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Effect of auxiliary ligands on cobalt(II) coordination polymers with 5-(imidazol-1-ylmethyl)isophthalate

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

The reactions of cobalt(II) salt with 5-(imidazol-1-ylmethyl)isophthalic acid (H₂L) as a main ligand and 1,10-phenanthroline (phen), 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (pybim) or 1,2-di(pyridin-4-yl)ethylene (dpe) as auxiliary ligand by hydrothermal method lead to the formation of four new complexes $[Co(L)(phen)]\cdot 2H_2O$ (1), $[Co(L)(pybim)(H_2O)]\cdot 2H_2O$ (2), $[Co(L)(pybim)]\cdot H_2O$ (3) and $[Co(L)(dpe)_{0.5}]$ (4), among them 2 and 3 were obtained by changing the metal-to-ligand ratio. While in the absence of any auxiliary ligand, complex [Co(L)] (5) was obtained. The complexes 1–5 have been characterized by single crystal and powder X-ray diffractions, IR, elemental and thermogravimetric analyses. Complexes 1 and 2 have double- and single-chain structures, while 2 and 3 are 3-connected uninodal and (3,6)-connected binodal 2D networks with (6^3) and $[(6^3)(6^6)]$ topology, respectively. All the complexes 1–4 show 3D supramolecular structures through hydrogen bonding/ π – π interactions. Complex 5 shows a (5,5)-connected binodal 3D net with $[(4^5)(6^5)]$ topology. The results imply that the auxiliary ligand as well as the metal-to-ligand ratio has great impact on the structure of the complexes.

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1. Introduction

During the past decades, considerable development and progress of synthesis and characterization of metal-organic frameworks (MOFs) have been achieved in coordination, materials and supramolecular chemistry, reflected by the fact that a growing interests of chemists were directed towards the field and a great number of MOFs with fascinating structures and interesting properties were prepared and reported [1-6]. The aim of crystal engineering is mainly to exploit new crystalline materials with intriguing architectures and potential applications in magnetism, heterogeneous catalysis, ion-recognition, nonlinear optics and adsorption [7,8]. Therefore, it becomes important to assemble coordination compounds with abundant structures for the exploration of crystalline materials. It is known that many factors can subtly influence on the assembly and structure of the complexes [9,10]. Among the factors, the option of organic ligands undoubtedly plays decisive role in the assembly of resultant coordination polymers [11]. Therefore, the structures and properties of MOFs may be adjustable through the alteration of organic ligands [12,13].

With such background in mind, recently we select 5-(imidazol-1-ylmethyl)isophthalic acid (H₂L) as the main organic bridging moieties to assembly coordination polymers in the presence of different auxiliary ligands. This is based mostly on the following considerations: (1) H₂L is an aromatic dicarboxylate-containing ligand, and may perform well in the assembly of coordination polymers with various structures for the well coordinating capacity of carboxylate group and its mutable coordination modes such as $\mu_1 - \eta^1 : \eta^0$ -monodentate, $\mu_1 - \eta^1 : \eta^1$ -chelating, and $\mu_2 - \eta^1 : \eta^1$ -bridging [14,15]. (2) H₂L can adopt different conformations in the selfassembly for the existence of a flexible imidazol-1-vlmethyl arm [16,17]. Therefore, the variable coordination modes and conformations of H₂L provide the feasibility to assemble polymers with various architectures by the adjustments of reaction conditions including the presence of different auxiliary ligands. In this contribution, three kinds of N-donor auxiliary ligands were introduced into the reactions, and four new coordination polymers [Co(L)(phen)] $\cdot 2H_2O$ (1), [Co(L)(pybim)(H₂O)] $\cdot 2H_2O$ (2), [Co(L)(pybim)] H_2O (**3**), and [Co(L)(dpe)_{0.5}] (**4**) have been obtained under the hydrothermal conditions with the employment of auxiliary ligands, 1,10-phenanthroline (phen), 2-(pyridin-2-yl)-1Hbenzo[*d*]imidazole (pybim), and 1,2-di(pyridin-4-yl)ethylene (dpe). Complex [Co(L)] (5) was obtained in the absence of any auxiliary ligands. Complexes 1-5 have been characterized by single-crystal X-ray structure determination, IR, elemental analysis, powder X-ray diffraction, and thermogravimetric analyses. In addition, preliminary magnetic property of 5 has also been investigated.





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Table 1
Crystal data and structure refinements for complexes 1-5.

