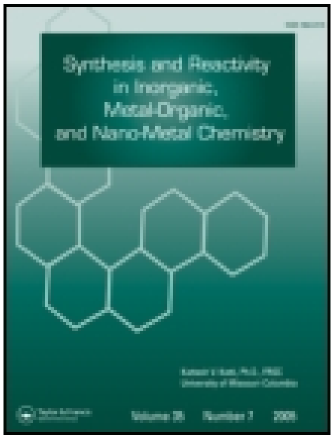
This article was downloaded by: [Boston University]
On: 07 October 2014, At: 20:03
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Two Novel Supramolecular Complexes Built by 2-propyl or 2-p-methoxyphenyl Imidazole Dicarboxylate Ligands

Chengjie Wang [a] , Zhifang Xiong [a] , Tao Wang [a] & Gang Li [a]
[a] Department of Chemistry , Zhengzhou University , Zhengzhou , Henan , P. R. China

Published online: 28 Dec 2012.

To cite this article: Chengjie Wang , Zhifang Xiong , Tao Wang & Gang Li (2013) Two Novel Supramolecular Complexes Built by 2-propyl or 2-p-methoxyphenyl Imidazole Dicarboxylate Ligands, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:2, 203-210, DOI: 10.1080/15533174.2012.740714

To link to this article: http://dx.doi.org/10.1080/15533174.2012.740714

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:203–210, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.740714

Two Novel Supramolecular Complexes Built by 2-propyl or 2-p-methoxyphenyl Imidazole Dicarboxylate Ligands

Chengjie Wang, Zhifang Xiong, Tao Wang, and Gang Li
Department of Chemistry, Zhengzhou University, Zhengzhou, Henan, P. R. China

Two complexes, [Cu(H_2PIDC)$_2$(H_2O)] (H_3PIDC = 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid) (1) and [Co(H_2MOPhIDC)$_2$ (H_2O)$_2$] (H_3MOPhIDC = 2-*p*-methoxyphenyl-1*H*-imidazole-4,5-dicarboxylic acid) (2), have been hydro(solvo)thermally synthesized and characterized by IR spectroscopy, elemental analysis, PXRD, and single-crystal X-ray diffraction. Both two complexes show three-dimensional supramolecular structures supported by intermolecular H-bonds. The thermal properties of the two complexes have been investigated as well.

Keywords Co(II), Cu(II), imidazole dicarboxylate, supramolecular complex

INTRODUCTION

In coordination chemistry field, synthesis and design of novel coordination compounds have attracted much interest not only owing to their interesting structural multiformity but also due to their potential applications.[1–8] Among them, the interactions among the molecules including weak intra- and intermolecular H-bonds, π-π stacking effects, and van der Waals interactions play a vital role in the construction of supramolecular structures. In this context, the derivatives of 4,5-imidazoledicarboxylic acid (H_3IDC) have been well studied because of their versatile coordination modes and potential hydrogen-bonding donors and acceptors.[9–24] In contrast to the well-studied ligand H_3IDC, complexes comprising 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIDC) or 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3EIDC) are still limited, especially of 2-proyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3PIDC). Indeed, to the best of our knowledge, only two examples of 2D coordination compounds reported by Wang et al.[25] and Li et al.[26] and one example of 0D complex gave by He et al.[27] bearing H_3PIDC ligands. Moreover, complexes bearing 2-(*p*-methoxyphenyl)-1*H*-imidazole-4,5-dicarboxylate (H_3MOPhIDC) have never been studied. These findings prompted us to prepare more complexes containing H_3PIDC or H_3MOPhIDC. Herein, we report the syntheses and structural determinations of two novel complexes, [Cu(H_2PIDC)$_2$(H_2O)] (**1**), and [Co(H_2MOPhIDC)$_2$(H_2O)$_2$] (**2**) (Scheme 1), and determine their powder X-ray diffraction (PXRD) and thermal behaviors.

EXPERIMENTAL

General Details

All chemicals were of reagent-grade quality obtained from commercial sources and used without further purification. The organic ligands H_3PIDC and H_3MOPhIDC were prepared according to the literature procedures.[28,29]

The C, H, and N analyses were carried out on a FLASH EA 1112 analyzer (USA). IR spectra were recorded on a BRUKER TENSOR 27 spectrophotometer (Germany) as KBr pellets in the 400–4000 cm^{-1} region. TG-DSC measurements were performed by heating the sample from 20 to 700°C at a rate of 10°C·min^{-1} in air on a Netzsch STA 409 PC differential thermal analyzer (Germany). The PXRD measurements were characterized on a RIGAKU D/MAX 2200 VPC diffractometer (Japan).

