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具有类 CsCl 拓扑的Co^{II}配位聚合物的合成,结构与磁性

林健斌 陈小明*
(中山大学化学与化学工程学院/教育部生物无机与合成化学重点实验室,广州 510275)

摘要: 本工作在溶剂热条件下合成了 2 例以二核或三核 Co^{II}为节点, 具有八连接类 CsCl 拓扑的配位聚合物:[Co(na)(ina)]和[Co_3(na)$_4$(1,4-chdc)](Hna=nicotinic acid,Hina=isonicotinic acid,1,4-H_2chdc=cyclohexane-1,4-dicarboxylic acid)。磁性研究表明,2 个配合物均呈现反铁磁行为。

关键词: CsCl; 拓扑结构; 反铁磁
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Syntheses, Structures and Magnetic Properties of Two Co^{II} Polymers with CsCl-like Topology

LIN Jian-Bin CHEN Xiao-Ming*
(*MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou* 510275)

Abstract: Two three-dimensional coordination polymers, namely [Co(na)(ina)] (**1**) and [Co_3(na)$_4$(1,4-chdc)] (**2**) (Hna=nicotinic acid, Hina=isonicotinic acid, 1,4-H_2chdc=cyclohexane-1,4-dicarboxylic acid), with 8-connected CsCl-like topology, have been solvothermally synthesized. The temperature-dependent magnetic susceptibilities were also determined, showing antiferromagnetism in both compounds. CCDC: 688479, **1**; 688480, **2**.

Key words: CsCl; topology; antiferromagnet

The design and synthesis of coordination polymers with three-dimensional (3D) frameworks featuring interesting topologies have been the focus of intense research activity in recent years[1~5]. The major structural types found in coordination polymers are low-connected topologies in which d-block metal ions are used as nodes for three-, four-, or six-connected[1,3~6]. The local connectivity numbers larger than six in coordination polymers are rare because of the low coordination sites of d-block metal ions and the sterically demanding nature of organic ligands[7]. Generally, there are two ways for constructing highly connected coordination polymers. One is employing *f*-block metal ions centers to construct seven- and eight-connected coordination polymers[8,9]. The other is based on metal clusters, which is effective to overcome the low coordination numbers of *d*-block metal ions and steric hindrance[10~12]. Herein, we report two new 3D coordination polymers, namely [Co(na)(ina)] (**1**) and [Co_3(na)$_4$(1,4-chdc)] (**2**) (Hna=nicotinic acid, Hina=isonicotinic acid, 1,4-H_2chdc=cyclohexane-1,4-dicarboxylic acid), which show 8-connected CsCl-like topology with Co_2 or Co_3

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*通讯联系人。E-mail:cxm@mail.sysu.edu.cn
第一作者:林健斌,男,25 岁,硕士研究生;研究方向:配位化学。

clusters acting as eight-connected nodes, respectively.

1 Experimental

1.1 Reagents and physical measurements

Commercially available reagents were used as received without further purification. Elemental analyses (C, H, N) were performed on a Vario EL elemental analyzer. The FTIR (KBr pellet) spectra were recorded from KBr pellets in the range of 400~4 000 cm^{-1} on a Bruker TENSOR 27 FTIR spectrometer. X-ray powder diffraction (XRPD) patterns were measured at a Rigaku D/M-2200T automated diffractometer. Magnetic susceptibility measurements of **1** and **2** were performed on a poly-crystalline sample fixed with GE7031 varnish on a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

1.2 Synthesis of [Co(na)(ina)] (1)

A DMF solution (7 mL) containing $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), isonicotinic acid (0.123 g, 1 mmol) and nicotinic acid (0.123 g, 1 mmol) was placed in a Parr Teflon-lined stainless-steel bomb (15 mL), which was sealed and placed in a programmable furnace. The temperature was raised to 160 ℃ and held at that temperature for 72 h, then cooled to room temperature at 5 ℃·h^{-1}. The resulting light blue crystals were collected (0.04 g, *ca.* 13.2% yield based on Co). Anal. calcd (%) for $C_{12}H_8CoN_2O_4$: C 47.55; H 2.66; N 9.24. Found(%): C 47.18; H 2.87; N 9.34. IR(cm^{-1}): 3 436.4 w, 3 062.8w, 1 627.8vs, 1 544.9s, 1 421.5vs, 1 200.9w, 1 047.0w, 858.3m, 765.7m, 700.1s, 565.9w, 443.6m.

