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Syntheses, structural diversities and magnetic properties of four new Co(II) coordination polymers with phthalic acid derivatives

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ABSTRACT

Four new 3D Co(II) coordination polymers, [Co(4apa)(H_2O)] (**1**), [Co(bpy)(3npa)] (**2**), [Co(bpy)$_{1.5}$(3adpa)] (**3**) and [Co(btx)$_{0.5}$(4npa)(H_2O)$_2$] (**4**) ($H_2$4apa = 4-aminophthalic acid, bpy = 4,4′-bipyridine, $H_2$3npa = 3-nitrophthalic acid, $H_2$3adpa = 3-(4-amino-1,3-dioxoisoindolin-2-yl)phthalic acid, btx = 1,4-bis(1,2,4-triazole-1-ylmethyl)benzene, $H_2$4npa = 4-nitrophthalic acid), have been synthesized and characterized by single crystal X-ray diffraction, PXRD and magnetic susceptibility measurements. An interesting *in situ* acylation reaction of 3-aminophthalic acid ($H_2$3apa) has been found in the formation of coordination polymer **3**. The Co(II) ions of each polymer lie in distorted octahedral environments and are bridged by $\mu_{1,3}$ carboxylate groups to form 2D (**1**), 1D (**2** and **3**) and dimer (**4**) structures, which are further assembled through ligands into different 3D structures due to the influence of the substituent groups. Studies of the temperature dependence of the magnetic susceptibilities in the range 2–300 K reveal antiferromagnetic interactions in **1**–**4** between the Co(II) ions transmitted by $\mu_{1,3}$ carboxylate groups.

1. Introduction

Functional coordination polymers have attracted considerable attention in the past decades due to their valuable properties, such as magnetism [1], luminescence [2], catalysis [3], and adsorption [4]. In this context, magnetic coordination polymers are of special interest. The magnetic properties of coordination polymers are attributed to (i) spin carriers such as metal ions providing the source of magnetic moments, and (ii) different bridging ligands providing superexchange pathways between the spin carriers. To better understand the magnetic properties of coordination polymers there have been many efforts in the strategy of synthesis and analysis of magneto-structural correlations [1,5], but it is still a great challenge to assemble spin carriers to the skeleton of coordination polymers with predetermined structures and targetted magnetic properties. The way to solve of this problem lies in the understanding of magneto-structural correlations more thoroughly through both experimental and theoretical investigations.

Co(II) ion is one of the interesting candidates of spin carriers and usually leads to fascinating magnetic properties. In an octahedral coordination geometry, its magnetic moment includes contributions from not only the spin angular momentum but also the orbital angular momentum, different from other first-row transition metal ions whose orbital angular momentums are always quenched by the ligand field. On the other hand, carboxylato ligands exhibit an extensively documented ability to bridge metal ions, forming 1D, 2D and 3D coordination networks [1a,f,6]. Carboxylate groups can adopt many types of bridging conformations, such as triatomic *syn-syn*, *anti-syn*, and *anti–anti*. Ferro- or antiferro-magnetic interactions can be effectively transmitted through such three atom bridges [7]. However, due to the structural diversities of Co(II) coordination polymers, a detailed understanding of magneto-structural correlations in such systems is still unclear [1c]. Our previous studies show that phthalic acid is a good bridging ligand to build molecular magnetic materials due to its flexibility of coordination modes [8]. As a continuation of this work, four phthalic acid derivatives ($H_2$4apa = 4-aminophthalic acid, $H_2$3npa = 3-nitrophthalic acid, $H_2$3apa = 3-aminophthalic acid, $H_2$4npa = 4-nitrophthalic acid) were selected because of their abilities to adopt various coordination modes like phthalic acid but with different substituent groups. It is noted that $H_2$3adpa ($H_2$3adpa = 3-(4-amino-1,3-dioxoisoindolin-2-yl)phthalic acid) was formed by the *in situ* acylation reaction of 3-aminophthalic acid ($H_2$3apa) in the formation of coordination polymer **3**. Furthermore, net neutral linear linkers 4,4′-bipyridine (bpy) and 1,4-bis(1,2,4-triazole-1-ylmethyl)benzene (btx) were employed as co-ligands. Four new 3D coordination polymers, [Co(4apa)(H_2O)] (**1**), [Co(bpy)(3npa)] (**2**), [Co(bpy)$_{1.5}$(3adpa)] (**3**) and [Co(btx)$_{0.5}$(4npa)(H_2O)$_2$] (**4**), were successfully synthesized and characterized. Studies of the temperature dependence of the magnetic susceptibilities in the range 2–300 K reveal antiferromagnetic interactions in **1**–**4**

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between the Co(II) ions transmitted by the *anti–syn* carboxylate groups.

2. Experimental

2.1. General considerations

All reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 CHN elemental analyzer. Powder X-ray diffraction measurements were measured on a D/Max-2500 X-ray diffractometer using Cu Kα radiation. Variable-temperature magnetic susceptibilities were measured on a SQUID MPMS XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms and sample holders.

