w), 1613(m), 1590(s), 1556(s), 1506(m), 1474(w), 1417(m), 1392(m), 1373(w), 1340(s), 1226(w), 1122(w), 1068(m), 1024(w), 920(w), 858(w), 827(s), 801(m), 756(w), 735(w), 721(m), 664(w).

2.5. Synthesis of $\{[\text{Mn}_2(3\text{-Nbdc})_2(\text{bib})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**4**)

A mixture of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.025 g, 0.10 mmol), 3-NbdcH₂ (0.021 g, 0.10 mmol), bib (0.042 g, 0.20 mmol), KOH (0.006 g, 0.10 mmol), and H₂O (7 mL) was placed in a 23 mL Teflon-lined autoclave. The vessel was heated to $120\text{ }^\circ\text{C}$ for 4 days, and then cooled to room temperature. Colorless block crystals were obtained. Elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{40}\text{Mn}_2\text{N}_4\text{O}_{14}$: C 52.38%, H 3.32%, N 16.45%. Found: C 52.27%, H 3.37%, N 16.41%. Selected IR (KBr, cm^{-1}): 3113(w), 1660(w), 1586(m), 1557(s), 1529(m), 1518(m), 1447(w), 1384(m), 1339(m), 1304(m), 1266(w), 1252(w), 1127(w), 1105(w),

Table 1
Crystal and structure refinement data for complexes **1–4**.

	1	2	3	4
Empirical formula	$\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_7\text{Ni}$	$\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_7\text{Co}$	$\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_8\text{Ni}$	$\text{C}_{52}\text{H}_{40}\text{Mn}_2\text{N}_4\text{O}_{14}$
Formula weight	470.08	484.32	502.12	1194.86
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$C2/c$	$P-1$	$P2(1)2(1)2(1)$	$P-1$
$a/\text{\AA}$	27.374(5)	10.0192(16)	8.403(5)	10.2120(5)
$b/\text{\AA}$	7.5696(14)	27.598(4)	10.985(7)	11.2640(6)
$c/\text{\AA}$	19.838(4)	17.5393(19)	24.235(14)	11.8008(8)
$\alpha/^\circ$	90	90	90	106.962(5)
$\beta/^\circ$	111.862(2)	123.252(6)	90	98.287(5)
$\gamma/^\circ$	90	90	90	97.359(4)
$V/\text{\AA}^3$	3815.1(12)	4055.7(10)	2237(2)	1263.89(13)
Z	8	8	4	2
$D_c/\text{g cm}^{-3}$	1.637	1.586	1.491	1.570
μ/mm^{-1}	1.069	0.897	0.920	0.583
$F(000)$	1936	1992	1040	612
θ Range/ $^\circ$	2.81 to 25.50	2.49 to 25.50	2.50 to 25.50	3.00 to 25.49
Reflections collected/unique	13489/3539	21102/7510	16859/4171	9233/4712
$R(\text{int})$	0.0580	0.0568	0.0635	0.0272
Completeness	99.8%	99.6%	99.9%	99.9%
Data/restraints/parameters	3539/0/281	7510/0/577	4171/0/298	4712/0/373
Goodness-of-fit	0.899	1.014	1.032	1.036
$R_1, wR_2 [I > 2\sigma(I)]$	0.0434, 0.1166	0.0495, 0.1021	0.0372, 0.0758	0.0411, 0.0935
R_1, wR_2 (all data)	0.0773, 0.1420	0.0917, 0.1189	0.0471, 0.0805	0.0546, 0.1029
Largest peak and hole / $e\text{\AA}^{-3}$	0.532 and -0.441	0.618 and -0.399	0.268 and -0.346	0.425 and -0.379

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