1.3 Synthesis of [Co_3(na)$_4$(1,4-chdc)] (2)

A DMF solution (6 mL) containing $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), nicotinic acid (0.123 g, 1 mmol) and 1,4-H_2chdc (0.172 g, 1 mmol) was placed in a Parr Teflon-lined stainless-steel bomb (15 mL), which was sealed and placed in a programmable furnace. The temperature was raised to 170 ℃ and held at that temperature for 72 h, then cooled to room temperature at 5 ℃·h^{-1}. The resulting deep blue crystals were collected (0.02 g, *ca.* 6.6% yield based on Co). Anal. calcd (%) for $C_{32}H_{26}Co_3N_4O_{12}$: C 46.01; H 3.14; N 6.71. Found(%): C 45.94; H 3.25; N 6.81. IR (cm^{-1}): 3 449.3w, 2 920.0w, 1 616.3vs, 1 570.0vs, 1 523.7s, 1 394.5vs, 1 284.5w, 1 195.8m, 1 043.4m, 1 101.5w, 858.3w, 756.1 m, 702.1m, 569.1w, 447.5m.

1.4 Crystal structure determination

Diffraction intensities were collected on a Bruker Apex CCD area-detector diffractometer (Mo $K\alpha$). Absorption corrections were applied by using multi-scan program SADABS[13]. The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package[14]. Anisotropic thermal parameters were applied to all the non-H atoms. The organic H atoms were generated geometrically. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table 1.

CCDC: 688479, **1**; 688480, **2**.

Table 1　Crystallographic data for complexes 1 and 2

Complex	**1**	**2**
Formula	$C_{12}H_8CoN_2O_4$	$C_{32}H_{26}Co_3N_4O_{12}$
Formula weight	303.13	835.37
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No.14)	$C2/c$ (No.15)
a / nm	0.975 1(2)	2.292 4(3)
b / nm	1.171 1(3)	1.039 37(15)
c / nm	1.148 1(3)	1.353 2(2)
β / (°)	112.694(4)	105.250(2)
V / nm^3	1.209 6(5)	3.110 7(8)
Z	4	4
D_c / ($g \cdot cm^{-3}$)	1.665	1.784

Continued Table 1

μ(Mo $K\alpha$) / mm^{-1}	1.429	1.657
Reflections collected	5 042	7 130
Unique reflns / R_{int}	2 369 / 0.023 2	2 711 / 0.042 4
R_1, wR_2 [$I>2\sigma(I)$]	0.036 1, 0.093 1	0.086 2, 0.250 4
R_1, wR_2 (all data)	0.042 1, 0.095 9	0.101 0, 0.264 7
GOF	1.046	1.036
$\Delta\rho_{min/max}$ / (e·nm^{-3})	766 / −440	1 021 / −1 868

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

2 Results and discussion

2.1 Crystal structure of 1

The crystal structure of **1** is shown in Fig.1. Selected bond lengths and angles are given in Table 2. Each Co Ⅱ ion is coordinated to three na and two ina ligands in a distorted octahedral N_2O_4 geometry (Co-N/O 0.199 9(2)~0.223 0(2) nm). Each na ligand acts as a μ_3-ligand with its carboxylate group bridging two Co Ⅱ ions that are separated by 0.411 9 nm. Each ina ligand acts as a μ_2-ligand with its carboxylate group chelating a Co Ⅱ ion. In other words, each dinuclear Co Ⅱ cluster