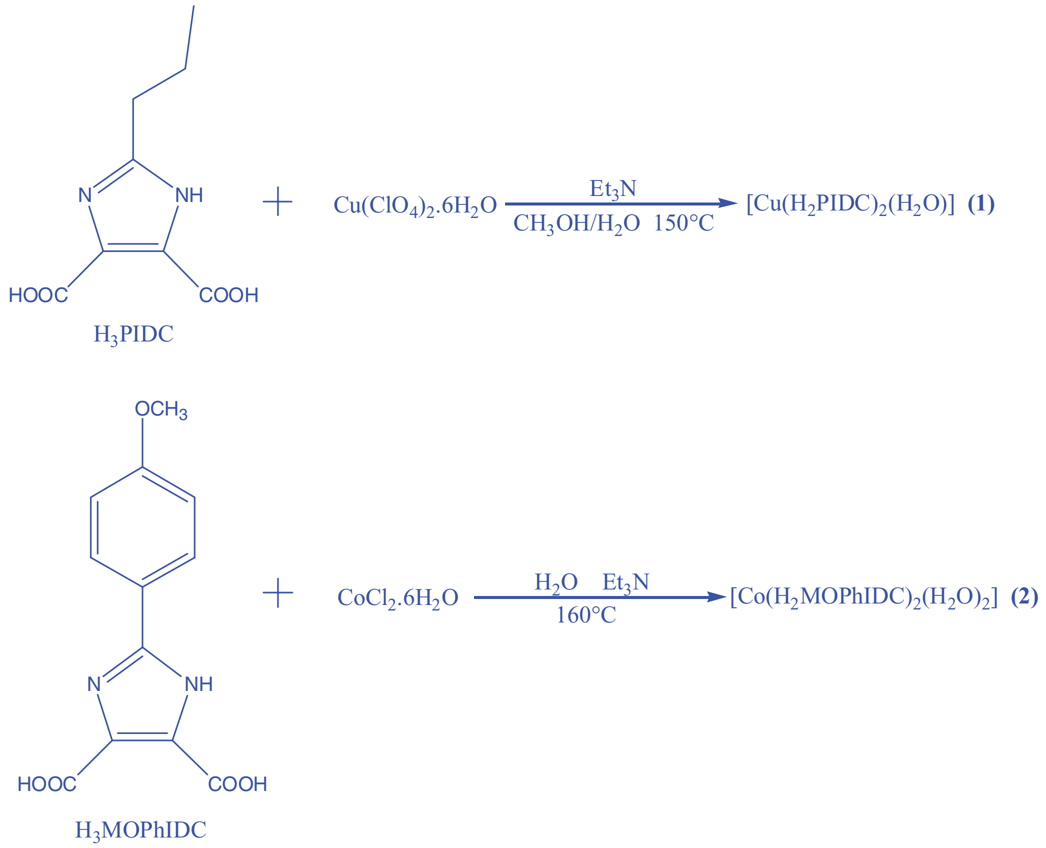
Preparation of [Cu(H_2PIDC)$_2$(H_2O)] (1)

A mixture of H_3PIDC (19.7 mg, 0.1 mmol), Cu(ClO_4)$_2$·6H_2O (74.2 mg, 0.2 mmol), CH_3OH/H_2O (3/4, 7 mL), and Et_3N (0.056 mL, 0.4 mmol) was sealed in a 25 mL Telfon-lined bomb and heated at 150°C for 72 h. The reaction mixture was then allowed to cool to room temperature, thus, blue solution was got. Then the blue resulting solution was put aside at room temperature. Good quality blue crystals of **1** were collected after one week. Crystals of **1** are stable in the air. Yield: 58% (based on Cu). Anal. Calcd. for $C_{16}H_{18}CuN_4O_9$ (%): C, 40.51; H, 3.80; N,11.81; O, 30.38. Found (%): C, 40.82; H, 3.58; N, 11.56; O, 30.98. IR (cm^{-1}, KBr): 3461 m, 3206 m, 2785 w, 1717 s, 1601 s, 1587 s, 1496 s, 1453 s, 1384 m, 1277 m, 1116 m, 1060 m, 993 w, 858 m, 772 m, 742 w, 527 w, 474 w.

Received 2 November 2011; accepted 13 October 2012.

The authors gratefully acknowledge the financial support by the National Natural Science Foundation of China (21071127, and 20501017), and by the Natural Science Foundation of Henan Educational Committee (2009A150028 and 2011A150029).

Address correspondence to Gang Li, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, Henan, P. R. China. E-mail: gangli@zzu.edu.cn.



SCH. 1. The syntheses of complexes **1** and **2** (color figure available online).

Preparation of [Co(H_2MOPhIDC)$_2$(H_2O)$_2$] (2)

A mixture of H_3MOPhIDC (26.3 mg, 0.1 mmol), $CoCl_2{\cdot}6H_2O$ (23.8 mg, 0.1 mmol), H_2O (7 mL), and Et_3N (0.056 mL, 0.4 mmol) was sealed in a 25 mL Telfon-lined bomb and heated at 160°C for 72 h. The reaction mixture was then allowed to cool to room temperature; yellow strip crystals of **2** were isolated. The crystals of **2** are stable in the air. Yield: 43% (based on Co). Anal. Calcd. for $C_{24}H_{22}CoN_4O_{12}$ (%): C, 46.65; H, 3.56; N,7.77%. Found (%): C, 46.38; H, 3.38; N, 7.49%. IR (cm^{-1}, KBr): 3485 m, 3219 m, 2952 w, 2846 w, 1924 w,1715 m, 1612 s, 1493 s, 1407 s, 1299 m, 1189 m, 1041 w, 867 w, 834 s, 701 m, 624 m, 523 m, 499 w, 462 w.