Compound	1	2	3	4	5
Formula	C24H20N4O6C0	C ₂₄ H ₂₃ N ₅ O ₇ Co	C24H19N5O5C0	C ₁₈ H ₁₃ N ₃ O ₄ Co	$C_{12}H_8N_2O_4C_0$
Formula weight	519.37	552.40	516.37	394.24	327.59
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	ΡĪ	$P2_1/c$	ΡĪ	$P2_1/n$	$P2_1/c$
a (Å)	10.154(10)	13.353(2)	9.7385(19)	10.985(5)	8.7187(12)
b (Å)	10.188(10)	11.0086(17)	9.8487(18)	10.132(5)	16.490(2)
<i>c</i> (Å)	13.595(13)	16.140(3)	14.1656(14)	14.190(5)	7.7481(11)
α (°)	80.837(10)	90.00	87.555(2)	90.00	90.00
β(°)	71.365(15)	93.408(7)	79.562(3)	93.051(5)	100.451(2)
γ (°)	60.11	90.00	64.531(2)	90.00	90.00
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
V (Å ³)	1155.4(19)	2368.4(7)	1205.4(3)	1577.1(12)	1095.5(3)
Z	2	4	2	4	4
D_{calc} (g cm ⁻³)	1.493	1.549	1.423	1.660	1.838
μ (mm ⁻¹)	0.791	0.781	0.756	1.119	1.578
F(000)	534	1140	530	804	612
θ for data collection (°)	1.58-28.00	3.03-27.62	1.46-26.00	2.29-28.00	2.38-26.60
Reflections collected	8019	24561	10161	9612	6055
Unique reflections	5502	5476	4678	3764	2275
Goodness-of-fit (GOF) on F^2	1.073	1.095	1.163	1.061	1.358
$R_1^{a}, wR_2^{b} [I > 2\sigma(I)]$	0.0608, 0.1744	0.0689, 0.1738	0.0593, 0.1383	0.0372, 0.0858	0.0938, 0.1687
R_1 , wR_2 (all data)	0.0720, 0.1820	0.0731, 0.1773	0.0793, 0.1443	0.0511, 0.0922	0.0958, 0.1695

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.

^b $wR_2 = |\sum w(|F_0|^2 - |F_c|^2)| / \sum |w(F_0)^2|^{1/2}$, where $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = (F_0^2 + 2F_c^2)/3$.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The ligand H₂L was prepared according to the previously reported method [18]. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu K α (λ = 1.5418 Å) radiation at room temperature. The magnetic measurement in the temperature range of 1.8-300 K was carried out on a Quantum Design MPMS7 SQUID magnetometer in a field of 2000 Oe. Diamagnetic corrections were made with Pascal's constants.

2.2. Preparation of [Co(L)(phen)]·2H₂O (**1**)

Reaction mixture of $Co(NO_3)_2$ ·6H₂O (29.1 mg, 0.1 mmol), H₂L (24.6 mg, 0.1 mmol), phen (18.0 mg, 0.1 mmol), and KOH (11.2 mg, 0.2 mmol) in 10 mL H₂O was sealed in a 16 mL Teflonlined stainless steel container and heated at 160 °C for 3 days. After cooling to the room temperature, red block crystals of **1** were collected by filtration and washed by water and ethanol for several times with a yield of 62%. *Anal.* Calc. for C₂₄H₂₀N₄O₆Co: C, 55.50; H, 3.88; N, 10.79. Found: C, 55.21; H, 4.16; N, 10.52%. IR (KBr pellet, cm⁻¹): 3443 (m, br), 1617 (s), 1577 (s), 1552 (s), 1516 (m), 1450 (s), 1421 (m), 1376 (s), 1290 (w), 1240 (w), 1220 (w), 1114 (m), 1090 (m), 938 (w), 852 (m), 782 (m), 745 (m), 729 (s), 663 (w).

2.3. Preparation of $[Co(L)(pybim)(H_2O)] \cdot 2H_2O(2)$

Complex **2** was obtained by an analogous hydrothermal procedure as that used for synthesis of **1** except that pybim (39.0 mg, 0.2 mmol) was used instead of phen. Dark red needle crystals of **2** were collected by filtration and after washed by water and ethanol several times in 59% yield based on H₂L. *Anal.* Calc. for $C_{24}H_{23}N_5O_7Co$: C, 52.18; H, 4.20; N, 12.68. Found: C, 52.46; H, 3.96; N, 12.42%. IR (KBr pellet, cm⁻¹): 3373 (m, br), 1609 (s), 1560 (s), 1449 (s), 1371 (s), 1310 (s), 1236 (m), 1191 (w), 1134 (w), 1109 (w), 1089 (m), 1027 (w), 945 (w), 835 (m), 802 (w), 774 (s), 753 (s), 720 (s), 659 (m), 634 (w), 532 (w).