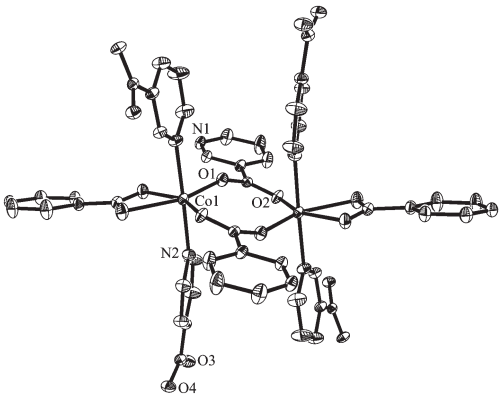

Fig.1 Dinuclear Co Ⅱ structure of complex **1**

Table 2 Selected bond lengths (nm) and angles (°) of complexes 1 and 2

Complex **1**					
Co(1)-O(1)	0.199 9(2)	Co(1)-O(4B)	0.213 2(2)	Co(1)-N(1C)	0.216 9(2)
Co(1)-O(2A)	0.202 0(2)	Co(1)-N(2)	0.215 6(2)	Co(1)-O(3B)	0.223 0(2)
O(1)-Co(1)-O(2A)	115.63(8)	O(4B)-Co(1)-N(2)	86.18(9)	O(1)-Co(1)-O(3B)	150.66(8)
O(1)-Co(1)-O(4B)	90.81(8)	O(1)-Co(1)-N(1C)	87.65(8)	O(2A)-Co(1)-O(3B)	93.58(7)
O(2A)-Co(1)-O(4B)	153.56(8)	O(2A)-Co(1)-N(1C)	89.45(8)	O(4B)-Co(1)-O(3B)	60.01(7)
O(1)-Co(1)-N(2)	92.49(9)	O(4B)-Co(1)-N(1C)	91.79(9)	N(2)-Co(1)-O(3B)	88.74(9)
O(2A)-Co(1)-N(2)	92.32(8)	N(2)-Co(1)-N(1C)	177.97(9)	N(1C)-Co(1)-O(3B)	90.15(9)
Complex **2**					
Co(1)-O(6)	0.207 5(5)	Co(2)-O(3)	0.199 6(5)	Co(2)-N(1D)	0.208 5(7)
Co(1)-O(4)	0.215 1(5)	Co(2)-O(2)	0.205 7(7)	Co(2)-O(1)	0.231 5(7)
Co(1)-N(2B)	0.215 9(6)	Co(2)-O(5)	0.206 0(6)	Co(2)-O(6)	0.233 7(6)
O(6)-Co(1)-O(6A)	91.8(3)	O(3)-Co(2)-O(2)	102.8(3)	O(5)-Co(2)-O(1)	83.2(2)
O(6)-Co(1)-O(4A)	91.7(2)	O(3)-Co(2)-O(5)	113.0(2)	N(1D)-Co(2)-O(1)	91.8(2)
O(6)-Co(1)-O(4)	92.8(2)	O(2)-Co(2)-O(5)	137.8(2)	O(3)-Co(2)-O(6)	97.8(2)
O(4A)-Co(1)-O(4)	173.5(3)	O(3)-Co(2)-N(1D)	95.2(2)	O(2)-Co(2)-O(6)	95.8(2)
O(6)-Co(1)-N(2B)	88.2(2)	O(2)-Co(2)-N(1D)	103.9(3)	O(5)-Co(2)-O(6)	58.9(2)
O(6)-Co(1)-N(2C)	179.9(3)	O(5)-Co(2)-N(1D)	94.6(3)	N(1D)-Co(2)-O(6)	153.3(2)
O(4)-Co(1)-N(2C)	87.3(2)	O(3)-Co(2)-O(1)	161.6(2)		
N(2B)-Co(1)-N(2C)	91.9(3)	O(2)-Co(2)-O(1)	58.9(2)		

Symmetry codes for **1**: A: −1−x, −y, −1−z; B: −x, 0.5+y, −0.5−z; C: x, 0.5−y, −0.5+z; for **2**: A: −x, y, 0.5−z; B: x, 1−y, −0.5+z; C: −x, 1−y, 1−z; D: 0.5−x, 0.5+y, 0.5−z.

binds simultaneously to four na and four ina ligands. By treating the dinuclear cluster as a single node and the ligand as linker, a CsCl-like[15] 3D network sustained by 8-connected nodes is formed, as illustrated in Fig.2.