X-Ray Crystallography

Crystal data and experimental details for compounds **1** and **2** are contained in Table 1. All measurements of **1** and **2** were made on a Bruker smart APEXII CCD diffractometer (Germany). with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Single crystals of **1** and **2** were selected and mounted on a glass fiber. All data were collected at a temperature of 296(2) K for complex **1** and 296.15 K for complex **2** using the ω-2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The two structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least square refinement for complex **1** was based on 3691 observed reflections and 268 variable parameters and for complex **2** was based on 2502 observed reflections and 197 variable parameters. All calculations were performed using the SHELX-97 crystallographic software package.[30] Selected bond lengths and angles are listed in Table 2.

RESULTS AND DISCUSSION

Crystal Structure of [Cu(H_2PIDC)$_2$(H_2O)] (1)

Single crystal X-ray diffraction shows that complex **1** is a discrete neutral mononuclear complex. The asymmetric unit of the compound contains one crystallographically independent Cu(II) ion, two H_2PIDC^- units with the same coordination mode, and one coordination water molecule (Figure 1). The Cu1 ion is five-coordinated, and the Addison parameter ($\tau = 0.027$) of Cu1 reveals that the geometry around the Cu(II) atom is a largely distorted square pyramidal geometry. The Cu1 atom is surrounded by two carboxylate oxygen atoms and two nitrogen atoms from two chelating H_2PIDC^-, and one oxygen atom from a

TABLE 1
Crystallographic data for complexes **1** and **2**

Formula	$C_{16}H_{18}N_4O_9Cu$	$C_{24}H_{22}N_4O_{12}Co$
Formula weight	473.88	617.39
T (K)	296(2)	296.15
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
Crystal size(mm^3)	0.21 × 0.18 × 0.15	0.20 × 0.20 × 0.20
a (Å)	8.5280(13)	6.3231(15)
b (Å)	11.4840(18)	7.7385(19)
c (Å)	12.500(2)	13.419(3)
α (°)	70.6170(15)	75.021(3)
β (°)	71.6650(17)	80.218(3)
γ (°)	73.3970(15)	83.354(3)
V (Å^3)	1073.5(3)	623.3(3)
Dc (Mg m^{-3})	1.466	1.645
Z	2	1
μ (mm^{-})	1.071	0.765
F(000)	486	317
Reflens collected/unique	7680/3691 R(int) 0.1139	5192/2502/R(int) 0.0359
Data/restraints/parameters	3691/15/268	2502/0/197
Final R indices [I > 2sigma(I)]	$R_1 = 0.0890$; $wR_2 = 0.1790$	$R_1 = 0.0427$; $wR_2 = 0.0908$
R indices (all data)	$R_1 = 0.2633$; $wR_2 = 0.2064$	$R_1 = 0.0664$; $wR_2 = 0.0995$
Goodness-of-fit on F^2	1.012	1.008

coordination water molecule. The Cu-L (L=N or O) distances are in the range of 1.950(9)–2.181(6) Å, and the L—Cu—L bond angles vary from 82.7(3)° to 164.4(3)°, all of which are comparable to those reported for other imidazole-based dicarboxyate Cu(II) complexes.[25,26]

Two kinds of hydrogen bonds can be observed in this compound: (a) hydrogen bonds between the coordinated water molecule and uncoordinated carboxylate oxygen atoms (O(9)-H(1W) … O(2)#1 2.869(8) Å, O(9)-H(2W) … O(6)#2 2.841(8) Å); and (b) hydrogen bonds among the uncoordinated