2.4. Preparation of $[Co(L)(pybim)] \cdot H_2O(3)$

Complex **3** was obtained by an analogous hydrothermal procedure as that used for synthesis of **2** except that pybim (19.5 mg, 0.1 mmol) was used, namely the metal-to-ligand ratio of Co(N- $O_3)_2$ · $6H_2O$:pybim was changed from 1:2 to 1:1. Pale red block crystals of **3** were isolated by filtration and washed by water and ethanol several times in 72% yield. *Anal.* Calc. for C₂₄H₁₉N₅O₅Co: C, 55.82; H, 3.71; N, 13.56. Found: C, 55.59; H, 3.93; N, 13.29%. IR (KBr pellet, cm⁻¹): 3417 (m, br), 1619 (s), 1563 (s), 1521 (m), 1481 (m), 1443 (s), 1419 (m), 1366 (s), 1325 (m), 1288 (m), 1235 (w), 1161 (w), 1100 (m), 1046 (w), 1026 (w), 981 (w), 940 (w), 842 (w), 784 (m), 748 (s), 723 (m), 694 (m), 661 (m), 633 (m), 571 (w).

2.5. Preparation of $[Co(L)(dpe)_{0.5}]$ (4)

Complex **4** was obtained by an analogous hydrothermal procedure as that used for synthesis of **1** except that dpe (18.2 mg, 0.1 mmol) was used instead of phen. Dark purple block crystals of **4** were collected by filtration and after washed by water and ethanol several times in 65% yield based on H₂L. *Anal.* Calc. for C₁₈H₁₃N₃O₄Co: C, 54.84; H, 3.32; N, 10.66. Found: C, 54.59; H, 3.48; N, 10.39%. IR (KBr pellet, cm⁻¹): 1623 (s), 1579 (s), 1513 (w), 1431 (w), 1345 (s), 1304 (w), 1284 (w), 1222 (w), 1112 (w), 1088 (w), 1063 (w), 1030 (w), 964 (w), 834 (m), 780 (m), 727 (m), 649 (w), 559 (w).

2.6. Preparation of [Co(L)] (5)

Complex **5** was obtained by an analogous hydrothermal procedure as that used for synthesis of **1** except that no auxiliary ligand

Table 2

Selected bond lengths (Å) and bond angles (°) for complexes 1-5.