2.2. Syntheses

2.2.1. [Co(4apa)(H2O)] (**1**)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.116 g, 0.40 mmol), 4-aminophthalic acid (0.054 g, 0.30 mmol), NaOH (0.016 g, 0.40 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 150 °C for 2 days, and then cooled to room temperature. Red block-shaped crystals were filtered off, washed with water and dried in air. Yield: 67% based on 4apa. *Anal.* Calc. for $C_8H_9CoNO_5$ (258.08): C, 37.23; H, 3.51; N, 5.43. Found: C, 37.45; H, 3.80; N, 5.59%.

2.2.2. [Co(bpy)(3npa)] (**2**)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.116 g, 0.40 mmol), 4,4′-bipyridine (0.016 g, 0.10 mmol), 3-nitrophthalic acid (0.042 g, 0.20 mmol), NaOH (0.008 g, 0.20 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 150 °C for 2 days, and then cooled to room temperature. Red block-shaped crystals were filtered off, washed with water and dried in air. Yield: 76% based on bpy. *Anal.* Calc. for $C_{18}H_{11}CoN_3O_6$ (424.23): C, 50.96; H, 2.61; N, 9.91. Found: C, 50.96; H, 2.62; N, 9.79%.

2.2.3. [Co(bpy)$_{1.5}$(3adpa)] (**3**)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.116 g, 0.40 mmol), 4,4′-bipyridine (0.048 g, 0.30 mmol), 3-aminophthalic acid (0.054 g, 0.30 mmol), NaOH (0.016 g, 0.40 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 150 °C for 2 days, and then cooled to room temperature. Red block-shaped crystals were filtered off, washed with water and dried in air. Yield: 64% based on bpy. *Anal.* Calc. for $C_{31}H_{20}CoN_5O_6$ (617.45): C, 60.30; H, 3.26; N, 11.34. Found: C, 60.04; H, 3.74; N, 11.56%.

2.2.4. [Co(btx)$_{0.5}$(4npa)(H$_2$O)$_2$] (**4**)

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.116 g, 0.40 mmol), 1,4-bis(1,2,4-triazol-1-ylmethyl) benzene (0.024 g, 0.10 mmol), 4-nitrophthalic acid (0.042 g, 0.20 mmol), NaOH (0.008 g, 0.20 mmol) and H_2O (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 150 °C for 2 days, and then cooled to room temperature. Red block-shaped crystals were filtered off, washed with water and dried in air. Yield: 73% based on btx. *Anal.* Calc. for $C_{14}H_{13}CoN_4O_8$ (424.21): C, 39.64; H, 3.09; N, 13.21. Found: C, 39.78; H, 3.00; N, 12.98%.

2.3. Crystal structure determination

Diffraction data of the four compounds were collected at 150 or 293 K on an Oxford Supernova diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by the direct method and refined with the full-matrix least-squares technique using the SHELXTL program package [9]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with

Table 1
Data collection and processing parameters for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_8H_7CoNO_5$	$C_{18}H_{11}CoN_3O_6$	$C_{31}H_{20}CoN_5O_6$	$C_{14}H_{13}CoN_4O_8$
Formula weight	256.08	424.23	617.45	424.21
T (K)	150(2)	150(2)	293(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*21/*c*	*C*2/*c*
a (Å)	10.3115(4)	7.1044(8)	11.5656(5)	37.186(3)
b (Å)	7.3868(3)	23.403(2)	21.4632(6)	5.9373(4)
c (Å)	14.2596(7)	10.8747(15)	11.8959(5)	14.9209(9)
α (°)	90	90	90	90
β (°)	126.966(3)	113.173(10)	108.644(4)	112.981(8)
γ (°)	90	90	90	90
V (Å^3)	867.82(6)	1662.2(3)	2798.01(19)	3032.8(4)
Z	4	4	1	8
ρ (g/cm^3)	1.960	1.695	1.466	1.858
μ (mm^{-1})	1.977	1.078	0.668	1.192
θ (°)	2.88–25.99	2.68–26.00	2.62–25.01	2.38–25.50
Index ranges	$-12 \leqslant h \leqslant 12$, $-9 \leqslant k \leqslant 8$, $-17 \leqslant l \leqslant 17$	$-8 \leqslant h \leqslant 4$, $-28 \leqslant k \leqslant 21$, $-12 \leqslant l \leqslant 13$	$-13 \leqslant h \leqslant 13$, $-25 \leqslant k \leqslant 24$, $-9 \leqslant l \leqslant 14$	$-44 \leqslant h \leqslant 44$, $-7 \leqslant k \leqslant 5$, $-17 \leqslant l \leqslant 18$
Reflections collected	3334	6888	10418	5769
Independent reflections (R_{int})	1707 (0.0282)	3269 (0.0282)	4930 (0.0282)	2810 (0.0282)
Data/restraints/ parameters	1707/0/140	3269/24/253	4930/15/389	2810/0/256
Goodness-of-fit (GOF) on F^2	1.044	0.949	1.062	1.016
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0356, 0.0846	0.0560, 0.1432	0.0801, 0.2429	0.0316, 0.0741
R_1, ωR_2 (all data)	0.0425, 0.0872	0.0987, 0.1832	0.1263, 0.2643	0.0410, 0.0770