TABLE 2
Selected bond distances (Å) and angles (°) for **1** and **2**

			1		
Cu(1)-N(3)	1.950(9)	Cu(1)-N(1)	1.957(8)	Cu(1)-O(1)	2.030(6)
Cu(1)-O(5)	2.032(6)	Cu(1)-O(9)	2.181(6)		
N(3)-Cu(1)-O(1)	95.1(3)	N(1)-Cu(1)-O(1)	82.7(3)	N(3)-Cu(1)-O(5)	82.8(3)
N(1)-Cu(1)-O(5)	95.5(3)	O(1)-Cu(1)-O(5)	166.0(3)	N(3)-Cu(1)-O(9)	97.7(3)
N(1)-Cu(1)-O(9)	97.9(3)	O(1)-Cu(1)-O(9)	97.9(3)	O(5)-Cu(1)-O(9)	96.1(2)
N(3)-Cu(1)-N(1)	164.4(3)				
			2		
Co(1)-O(1a)	2.045(2)	Co(1)-O(6)	2.110(2)	Co(1)-O(1)	2.045(2)
Co(1)-O(6a)	2.110(2)	Co(1)-N(1)	2.245(2)	Co(1)-N(1a)	2.245(2)
O(1)-Co(1)-O(1a)	180.0(1)	O(1)-Co(1)-O(6)	90.2(8)	O(1a)-Co(1)-O(6)	89.8(8)
O(1)-Co(1)-O(6a)	89.8(8)	O(1a)-Co(1)-O(6a)	90.2(8)	O(1)-Co(1)-N(1)	79.2(7)
O(1a)-Co(1)-N(1)	100.8(7)	O(1a)-Co(1)-N(1a)	79.2(7)	O(1)-Co(1)-N(1a)	100.8(7)
O(6a)-Co(1)-O(6)	180.0	O(6)-Co(1)-N(1)	89.2(8)	O(6a)-Co(1)-N(1)	90.8(8)
O(6)-Co(1)-N(1a)	90.8(8)	O(6a)-Co(1)-N(1a)	89.2(8)	N(1a)-Co(1)-N(1)	180.0

