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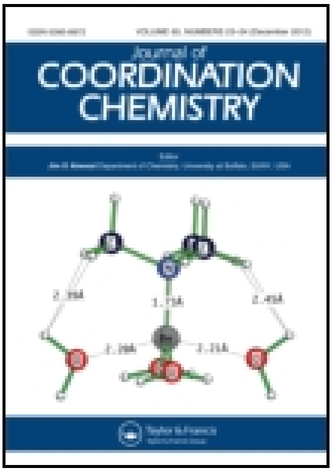

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Syntheses, structures, and properties of Cd^{II} and Co^{II} complexes with 5-(pyridin-4-yl)isophthalate

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Syntheses, structures, and properties of Cd^{II} and Co^{II} complexes with 5-(pyridin-4-yl)isophthalate

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A N-donor containing carboxylic ligand, 5-(pyridin-4-yl)isophthalic acid (H_2L), was applied to construct two new coordination polymers $[Cd(L)(DMF)]_n$ (**1**, DMF = *N*,*N*-dimethylformamide) and $\{[Co(L)(H_2O)_2]\cdot 0.5CH_3OH\cdot 1.5H_2O\}_n$ (**2**) under different conditions. The complexes were characterized by IR, elemental, and thermogravimetric analyses, powder and single crystal X-ray diffraction. In **1** each L^{2-} links four Cd^{II} to form a 3-D framework, while in **2** each L^{2-} connects three metals to form a 2-D layer structure, which is further connected together by hydrogen bonds to form a 3-D architecture. The thermal stability of the complexes and the photoluminescence of **1** were investigated.

Keywords: Cd^{II} complex; Co^{II} complex; Crystal structure; Photoluminescence

1. Introduction

Coordination polymers or metal–organic frameworks (MOFs) have received attention for intriguing architectures and topologies, and potential applications in gas storage/separation, catalysis, magnetism, photoluminescence, etc. [1, 2]. Most studies have focused on the design and construction of MOFs and attempts to develop structure–property relationships [2, 3]. However, obtaining desired architectures of MOFs constructed by organic ligands and metal salts is still a long-term challenge to chemists; assembly is complicated and minor changes in the chemical environment, reaction temperature, pH, solvent, counterions, etc., can have subtle but important influence on the formation and structure of the complexes [4–7]. Carefully selected organic ligands have a decisive role in the construction of MOFs.

Carboxylates are of special interest because of their variable coordination modes such as terminal monodentate, chelating, bridging bidentate, bridging tridentate [8], and also

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because of their ability to act as hydrogen bond acceptors and donors to assemble supramolecular structures [9]. N-donor ligands such as 1,3,5-tris(1-imidazolyl)benzene, 3,4′-bipyridine and 1,3-bis(4-pyridyl)propane are widely used for constructing coordination complexes [10–12]. The application of these N-donor ligands in the MOFs synthesis often results in structures with unique motifs and interesting properties [11–13].

Based on the above arguments, in this work we employed a carboxylate- and pyridyl-containing ligand, 5-(pyridin-4-yl)isophthalic acid (H_2L), which has remarkable features as follows: (a) it is a rigid ligand which may favor the construction of coordination architectures with high thermal stability; (b) the carboxylate can have different coordination modes to satisfy the coordination geometric requirement of metal centers; and (c) the ligand can offer additional hydrogen bonding to consolidate the structure. Only a small number of MOFs based on this ligand has been reported hitherto, thus it is necessary to enrich the variety of 5-(pyridin-4-yl)isophthalate-based MOFs [14]. Herein we report the syntheses and crystal structures of two new complexes based on L^{2-}, $[Cd(L)(DMF)]_n$ (**1**, DMF = *N*,*N*-dimethylformamide) and $\{[Co(L)(H_2O)_2] \cdot 0.5CH_3OH \cdot 1.5H_2O\}_n$ (**2**). They are also characterized by IR, elemental, and thermogravimetric analyses (TGA), powder and single crystal X-ray diffractions, and the luminescence of **1** has been studied.

2. Experimental

2.1. *Materials and methods*

All commercially available chemicals and solvents are of reagent grade and used as received. H_2L was synthesized according to the literature [14a]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. TGA were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10^\circ C\,min^{-1}$. FT-IR spectra were recorded from 400 to $4000\,cm^{-1}$ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature. Luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions.