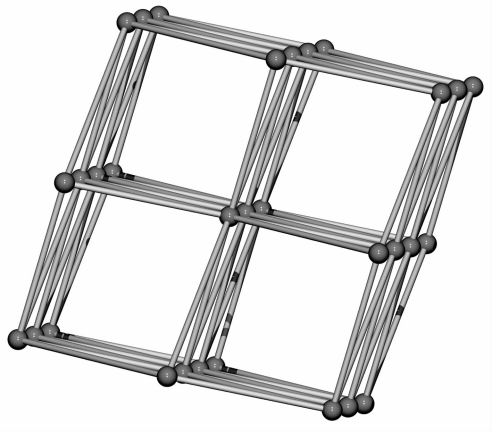

Fig.2　CsCl-like net

2.2　Crystal structure of 2

The crystal structure of **2** is shown in Fig.3 (a). Selected bond lengths and angles are given in Table 2. Two Co$^{\text{II}}$ ions are crystallographically unique, and both have distorted octahedral environments. Co(1) is located at a twofold axis, and coordinated to four na and two 1,4-chdc ligands in a distorted octahedral N_2O_4 geometry (Co-N/O 0.207 5(5)~0.215 9(6) nm). Co(2) is coordinated to three na and one 1,4-chdc ligands in a distorted octahedral NO_5 geometry (Co-N/O 0.199 6(5)~0.233 7(6) nm). One na acts as a μ_3-ligand with its carboxylate group bridging two Co$^{\text{II}}$ ions that are separated by 0.383 1 nm, the other acts as a μ_2-ligand with its carboxylate group chelating a Co atom. Each 1,4-chdc acts as a μ_4-ligand with each carboxylate group connects two Co$^{\text{II}}$ ions with the μ_2-η^1:η^2 mode. In other words, each trinuclear Co$^{\text{II}}$ cluster binds to eight na ligands and two 1,4-chdc ligands simultaneously. By treating the trinuclear as a single node, the 8-connected node connects to eight neighbors through these ten ligands (Fig.3(b)), forming a CsCl-like 3D network similar to complex **1**, as illustrated in Fig.2.

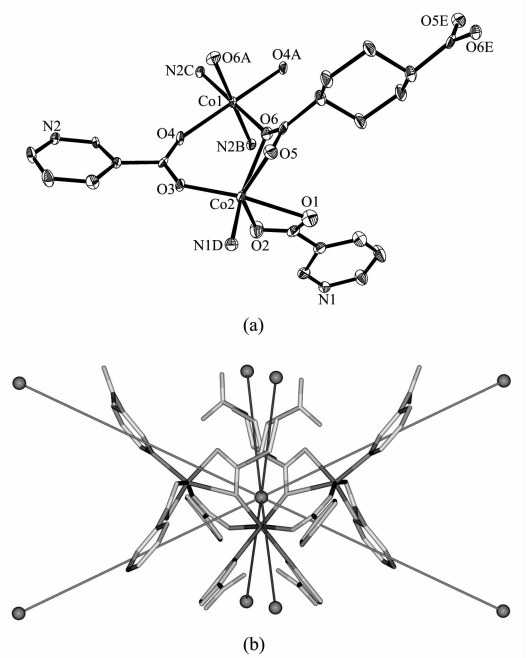

Fig.3　(a) Coordination environments in **2** (symmetry codes: A: $-x$, y, 0.5$-z$; B: x, 1$-y$, $-$0.5$+z$; C: $-x$, 1$-y$, 1$-z$; D: 0.5$-x$, 0.5$+y$, 0.5$-z$; E: $-x$+1/2, $y$$-$1/2, $-z$+1/2); (b) view of the 8-connected trinuclear connected to eight neighbors in **2**

2.3　Magnetic properties

The phase purities of **1** and **2** used for magnetic measurement have been confirmed by XRPD (Fig.4). The variable-temperature magnetic susceptibilities of **1** and **2** were measured in the temperature range from 300 to 2 K (Fig.5), at a magnetic field strength of 1 000 Oe.