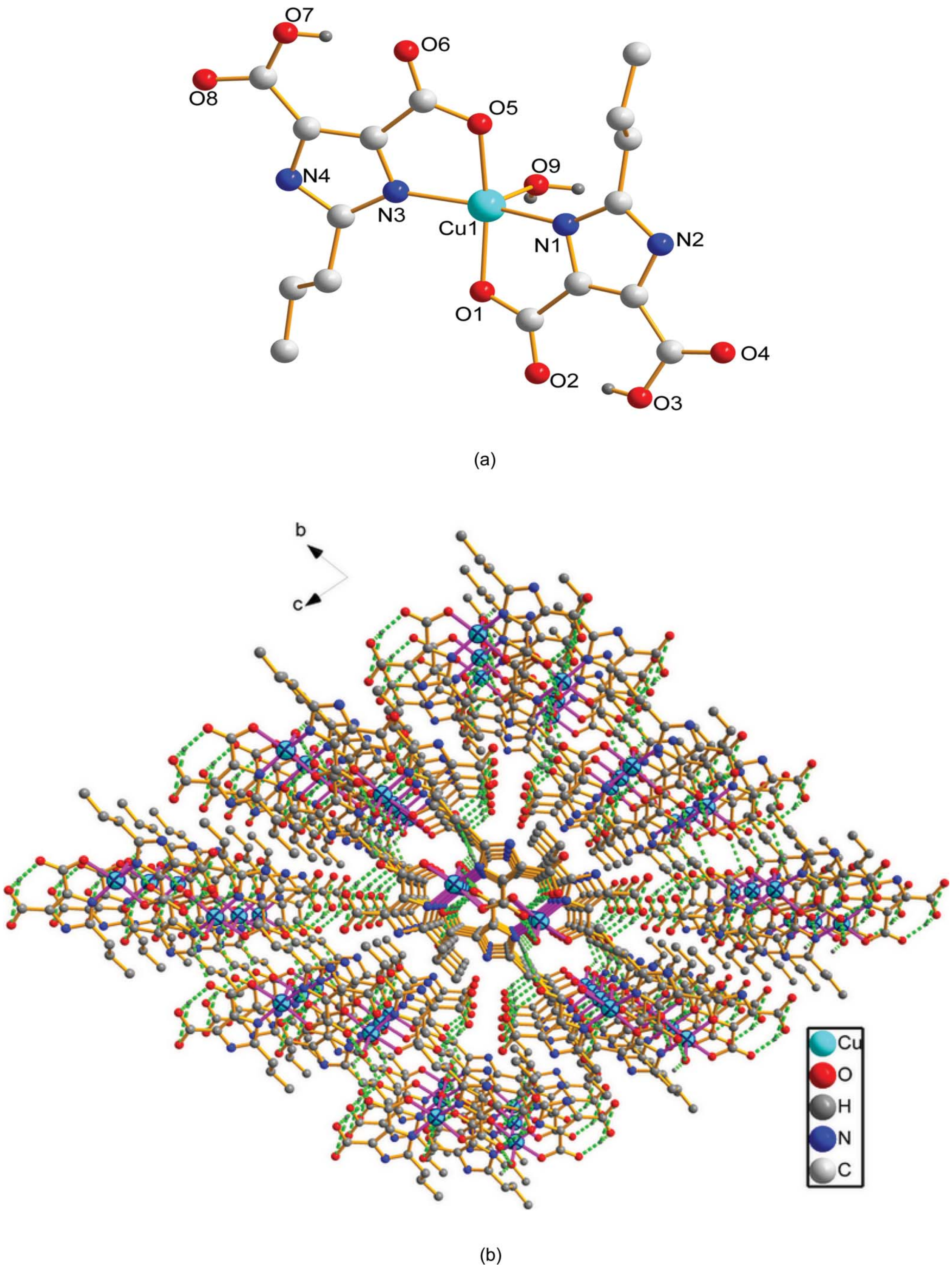


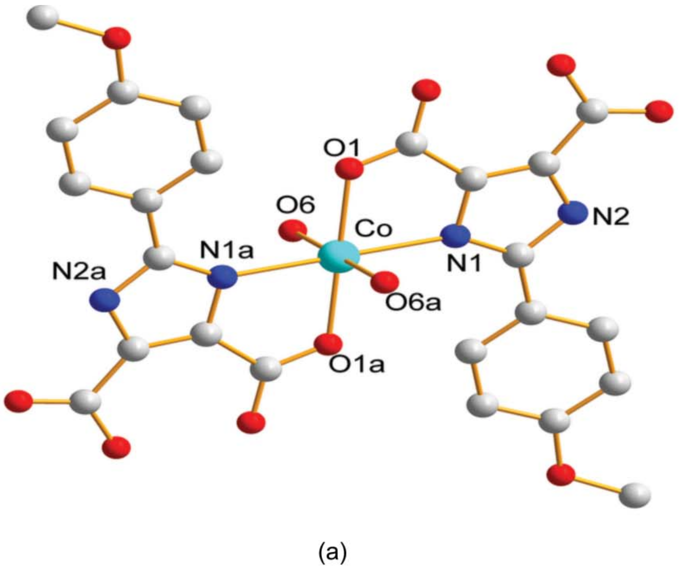
FIG. 1. (a) Molecular structure of complex 1 (partial H atoms omitted for clarity). (b) Crystal packing view from the a-axis of 1 (color figure available online).

carboxylate oxygen atoms (O(3) - H(3) ... O(2) 2.581(9) Å, O(7)- H(7) ... O(6) 2.564(10) Å). Thus, the previous H-bond interactions together with van der Waals forces represent the main contribution for the stabilization of the crystal packing (Figure 1).

To the best of our knowledge, only one 0D Cu(II) complex and two 2D sheet Cu(II) polymers of complexes constructed by H_3PIDC ligand can be found in the recent publications.[25–27] Compound **1** is the second example of mononuclear Cu(II) complex built by H_3PIDC ligand.

Crystal Structure of [Co(H_2MOPhIDC)$_2$(H_2O)$_2$] (2)

Complex **2** with one crystallographically independent Co(II) ion in the crystal lattice, it is a discrete neutral mononuclear complex. As shown in Figure 2, the Co(II) atom is six-coordinated in a slightly distorted octahedral environment with two oxygen



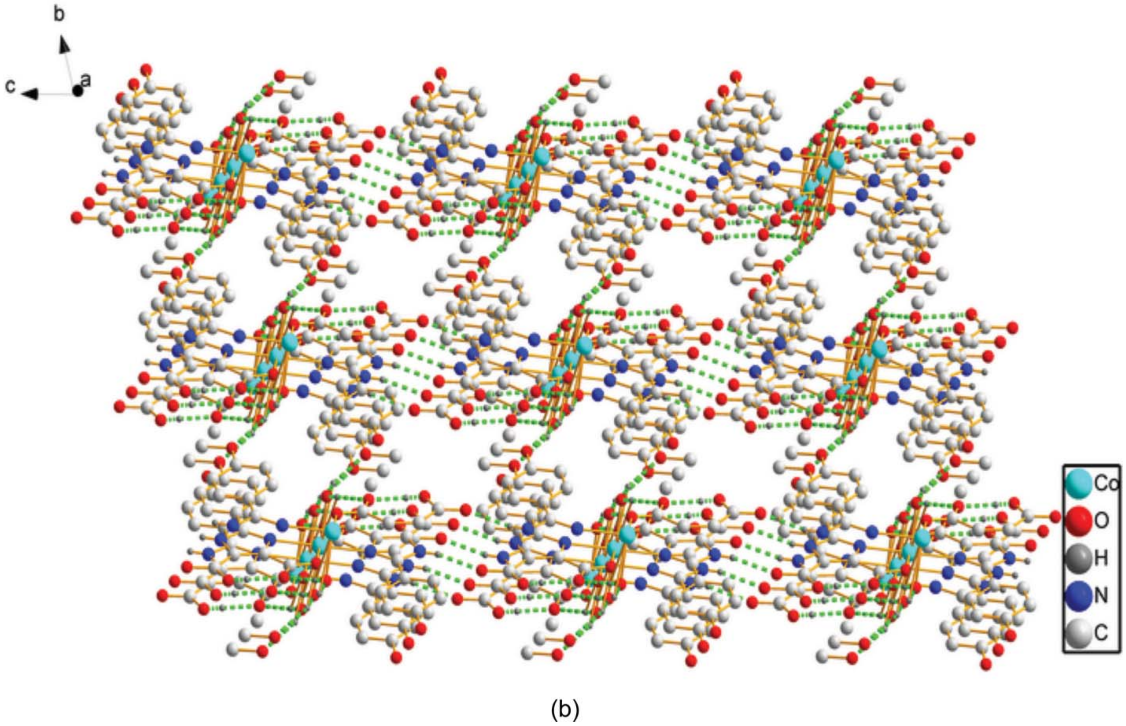


FIG. 2. (a) Diagram showing the molecular structure of complex 2 (H atoms omitted for clarity). (b) The 3D supramolecular architecture of 2 along a-axis supported by H-bonds (color figure available online).