2.2. *Syntheses of complexes*

2.2.1. $[Cd(L)(DMF)]_n$ (1). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol), H_2L (12.2 mg, 0.05 mmol), concentrated hydrochloric acid (50 µL), and DMF (3 mL) was treated by ultrasonic vibration. The mixture was then sealed into a Teflon-lined stainless steel container and heated at 120°C for 3 days. After cooling to room temperature, colorless block crystals of **1** were obtained in 54% yield. Anal. Calcd for

$C_{16}H_{14}CdN_2O_5$ (%): C, 45.04; H, 3.31; N, 6.57. Found (%): C, 44.99; H, 3.29; N, 6.54. IR (KBr pellet, cm^{-1}): 3424 (s), 1658 (s), 1616 (s), 1571 (s), 1442 (m), 1416 (m), 1358 (s), 1292 (w), 1217 (w), 1099 (w), 777 (w), 729 (m), 644 (w), 506 (w).

2.2.2. $\{[Co(L)(H_2O)_2]\cdot 0.5CH_3OH\cdot 1.5H_2O\}_n$ (2). Compound **2** was prepared by the layering method. A buffer layer of a $CH_3OH:H_2O$ (1 : 1) solution (8 mL) was carefully layered over a solution of H_2L (24.3 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) in H_2O (3 mL). Then a solution of $Co(NO_3)_2\cdot 6H_2O$ (29.2 mg, 0.1 mmol) in CH_3OH (3 mL) was layered over the buffer layer. Block reddish-purple crystals of **2** were obtained after 2 months in 42% yield. Anal. Calcd for $C_{13.50}H_{16}CoNO_8$ (%): C, 42.76; H, 4.26; N, 3.69. Found (%): C, 43.12; H, 4.17; N, 3.72. IR (KBr pellet, cm^{-1}): 3416 (s), 1614 (s), 1558 (s), 1508 (m), 1446 (s), 1374 (s), 1235 (w), 1074 (w), 1024 (w), 777 (m), 734 (m), 647 (m).

2.3. *X-ray structure determination*

Structural data for **1** were collected on a Bruker Smart Apex CCD with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and refined with full-matrix least-squares using the SHELXS-97 and SHELXL-97 programs [15]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of ligands were generated geometrically. For C102 and C103 in **1**, the locations of difference Fourier peaks suggested disorder in which two orientations of the methyl were rotated by 60° relative to each other. The single X-ray diffraction measurements for **2** were made on a Rigaku Rapid II imaging plate area detector with Mo-Kα radiation (0.71075 Å) using MicroMax-007HF microfocus rotating anode X-ray generator and VariMax-Mo optics at 200 K. The structure of **2** was solved by direct methods with *SIR92* and expanded using Fourier techniques by *DIRFID-99* [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water with O5, O6, and O8 were located directly; hydrogen atoms of water and methanol with O7 and O21 were not found, while all the other hydrogen atoms were generated geometrically and refined isotropically using the riding model. All calculations for **2** were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97 [17]. The details of the crystal parameters, data collection, and refinement for the complexes are summarized in table 1 and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the crystal structure of 1*

The asymmetric unit of **1** consists of one Cd^{II}, one L^{2-}, and one coordinated DMF. As depicted in figure 1(a), Cd1 is seven-coordinate with a pentagonal bipyramid coordination geometry by one nitrogen (N11A) and one oxygen (O1C) atoms from two different L^{2-}, two pairs of oxygen atoms (O1B, O2B and O3, O4) from another two distinct L^{2-}, respectively, and one oxygen atom (O101) from coordinated DMF. Each

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{16}H_{14}CdN_2O_5$	$C_{13.50}H_{16}CoNO_8$
Formula weight	426.69	379.20
Temperature (K)	293(2)	200
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	9.238(5)	8.967(4)
b	18.225(9)	10.165(4)
c	9.743(5)	10.213(5)
α	90.00	115.635(15)
β	104.940(9)	90.746(18)
γ	90.00	110.684(18)
Volume (Å^3), Z	1584.9(14), 4	769.8(6), 2
Calculated density (g cm^{-3})	1.788	1.636
Absorption coefficient (mm^{-1})	1.407	1.157
F(000)	848	390
Reflections collected	8466	5805
Independent reflection	3264	2698
Goodness-of-fit on F^2	1.199	1.230
Final R indices [$I > 2\sigma(I)$]^{a,b}	$R_1 = 0.0517$, $wR_2 = 0.1085$	$R_1 = 0.0698$, $wR_2 = 0.1884$
R indices (all data)	$R_1 = 0.0607$, $wR_2 = 0.1117$	$R_1 = 0.0712$, $wR_2 = 0.1889$

[a] $R_1 = \Sigma F_o - F_c / \Sigma F_o$.