1			
Co(1)-O(3) Co(1)-N(2) Co(1)-O(2)#1 O(3)-Co(1)-N(1) O(1)#1-Co(1)-O(3)	2.084(3) 2.155(3) 2.315(3) 119.37(12) 91.73(12)	Co(1)-N(1) Co(1)-O(1)#1 Co(1)-N(12)#2 O(3)-Co(1)-N(2) O(3)-Co(1)-N(12)#2	2.144(3) 2.156(3) 2.115(3) 89.32(12) 90.99(12)
N(1)-Co(1)-N(2) N(1)-Co(1)-N(12)#2 N(2)-Co(1)-N(12)#2	78.21(11) 97.09(11) 174.74(10)	O(1)#1-Co(1)-N(1) O(1)#1-Co(1)-N(2) O(1)#1-Co(1)-N(12)#2	146.85(10) 91.99(12) 93.25(12)
$\begin{array}{c} 2\\ Co(1)-O(5)\\ Co(1)-N(2)\\ Co(1)-O(1)\#1\\ O(5)-Co(1)-N(1)\\ O(5)-Co(1)-N(1)\\ O(2)\#1-Co(1)-O(5)\\ N(1)-Co(1)-N(1)\\ O(2)\#1-Co(1)-N(1)\\ O(1)\#1-Co(1)-N(2)\\ O(1)\#1-Co(1)-N(1)\\ O(1)\#1-Co(1)-O(2)\#1 \end{array}$	2.033(3) 2.070(3) 2.191(3) 85.60(12) 88.55(11) 155.24(11) 170.55(11) 97.18(11) 150.33(11) 100.06(11) 60.44(9)	$\begin{array}{c} Co(1)-N(1)\\ Co(1)-N(11)\\ Co(1)-O(2)\#1\\ O(5)-Co(1)-N(2)\\ O(1)\#1-Co(1)-O(5)\\ N(1)-Co(1)-N(2)\\ O(1)\#1-Co(1)-N(1)\\ N(2)-Co(1)-N(11)\\ O(2)\#1-Co(1)-N(11)\\ O(2)\#1-Co(1)-N(11)\\ O(2)\#1-Co(1)-N(11)\\ \end{array}$	2.254(3) 2.111(3) 2.152(2) 108.36(12) 95.22(11) 76.58(12) 87.88(11) 98.31(11) 96.18(11) 91.24(11)
$\begin{array}{l} \textbf{3} \\ Co(1)-N(1) \\ Co(1)-N(11) \\ Co(1)-O(3)\#2 \\ N(1)-Co(1)-N(2) \\ O(1)\#1-Co(1)-N(1) \\ N(2)-Co(1)-N(11) \\ O(3)\#2-Co(1)-N(2) \\ O(3)\#2-Co(1)-N(11) \end{array}$	2.200(3) 2.077(3) 2.018(3) 75.80(13) 91.31(12) 96.03(13) 123.66(13) 97.33(12)	$\begin{array}{c} Co(1)-N(2)\\ Co(1)-O(1)\#1\\ \\ N(1)-Co(1)-N(11)\\ O(3)\#2-Co(1)-N(1)\\ O(1)\#1-Co(1)-N(2)\\ O(1)\#1-Co(1)-N(11)\\ O(1)\#1-Co(1)-O(3)\#2\\ \end{array}$	2.072(3) 2.089(3) 171.47(12) 89.40(12) 99.78(12) 87.62(13) 135.19(11)
$\begin{array}{c} \textbf{4} \\ Co(1)-O(1) \\ Co(1)-O(3)\#1 \\ O(1)-Co(1)-N(21) \\ O(1)-Co(1)-N(1)\#2 \\ N(1)\#2-Co(1)-N(21) \end{array}$	1.9903(17) 2.0082(17) 111.56(7) 109.11(7) 102.99(8)	$\begin{array}{c} Co(1)-N(21)\\ Co(1)-N(1)\#2\\ O(1)-Co(1)-O(3)\#1\\ O(3)\#1-Co(1)-N(21)\\ O(3)\#1-Co(1)-N(1)\#2 \end{array}$	2.0358(19) 2.048(2) 96.66(7) 129.77(7) 105.76(7)
$\begin{array}{c} \textbf{5} \\ Co(1)-O(1) \\ Co(1)-O(4) \ \#2 \\ Co(1)-N(1) \ \#4 \\ O(1)-Co(1)-O(3) \ \#1 \\ O(1)-Co(1)-O(2) \ \#3 \\ O(3) \ \#1-Co(1)-O(4) \ \#2 \\ O(3) \ \#1-Co(1)-N(1) \ \#4 \\ O(4) \ \#2-Co(1)-N(1) \ \#4 \end{array}$	2.106(5) 1.9650(18) 2.085(6) 89.2(2) 91.6(2) 145.4(2) 87.4(2) 89.0(2)	Co(1)-O(3)#1 Co(1)-O(2)#3 O(1)-Co(1)-O(4)#2 O(1)-Co(1)-N(1)#4 O(2)#3-Co(1)-O(3)#1 O(2)#3-Co(1)-O(4)#2 O(2)#3-Co(1)-N(1)#4	2.015(5) 1.992(5) 85.6(2) 165.1(2) 95.0(2) 119.3(2) 103.2(2)
	$\begin{array}{c} 1 \\ \hline \\ Co(1)-O(3) \\ Co(1)-N(2) \\ Co(1)-N(2) \\ O(3)-Co(1)-N(1) \\ O(3)-Co(1)-N(1) \\ O(1)^{\#}1-Co(1)-O(3) \\ N(1)-Co(1)-N(2) \\ N(1)-Co(1)-N(12)^{\#}2 \\ N(2)-Co(1)-N(12)^{\#}2 \\ 2 \\ Co(1)-O(5) \\ Co(1)-N(2) \\ Co(1)-O(1)^{\#}1 \\ O(5)-Co(1)-N(1) \\ O(5)-Co(1)-N(1) \\ O(5)-Co(1)-N(1) \\ O(5)-Co(1)-N(1) \\ O(2)^{\#}1-Co(1)-O(5) \\ N(1)-Co(1)-N(1) \\ O(2)^{\#}1-Co(1)-N(1) \\ O(2)^{\#}1-Co(1)-N(1) \\ O(1)^{\#}1-Co(1)-N(2) \\ O(1)^{\#}1-Co(1)-N(2) \\ O(1)^{\#}1-Co(1)-N(2) \\ O(1)^{\#}1-Co(1)-N(2) \\ O(1)^{\#}1-Co(1)-N(2) \\ O(1)^{\#}1-Co(1)-N(1) \\ Co(1)-O(3)^{\#}2 \\ N(1)-Co(1)-N(1) \\ O(3)^{\#}2-Co(1)-N(1) \\ O(3)^{\#}2-Co(1)-N(1) \\ O(1)-Co(1)-N(2) \\ O(1)^{\#}2-Co(1)-N(2) \\ O(1)-Co(1)-N(2) \\ O(3)^{\#}1-Co(1)-O(4)^{\#}2 \\ O(3)^{\#}1-Co(1)-N(1)^{\#}4 \\ O(4)^{\#}2-Co(1)-N(1)^{\#}4 \\ O(4)^{\#}2-Co(1)-N(1)^{\#}4 \\ O(4)^{\#}2-Co(1)-N(1)^{\#}4 \\ O(1)-Co(1)-N(1)^{\#}4 \\ O(4)^{\#}2-Co(1)-N(1)^{\#}4 \\ O(1)-Co(1)-N(1)^{\#}4 \\ O(1)-Co(1)-N(1$	1 $Co(1)-O(3)$ 2.084(3) $Co(1)-N(2)$ 2.155(3) $O(3)-Co(1)-N(1)$ 119.37(12) $O(1)H1-Co(1)-N(2)$ 78.21(11) $N(1)-Co(1)-N(12)#2$ 97.09(11) $N(2)-Co(1)-N(12)#2$ 174.74(10)2 $Co(1)-O(5)$ 2.033(3) $Co(1)-O(5)$ 2.033(3) $Co(1)-O(5)$ 2.070(3) $Co(1)-O(5)$ 2.070(3) $Co(1)-O(5)$ 2.070(3) $Co(1)-O(1)+N(1)$ 85.60(12) $O(5)-Co(1)-N(1)$ 170.55(11) $O(2)#1-Co(1)-N(1)$ 97.18(11) $O(1)#1-Co(1)-N(1)$ 170.55(11) $O(1)#1-Co(1)-N(1)$ 100.06(11) $O(1)+1-Co(1)-N(1)$ 100.06(11) $O(1)+1-Co(1)-N(1)$ 100.06(11) $O(1)-N(1)$ 2.077(3) $Co(1)-O(1)-N(1)$ 91.31(12) $N(1)-Co(1)-N(1)$ 91.31(12) $N(1)-Co(1)-N(1)$ 91.31(12) $N(2)-Co(1)-N(1)$ 91.3(12) 4 $Co(1)-O(1)-N(1)$ $Co(1)-O(1)-N(1)#2$ 109.3(17) $Co(1)-O(1)-N(1)#2$ 109.3(17) $O(1)-Co(1)-N(1)#2$ 109.1(7) $N(1)+2-Co(1)-N(1)#2$ 109.5(18) $Co(1)-O(1)+1/2$ 100.5(18) $Co(1)-O(1)+1/2$ 101.5(7) $O(1)-Co(1)-O(2)#3$ 91.6(2) $O(1)+1/2+1$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Symmetry transformations used to generate equivalent atoms:

For **1**, #1 –1 + x, 1 + y, z; #2 2 – x, 2 – y, 1 – z; for **2**, #1 x, 1 + y, z; for **3**, #1 –1 + x, 1 + y, z; #2 x, 1 + y, z; for **4**, #1 x, 1 + y, z; #2 –1/2 + x, 3/2 – y, -1/2 + z; for **5**, #1 1 – x, 1/2 + y, 5/2 – z; #2 1 – x, -y, 2 – z; #3 x, 1/2 – y, -1/2 + z; #4 1 + x, 1/2 – y, 1/2 + z.

was added. Dark purple block crystals of **5** were obtained in 72% yield. *Anal.* Calc. for $C_{12}H_8N_2O_4Co$: C, 47.55; H, 2.66; N, 9.24. Found: C, 47.82; H, 2.92; N, 9.09%. IR (KBr pellet, cm⁻¹): 1632 (s), 1612 (s), 1571 (s), 1546 (m), 1513 (m), 1456 (m), 1435 (m), 1378 (s), 1333 (m), 1284 (m), 1243 (w), 1218 (w), 1108 (m), 1088 (m), 1030 (w), 944 (w), 834 (w), 780 (m).

2.7. X-ray crystallography

The crystallographic data collections for complexes **1** and **3–5** were carried out on a Bruker SMART APEX CCD area-detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. The diffraction data were integrated by using the SAINT program [19], which was also used for the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption correction was applied using the SAINT program [20]. The crystallographic data for **2** were collected on a Rigaku XtaLABmini diffractometer at 293 K with Mo K α radiation



Fig. 1. (a) The coordination environment of Co(II) in **1** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms and lattice water molecules are omitted for clarity. (b) The 1D double chain of **1**.



Scheme 1. Coordination modes of the L^{2–} ligand in complexes 1–5.