TABLE 3
Distances (Å) and angle (°) of hydrogen bonds for **1** and **2**

D—H . . . A	d(H . . . A)	d(D . . . A)	∠(DHA)
	1		
O(3)-H(3) . . . O(2)	1.76	2.581(9)	175.9
O(7)-H(7) . . . O(6)	1.76	2.565(1)	167.9
O(9)-H(1W) . . . O(2)#1	2.04	2.869(8)	164.3
O(9)-H(2W) . . . O(6)#2	2.40	2.841(8)	112.8
	2		
O(3)-H(3) . . . O(2)	1.67	2.492(3)	176.2
O(6)-H(6A) . . . O(5)#1	2.15(4)	2.900(3)	159(4)
O(6)-H(6B) . . . O(2)#2	1.95(4)	2.728(3)	169(4)
N(2)-H(2) . . . O(4)#3	2.04(3)	2.835(3)	168(3)

Symmetry codes for **1**: #1: –x + 1, –y, –z; #2: –x + 1, –y + 1, –z. For **2**: #1: –x + 1, –y, 1 – z; #2: –x – 1, 1 – y, 1 – z; #3: –x, 1 – y, –z.

atoms (O1, O1a) and two nitrogen atoms (N1, N1a) from two different $H_2MOPhIDC^-$ ligands in the equatorial plane, and two oxygen atoms (O6,O6a) from two water molecules in axial positions. The bond lengths of Co-O and Co-N from $H_2MOPhIDC^-$ are 2.0446(18) Å and 2.245(2) Å, respectively, while the Co-O_{water} distance is 2.110(2) Å. The bond angles around each Co(II) ion vary from 79.17(7)° to 180.0(1)°.

In the solid-state structure of complex **2**, the imidazole dicarboxylate ligands have one kind of coordination mode. There are two types of hydrogen bonds formed by coordination water and $H_2MOPhIDC^-$, namely, O-H . . . O and N-H . . . O. The H-bonding parameters are listed in Table 3. Obviously, as can be seen from Figure 2, countless of $[Co(H_2MOPhIDC)_2(H_2O)_2]$ units are interconnected together by the interaction of the intermolecular and intramolecular hydrogen bonds to form a 3-D supermolecular structure.

So far, complexes bearing $H_3MOPhIDC$ ligand have never been reported. The successful preparation of complex **2** gives us more chance to study the structures and properties of this kind of complex.

IR Spectroscopy

The IR spectra (400–4000 cm^{-1}) display characteristic absorption bands for water molecules, carboxylate, imidazolyl units, and phenyl units. Compounds **1** and **2** show strong broad absorption bands in the range of 3400–3500 cm^{-1}, which indicates the presence of the $\nu_{O\text{-}H}$ and $\nu_{N\text{-}H}$ stretching frequencies of the coordinated water molecules and imidazole ring, respectively. The coordination of the carboxylate units can be seen from the absorption bands in the frequency range 1295–1623 cm^{-1} in **1** and **2** due to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively. The frame vibration of phenyl ring is observed at 1493 cm^{-1} for **2**. In conclusion, the infrared spectral data of the complexes **1** and **2** are consistent with crystal structure analysis.

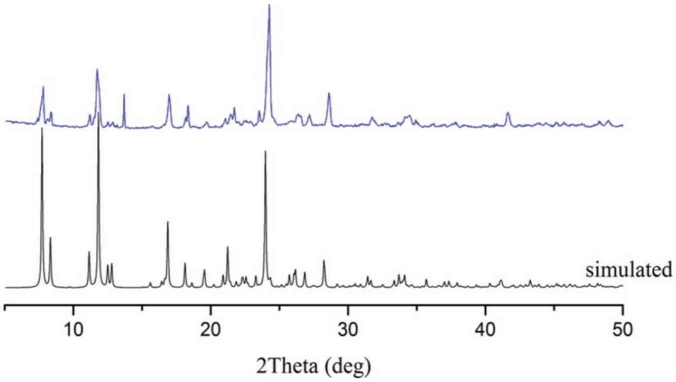


FIG. 3. XRPD pattern of the single crystal of complex 1 (color figure available online).

XRPD

X-ray powder diffraction (XRPD) was used to check the purity of complexes **1** and **2**. As shown in Figures 3 and 4, all the peaks revealed in the measured patterns closely match those in the simulated patterns generated from single-crystal diffraction data, indicating single phases of **1** and **2** are formed.