[b] $wR_2 = \Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o)^{21/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.[a]

1			
Cd1–N11A	2.299(4)	Cd1–O4	2.302(4)
Cd1–O101	2.375(5)	Cd1–O2B	2.382(4)
Cd1–O1C	2.396(4)	Cd1–O1B	2.494(4)
Cd1–O3	2.531(4)		
N11A–Cd1–O4	135.12(14)	N11A–Cd1–O101	90.95(18)
O4–Cd1–O101	86.30(16)	N11A–Cd1–O2B	85.85(14)
O4–Cd1–O2B	137.08(13)	O101–Cd1–O2B	79.76(16)
N11A–Cd1–O1C	97.22(15)	O4–Cd1–O1C	90.95(14)
O101–Cd1–O1C	170.75(17)	O2B–Cd1–O1C	96.43(13)
N11A–Cd1–O1B	137.13(13)	O4–Cd1–O1B	87.69(12)
O101–Cd1–O1B	94.96(17)	O2B–Cd1–O1B	53.85(13)
O1C–Cd1–O1B	76.09(13)	N11A–Cd1–O3	81.29(14)
O4–Cd1–O3	53.83(13)	O101–Cd1–O3	85.55(17)
O2B–Cd1–O3	160.29(15)	O1C–Cd1–O3	99.94(14)
O1B–Cd1–O3	141.46(12)		
2			
Co1–N11A	2.099(6)	Co1–O5	2.093(6)
Co1–O3B	2.058(5)	Co1–O6	2.109(6)
Co1–O1	2.186(5)	Co1–O2	2.221(5)
O3B–Co1–O5	86.5(2)	O3B–Co1–N11A	115.2(2)
O5–Co1–N11A	96.2(2)	O3B–Co1–O6	90.1(2)
O5–Co1–O6	174.3(2)	N11A–Co1–O6	89.3(2)
O3B–Co1–O1	96.0(2)	O5–Co1–O1	91.5(2)
N11A–Co1–O1	148.1(2)	O6–Co1–O1	84.3(2)
O3B–Co1–O2	155.27(19)	O5–Co1–O2	89.0(2)
N11A–Co1–O2	89.5(2)	O6–Co1–O2	92.2(2)
O1–Co1–O2	59.75(19)		

[a] Symmetry transformations used to generate equivalent atoms: A: $x-1$, y, $z-1$; B: $-x$, $y-1/2$, $-z+3/2$; C: x, $-y+1/2$, $z-1/2$ for **1**; A: $x-1$, $y-1$, $z-1$; B: x, y, $z-1$ for **2**.

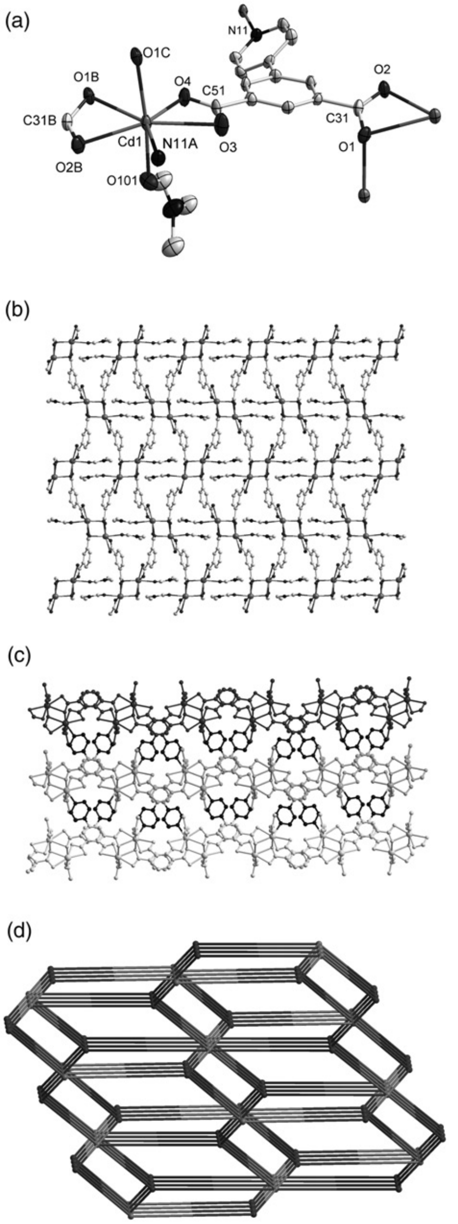
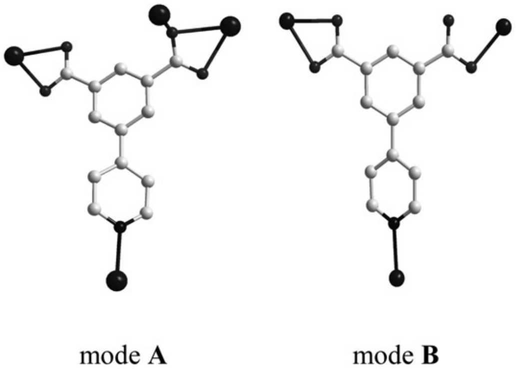