 $(\lambda = 0.71075 \text{ Å})$. The structures of **1–5** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [21]. In **1–5**, all hydrogen atoms attached to C atoms were generated geometrically. The hydrogen atoms of free water molecules of O6 in **1** and O7 in **3** could not



Fig. 2. (a) The coordination environment of Co(II) in 2 with the ellipsoids drawn at the 30% probability level. The hydrogen atoms and lattice water molecules are omitted for clarity. (b) 1D chain of 2.

be located and thus were not included in the refinement, while the ones of other water molecules in **1**–**3** and the ones of NH in **2** and **3** were found at reasonable positions in the difference Fourier maps and fixed there. The details of crystal parameters, data collection, and refinements for the complexes are summarized in Table 1; selected bond lengths and angles are listed in Table 2. The hydrogen bonding data for **1**, **2**, and **4** are listed in Table S1.

3. Results and discussion

3.1. Crystal structure description of [Co(L)(phen)]·2H₂O (**1**)

The single-crystal X-ray structure analysis revealed that complex 1 is composed of one-dimensional (1D) double-chains based on Co(II), L^{2-} and phen ligands and free water molecules. There are one Co(II), one L²⁻ ligand, one phen molecule, and two lattice water molecules in the asymmetric unit of complex 1. As shown in Fig. 1a, each Co(II) is six-coordinated by one nitrogen atom from imidazolyl group, two nitrogen ones from phen molecule, and three carboxylate oxygen atoms from two different L²⁻ ligands to furnish a distorted octahedral coordination geometry. The carboxylate groups in the L²⁻ ligand exhibit μ_1 - η^1 : η^1 -chelating and μ_1 - η^1 : η^0 -monodentate mode, respectively (Scheme 1). Each L²⁻ ligand connects three Co(II) atoms to form a 1D polymeric ladder structure with the nearest intrachain Co...Co distance of 10.100(4)Å (Fig. 1b). As depicted in Fig. S1a, the adjacent chains form a twodimensional (2D) network through the strong offset π - π stacking interactions with the centroid-centroid distance between the central benzene rings of 3.592(3) Å. The 2D networks are further linked together by weak C-H···O interactions to give a threedimensional (3D) supramolecular framework (Fig. S1b). The hydrogen bonding data are summarized in Table S1.

3.2. Crystal structure description of $[Co(L)(pybim)(H_2O)] \cdot 2H_2O(2)$

Complex **2** crystallizes in monoclinic crystal system with $P2_1/c$ space group (Table 1). The asymmetric unit of **2** consists of one Co(II), one L^{2-} ligand, one pybim, one coordinated and two lattice water molecules. Each Co(II) is six-coordinated with distorted octahedral coordination geometry by two carboxylate oxygen atoms from one L^{2–}, one oxygen atom from the coordinated water molecule, one nitrogen atom from imidazolyl group of L^{2-} , and two nitrogen atoms from the pybim molecule (Fig. 2a). It is noteworthy that only one of two carboxylate groups of L^{2-} coordinates with Co(II) in μ_2 - η^1 : η^1 -chelating coordination mode, while the other one is free of coordination, which is different from those in 1. Thus the L^{2–} ligand in **2** just acts as a μ_2 -connector, linking Co(II) atoms to form a 1D chain (Fig. 2b). In addition to the coordination interactions, there are hydrogen bonds (Table S1) and π - π stacking interactions in 2 which further link the ID chains into a 2D network (Fig. S2a). More interestingly, the coordinated pybim molecules are arranged at the same side of 1D chain and there are π - π interactions with centroid-centroid distance 3.808(6) Å between the pybim molecules from two adjacent chains (Fig. S2b). Finally, a sandwich-like 2D double-deck network is formed as illustrated in Fig. S2c.

3.3. Crystal structure description of $[Co(L)(pybim)] \cdot H_2O(3)$

Complex **3** was obtained by a similar procedure used for preparation of **2**, except that the ratio of metal-to-ligand was changed. Single-crystal X-ray diffraction analysis reveals that complex **3** is in triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit of **3** contains one Co(II), one L^{2–} ligand, one pybim molecule, and one lattice water molecule. Each Co(II) is five-coordinated with



Fig. 3. (a) The coordination environment of Co(II) in **3** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms and lattice water molecules are omitted for clarity. (b) 2D network of **3**. (c) Schematic representation of 2D network with (6^3) topology: green, L^{2-} ligand; red, Co(II). (Color online.)

distorted trigonal bipyramidal coordination geometry by two carboxylate oxygen atoms from two different L²⁻ ligands, two nitrogen ones from coordinated pybim molecule, and one nitrogen from the imidazolyl group of L²⁻ (Fig. 3a). The equatorial plane is defined by two carboxylate oxygen atoms and one nitrogen atom from the pybim molecule, while the other two nitrogen atoms occupy the axial positions. Both carboxylate groups of L²⁻ in **3** adopt $\mu_1-\eta^1:\eta^0$ -monodentate coordination mode (Scheme 1). In **3** each L²⁻ ligand bridges three different Co(II) atoms and in turn each Co(II) is coordinated by three different L²⁻ ligands. Such kind of connections extends infinitely to form a 2D network (Fig. 3b). Both of L²⁻ and Co(II) in **3** can be regarded as 3-connectors, thus the network of **3** can be simplified into a uninodal 3-connected 2D network with Point (Schläfli) symbol of (6³) (Fig. 3c), calculated by TOPOS [22].