Thermogravimetric Analysis

The TG-DSC curves have been obtained under flowing air for crystalline samples of **1** and **2** in the temperature range of 20–700°C. As shown in Figure 5, complex **1** shows four-step weight loss process. The complex is stable until 30.0°C, and then first loses weight from 30.0°C to 199.0°C (observed 4.25%) corresponding to the loss of coordinated water molecule. The second, the third and the fourth weight loss steps are from 199.0°C to 344.0°C and from 344.0°C to 416.0°C and from 416.0°C to 509.0°C, respectively. The total weight loss of the three steps is 79.15% (calcd. 79.34%) corresponds to the decomposition of the organic ligand. Finally, a plateau region is observed from 509.0°C to 689.0°C. A blue amorphous residue of CuO remained (observed 16.60%, calcd. 16.88%). There are two weak endothermic peaks at 141.6°C and 376.0°C, one

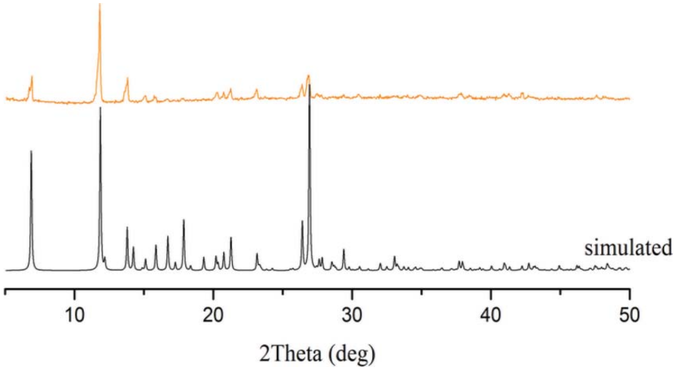


FIG. 4. XRPD pattern of the single crystal of complex 2 (color figure available online).

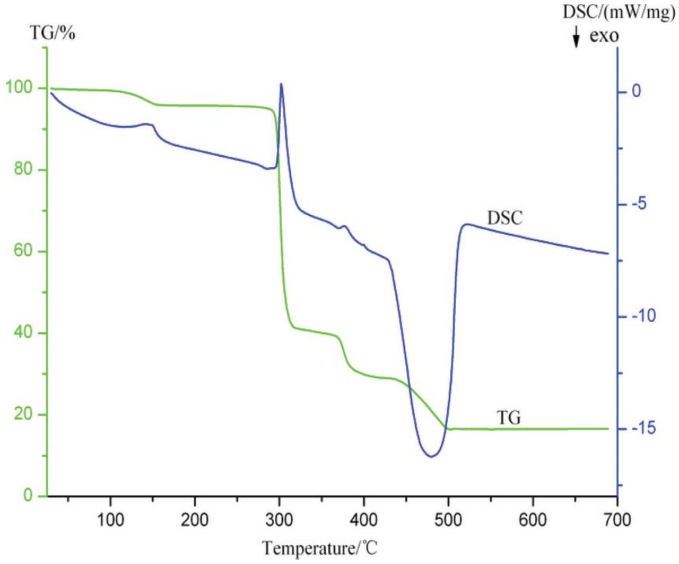


FIG. 5. TG-DSC curves of complex 1 (color figure available online).

middle endothermic peak at 302.2°C, and one strong exothermic peak at 479.8°C on the DSC curve of compound **1**.

As can be seen from Figure 6, there are two weak endothermic peaks at 198.9°C and 312.1°C, and one strong exothermic peak at 443.9°C on the DSC curve of complex **2**. The first weight loss of 5.69% (calcd. 5.83%) occurs from 142.0°C to 224.0°C, which is attributed to the loss of coordinated water molecules. The second weight loss of 36.71% (calcd. 36.28%) between 224.0°C and 354.0°C corresponds to the loss of two -COOH and two COO^- and two $-OCH_3$. The third weight loss of 44.28% (calcd. 44.38%) ranges from 354.0°C to 607.0°C corresponding to the loss of the remaining organic ligand. The remaining weight of 13.32% corresponds to the percentage (calcd.13.44%) of the Co and O components, indicating that the final product is $0.5Co_2O_3$.

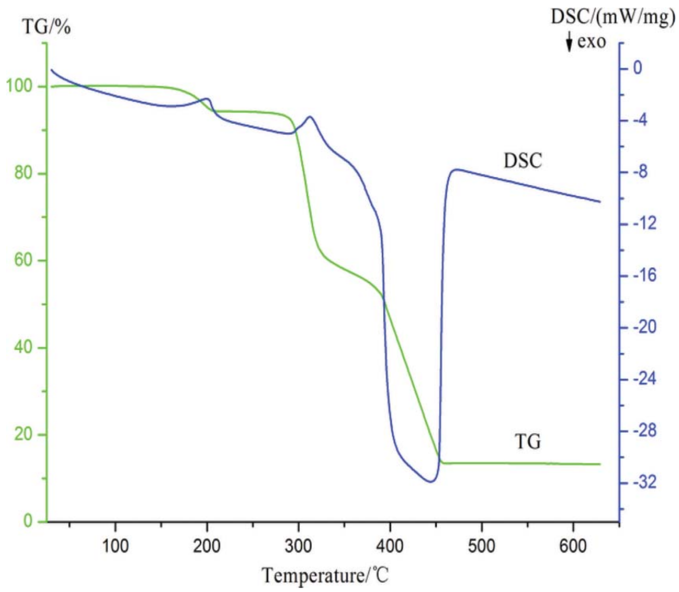


FIG. 6. TG-DSC curves of complex 2 (color figure available online).