Figure 1. (a) Coordination environment of Cd1 in **1** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. (b) The 2-D layer structure of **1** formed by neglecting the pyridines of L^{2-}. (c) The 3-D framework of **1**. (d) Schematic representation of the (3,6)-connected 2-nodal 3-D network of **1** with $(4.6^2)_2(4^2.6^{10}.8^3)$ topology.

L^{2-} in **1** is a μ_4-bridge to link four Cd^{II} (mode **A**, scheme 1): the pyridine nitrogen links the first Cd^{II}, one μ_2-η^2:η^1 carboxylate connects two Cd^{II} and the other μ_1-η^1:η^1 carboxylate ligates the fourth one. Two adjacent Cd^{II} are connected by two μ_2-η^2:η^1 carboxylates to form a dimeric unit with a Cd$\cdots$Cd separation of 3.85 Å. If the



Scheme 1. Coordination modes of L^{2-} in **1** and **2**.

coordination of pyridine of L^{2-} is neglected, the Cd^{II} centers are bridged by carboxylates of L^{2-} to give a 2-D network in the *bc* plane, as illustrated in figure 1(b). Then the layers are further linked by the pyridine groups to generate a 3-D framework (figure 1c).

To further understand the structure of **1**, topological analysis by reducing multidimensional structure to simple node-and-linker net was performed. Based on the simplification principle [18], each dimeric unit connects six L^{2-}, which can be viewed as a six-connector. Meanwhile, each L^{2-} can be regarded as a three-connected node since it links three dimeric Cd^{II} units. Hence, the overall structure of **1** is a (3,6)-connected 2-nodal 3-D net with stoichiometry $(3\text{–c})_2(6\text{–c})$, as shown in figure 1(d). Topology analysis by *TOPOS* suggests that the Point (Schläfli) symbol of the net is $(4.6^2)_2(4^2.6^{10}.8^3)$ [19].

3.2. *Description of the crystal structure of 2*

Single crystal X-ray diffraction analysis revealed that **2** crystallizes in the triclinic $P\bar{1}$ space group. In the asymmetric unit of **2**, there are one Co^{II}, one L^{2-}, two coordinated water molecules, 0.5 free methanols, and 1.5 free water molecules. As depicted in figure 2(a), each Co1 is six-coordinate with distorted octahedral coordination geometry by one oxygen (O3B) and one nitrogen (N11A) atoms from two distinct L^{2-}, two oxygen atoms (O1, O2) from another L^{2-} forming the equatorial plane, and two water molecules (O5, O6) at an apical position. L^{2-} in **2** adopts the coordination mode **B** (scheme 1) as a μ_3-bridge linking three Co^{II} through the pyridine nitrogen, one μ_1-$\eta^1:\eta^0$ carboxylate and a μ_1-$\eta^1:\eta^1$ one. Therefore, Co^{II} are connected by L^{2-} to form a 2-D network with large meshes filled with free water and methanol (figure 2b). The layers are linked by hydrogen bonds to generate a 3-D structure (figure 2c). The hydrogen bonding data are summarized in table S1.

3.3. *Comparison of the structures*

Complexes **1** and **2** have 3-D and 2-D framework structures with different topologies (vide supra), which can be ascribed to the different coordination numbers and geometries of Cd^{II} and Co^{II} as well as the different coordination modes of the ligand (scheme 1). Previously reported metal complexes with phthalate or isophthalate