3.4. Crystal structure description of $[Co(L)(dpe)_{0.5}]$ (4)

When 1.2-di(pyridin-4-yl)ethylene (dpe) was introduced into the reaction system as auxiliary ligand, complex 4 was obtained. Crystallographic analysis revealed that complex 4 crystallizes in monoclinic system with $P2_1/n$ space group. There are one Co(II), one L²⁻ ligand, and half molecule of dpe in the asymmetric unit of 4. As shown in Fig. 4a, each Co(II) is four-coordinated by one imidazolyl nitrogen atom of L²⁻, one pyridyl nitrogen atom of dpe, two carboxylate oxygen atoms from two different L^{2-} ligands to furnish distorted tetrahedral coordination geometry. Both carboxylate groups of L²⁻ in **4** adopt μ_1 - η^1 : η^0 -monodentate coordination mode (Scheme 1). Thus, in ${\bf 4}$ each L^{2-} ligand links three different Co(II) atoms as a 3-connector and in turn each Co(II) is coordinated by three different L²⁻ ligands. Such kind of connections proceeds infinitely to form 2D network, which is pillared by μ_2 -bridge dpe to form a new 2D laver (Fig. 4b). The topological analysis was carried out to get insight of the structure of 4. As mentioned above, each L^{2-} ligand is neighbored by three Co(II) ions which can be viewed as a 3-connector, each dpe ligand could be considered as a 2-connector, while each Co(II) can be regarded as a 4-connected node. Thus, the resulting structure of 4 is a (3,4)connected binodal 2D net with Point (Schläfli) symbol of (6³)(6⁶) (Fig. 4c). If weak C-H···O interactions is considered, a 3D supramolecular framework is formed through interesting $2D + 2D \rightarrow 3D$ parallel interpenetration (Fig. 4d).

3.5. Crystal structure description of [Co(L)] (5)

Complex 5 is in monoclinic crystal system with $P2_1/c$ space group. As shown in Fig. 5a, the asymmetric unit of complex 5 contains one Co(II) and one L²⁻ ligand. Each Co(II) is five-coordinated by four carboxylate oxygen atoms from four different L^{2–} ligands and one imidazolyl nitrogen atom from L²⁻ ligand to furnish distorted trigonal bipyramidal coordination geometry. Both of two carboxylate groups of L²⁻ ligand in **5** adopt μ_2 - η^1 : η^1 -bridging coordination mode (Scheme 1). Thus in complex 5 each L^{2-} ligand bridges five different Co(II) atoms and each Co(II) is coordinated by five different L²⁻ ligands. Such kind of linkage infinitely expands to give a 3D architecture (Fig. 5c), where 2D layer structure can be isolated if the coordination of imidazolyl group is ignored (Fig. 5b). Within the 2D structure there are $[Co_2(OCO)_2]$ subunits and 1D Co(II)-carboxylate chains formed through the connections of carboxylate groups and Co(II) atoms with the nearest Co---Co distance of 4.081(3) Å. In 5, both L^{2-} ligands and metal ions act as 5-connected nodes, and thus 5 can be described as a (5,5)-connected binodal 3D net with the Point (Schläfli) symbol of $(4^5)(6^5)$ (Fig. 5d).

3.6. Preparation and structural comparison of complexes 1-5

Complexes **1–5** were readily prepared by reactions of H_2L ligand with cobalt(II) salt in the presence or absence of the N-donor auxiliary ligand under hydrothermal conditions and characterized by single-crystal X-ray structure determination, elemental analysis, and IR as described above. The pure phase of the synthesized **1–5** was confirmed by powder X-ray diffraction (PXRD) measurements. As shown in Fig. S3, each PXRD pattern of the as-synthesized sample is consistent with the simulated one.