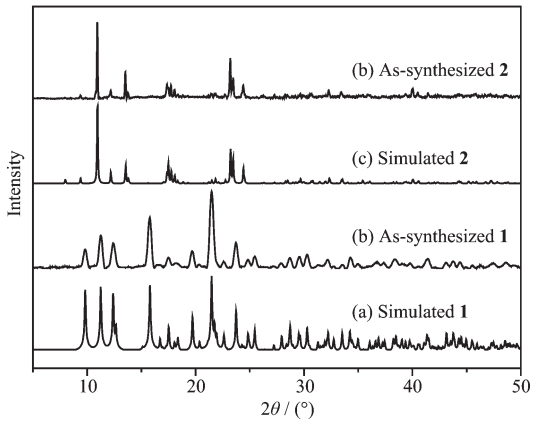

Fig.4　XRPD patterns of **1** and **2**

For **1**, the $\chi_m T$ value at room temperature is *ca.* 5.23 cm^3·mol^{-1}·K, higher than the spin-only value of 3.75 cm^3·mol^{-1}·K expected for two noncoupled Co$^{\text{II}}$ ions with g=2.0, owing to a significant orbital contribution of a high-spin octahedral Co$^{\text{II}}$. The $\chi_m T$ product decreases with decreasing temperature, which is a typical behavior of the antiferromagnetically coupled magnetic pair. The magnetic susceptibility in the range of 300~50 K can be well fitted by the Curie-Weiss law

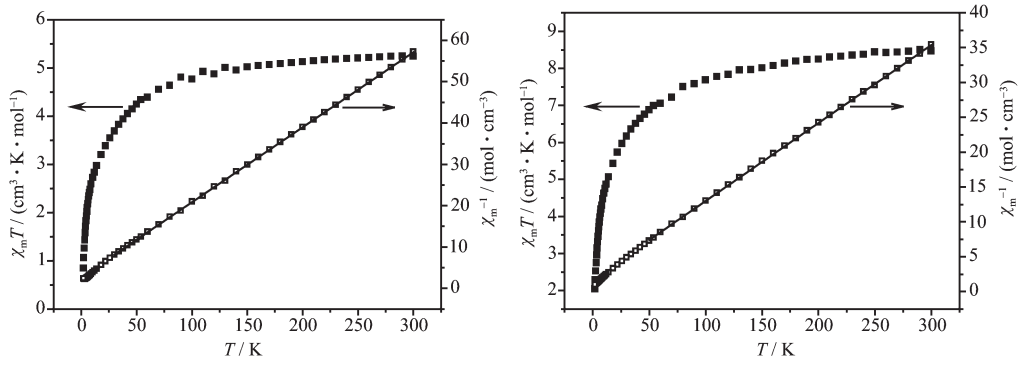

Fig.5 $\chi_m T$-T and χ_m^{-1}-T for **1** (left) and **2** (right) from 300 to 2 K at 1 000 Oe

with a Curie constant C=5.51 cm^3·mol^{-1}·K and a Weiss constant θ of −14.6 K, which is a further indication of the weak antiferromagnetic interactions in **1**.

For **2**, the $\chi_m T$ value at room temperature is *ca.* 8.45 cm^3·mol^{-1}·K, higher than the spin-only value of 5.625 cm^3·mol^{-1}·K expected for three noncoupled Co$^{\text{II}}$ ions with g=2.0, owing to a significant orbital contribution of a high-spin octahedral Co$^{\text{II}}$. The $\chi_m T$ product decreases with decreasing temperature, which is a typical behavior of the antiferromagnetically coupled magnetic pair. The magnetic susceptibility in the range of 300~50 K obeys the Curie-Weiss law with a Curie constant C=8.94 cm^3·mol^{-1} K and a Weiss constant θ of −16.3 K in **2**. The absolute values of Weiss constant θ of **2** is larger than **1**. According to the crystal structures, the single bridging oxygen can be assumed that the superexchange interactions between Co$^{\text{II}}$ ions of **2** is stronger than **1**.

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