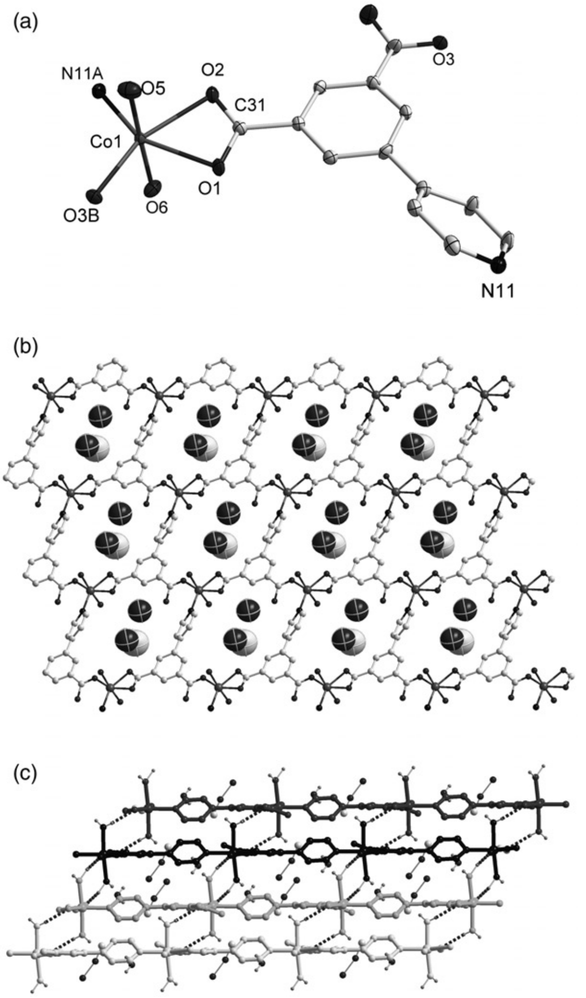


Figure 2. (a) Coordination environment of Co^{II} in **2** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms, free water, and methanol are omitted for clarity. (b) The 2-D layer structure of **2** with water molecules and methanols encapsulated inside large meshes. Hydrogen atoms are omitted for clarity. (c) The 3-D structure of **2** formed by hydrogen bonds, indicated by dashed lines.

derivatives also show diverse structures and topologies [20]. The results of present and previous studies [8, 9, 20] imply that the multicarboxylate ligands are powerful and important in the construction of MOFs.

3.4. *PXRD and thermal stabilities*

The phase purity of bulk products of the complexes was further confirmed by PXRD, and each PXRD pattern of the as-synthesized sample is consistent with the simulated one, as illustrated in figure S1.

TGA were carried out for **1** and **2** and the results of the TGA are shown in figure S2. Complex **1** shows a weight loss of 17.41% (Calcd 17.13%) before 285°C, which

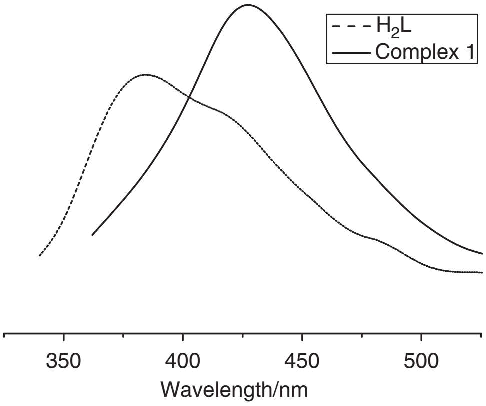


Figure 3. Emission spectra of H_2L and **1** in the solid state at room temperature.

corresponds to release of coordinated DMF; the residue is stable up to *ca* 380°C. Complex **2** shows a weight loss of 19.21% (Calcd 20.83%) before 335°C, which corresponds to the release of methanol, free and coordinated water.

3.5. *Photoluminescence property of 1*

Inorganic–organic hybrid coordination polymers with d^{10} metal centers have been investigated for fluorescence [21]. Fluorescence emission spectra of H_2L and **1** were measured in the solid state at room temperature (figure 3). Upon excitation at 350 nm, free H_2L exhibits maximum emission at 384 nm and **1** shows similar emission at 427 nm. Thus, the emission band of **1** should be ascribed to intraligand π–π^* transition [21]. The observed red shift of the emission maximum between **1** and H_2L originates from coordination interactions between the metal and ligand [22].

4. Conclusion

Two new coordination complexes with distinct architectures based on H_2L, $[Cd(L)(DMF)]_n$ (**1**), and $\{[Co(L)(H_2O)_2] \cdot 0.5CH_3OH \cdot 1.5H_2O\}_n$ (**2**), have been constructed and structurally characterized. Photoluminescence of **1** is investigated. The results suggest that it is a useful strategy to employ carboxylate- and pyridyl-containing ligands to design and synthesize MOFs with intriguing architecture and properties.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-894153 (**1**) and 894154 (**2**). Copies of the data can be obtained at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1 223 336 033; Email: deposit@ccdc.cam.ac.uk).

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