The results of structural analyses indicate that complexes **1–5** have diverse architectures from 1D chain to 3D frameworks with different topologies. The structural diversity of **1–5** is closely related with auxiliary ligands introduced into the reaction system. Complexes **1**, **2** and **4** with different auxiliary ligands exhibit different structures. Complex **5** is structurally different from the other



Fig. 4. (a) The coordination environment of Co(II) in **4** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) 2D pillared-network of **4**. (c) Schematic representation of the binodal (3,4)-connected 2D net of **4** with $(6^3)(6^6)$ topology: the big spheres, Co(II); the small spheres, L²⁻ ligand. (d) The 3D framework of **4** constructed by hydrogen bonding interactions.

four in the absence of any auxiliary ligand. Moreover, complexes **2** and **3** display different architectures with the same auxiliary ligand, which may be ascribed to the different metal-to-ligand ratio. In addition, it is noteworthy that the metal centers show different coordination number and geometry in these complexes, namely, six-coordinated with distorted octahedral coordination geometry in **1** and **2**; five-coordinated with distorted trigonal bipyramidal geometry in **3** and **5**, and four-coordinated with tetrahedral coordination geometry in **4**. The results imply that the auxiliary ligand as well as the metal-to-ligand ratio has great impact on the structure of the resultant complexes.

3.7. Thermal stability of complexes 1-5

Complexes **1–5** were subjected to thermogravimetric analysis (TGA) to ascertain their thermal stability, and the TGA curves of **1–5** are shown in Fig. S4. In the TGA curve of complex **1** there is a weight loss of 7.18% within the temperature range of 96–128 °C, corresponding to the release of two lattice water molecules

(Calc. 6.93%), and from 366 to 553 °C, there is a steep weight loss which could be assigned to the decomposition of the framework. The total weight loss in the temperature range 30–660 °C is 85.8%, which is in agreement with the weight loss calculated for the loss of ligands and water molecules leading to the formation of CoO as final residuals above 560 °C (85.6%). For **2**, a weight loss of 9.52% in the temperature range of 92–166 °C corresponds to the liberation of coordinated and lattice water molecules (Calc. 9.78%). Then the decomposition of the framework started at 353 °C. For **3**, a weight loss of 3.76% within the temperature range of 136–210 °C is assigned to the release of lattice water molecules (Calc. 3.48%), and the decomposition of the residue can be observed at 346 °C. No obvious weight loss could be observed before the decomposition of the frameworks occurred at about 400 °C for **4** and **5**.

3.8. Magnetic property of complex 5

The Co(II) atoms are bridged by carboxylate groups to form 1D Co(II)-carboxylate chains in **5**, which may mediate magnetic inter-



Fig. 5. (a) The coordination environment of Co(II) in **5** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) The 2D network in **5**. (c) The 3D structure of **5** with different 2D layers shown in different color. (d) The schematic representations of the binodal (5,5)-connected 3D net of **5** with $(4^5)(6^5)$ topology: green, L^{2-} ligand; red, Co(II). (Color online.)



Fig. 6. Temperature dependences of magnetic susceptibility of χ_M and $\chi_M T$ for 5. The solid line represents the fitted curve.

actions while in **1–4**, the Co(II) atoms are linked by L ligands and no magnetic interactions can be expected [23]. The temperature dependence of magnetic susceptibility of **5** was investigated from 300 to 1.8 K with an applied magnetic field of 2000 Oe. The magnetic behaviors of **5** in the forms of $\chi_{\rm M}$ and $\chi_{\rm M}T$ versus *T* are depicted in Fig. 6. The $\chi_{\rm M}^{-1}$ value (above 50 K) obeys the Curie– Weiss law well with a Weiss constant (θ) of –10.09 K and a Curie constant (*C*) of 2.87 emu K mol⁻¹ (Fig. S5).

The negative value of θ and the shape of the $\chi_{M}T$ versus *T* curve suggests there may exist antiferromagnetic interactions between

the neighboring Co(II) centers [24]. In order to estimate the strength of the magnetic interactions in **5**, the following was used [25]:

$$\chi_{\rm M}T = A\exp(-E_1/kT) + B\exp(-E_2/kT) \tag{1}$$

Here, A + B equals the curie constant (*C*), and E_1 , E_2 represent the 'activation energies' corresponding to the spin–orbit coupling and the antiferromagnetic exchange interaction, respectively. The obtained values of A + B = 2.89 emu K mol⁻¹ and $E_1/k = 33.94$ K agree with those given in a previous report [25]. The value of $-E_2/k = -0.94$ K, corresponding to J = -1.88 K, further proved that the antiferromagnetic interactions exist between neighboring Co(II) atoms in **5** [26].

4. Conclusion

Five new Co(II) coordination polymers have been synthesized through the hydrothermal reactions. The structures of the resultant complexes varied from 1D chain to 3D framework with different topologies. The structural diversity of the complexes is achieved by the presence of auxiliary ligands and the alteration of metal-to-ligand ratio.

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Appendix A. Supplementary data

CCDC 877980–877984 contain the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.06.020.

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