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 851963 for **1** and 851964 for **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44–1223–336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

REFERENCES

1. Fang, R.Q.; Zhang, X.M. Diversity of coordination architecture of metal 4,5-dicarboxyimidazole. *Inorg. Chem.* **2006**, *45*, 4801–4810.
2. Wang, Y.L.; Yuan, D.Q.; Bi, W.H.; Li, X.; Li, X.J.; Li, F.; Gao, R. Syntheses and characterization of two 3D cobalt-organic frameworks from 2D honeycomb building blocks. *Cryst. Growth Des.* **2005**, *5*, 1849–1855.
3. Lu, W.G.; Jiang, L.; Feng, X.L.; Lu, T.B. Four 3D porous metal-organic frameworks with various layered and pillared motifs. *Cryst. Growth Des.* **2008**, *8*, 986–994.
4. Yao, Y.L.; Che, Y.X.; Zheng, J.M. The coordination chemistry of benzimidazole-5,6-dicarboxylic acid with Mn(II), Ni(II), and Ln(III) complexes (Ln = Tb, Ho, Er, Lu). *Cryst. Growth Des. 2008*, *8*, 2299–2306.
5. Moulton, B.; Zaworotko, M.J. From molecules to crystal engineering: supramolecular isomerism and polymorphism in network solids. *Chem. Rev.* **2001**, *101*, 1629–1658.
6. Lin, J.D.; Cheng, J.W.; Du, S.W. Five d^{10} 3D metal−organic frameworks constructed from aromatic polycarboxylate acids and flexible imidazole-based ligand. *Cryst. Growth Des.* **2008**, *8*, 3345–3353.
7. Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. Crystallized frameworks with giant pores: Are there limits to the possible. *Chem. Rev.* **2005**, *38*, 217–225.
8. Ockwig, N.W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O.M. Reticular chemistry:occurrence and taxonomy of nets and grammar for the design of frameworks. *Chem. Rev*. **2005**, *38*, 176–182.
9. Liu, H.; Qin, H.; Zong, X.M.; Hong, W.; Jiao, Y.F.; Zhou, S.J.; Cui, J.W. Two-dimensional lanthanide coordination polymers constructed from Ce3+/Pr3 +cation imidazole-4,5-dicarboxylate and in situ generated oxalate anions. *Chin. J. Struct. Chem.* **2011**, *7*, 1030–1036.
10. Lu, W.G.; Jiang, L.; Feng, X.L.; Lu, T.B. Four 3D porous metal-organic frameworks with various layered and pillared motifs. *Cryst. Growth Des.* **2008**, *8*, 986–994.
11. Yue, S.T.; Wei, Z.Q.; W, N.; Liu, W.J.; Chang, L.M.; Liu, Y.L.; Mo, H.H.; Cai, Y.P. Three novel microporous 3D heterometallic 3d-4f coordination polymers: synthesis, crystal structures and photoluminescence properties. *Inorg. Chem. Commun.* **2011**, *14*, 1396–1399.
12. Zheng, S.R.; Cai, S.L., Fan, J.; Xiao, T.T.; Zhang, W.G. Three new complexes synthesized from an imidazole - based dicarboxylate ligand containing hydroxymethyl group. *Inorg. Chem. Commun*. **2011**, *14*, 1097–1101.
13. Gu, Z.G.; Fang, H.C.; Yin, P.Y.; Tong, L.; Ying, Y.; Hu, S.J.; Li, W.S.; Cai, Y.P. A Family of three-dimensional lanthanide-zinc heterometal-organic frameworks from 4,5-imidazoledicarboxylate and oxalate. *Cryst. Growth Des*. **2011**, *11*, 2220–2227.
14. Ou, G.C.; Zhou, Q.; Ng, S.W. [4-Carboxyimidazole-5-carboxylato(2-)-.kapp. 2N1, O5](5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-.kappa.4N,N',N",N"',)nickel(II) monohydrate. *Acta Cryst*. **2009**, *E65*, m1556.
15. Li, Z. Y., Zhang, Z.M.; Dai, J.W.; Huang, H.Z.; Li, X.X.; Xue, S.T.; Liu, Y.L. Three novel lanthanide complexes with imidazole-4,5-dicarboxylate

ligand: hydrothermal syntheses, structural characterization, and properties. *J. Mol. Struct*. **2010**, *963*, 50–56.

16. Ghosh, A.; Prabhakara, R.K.; Sanguramath. R.A.; Rao, C.N. R. Two-and Three-dimensional lead-1H-imidazole-4,5-dicarboxylates. *J. Mol. Struct*. **2009**, *927*, 37–42.
17. Luo, Z.R.; Zhuang, J.C.; Wu, Q.L.; Yin, X.H.; Tan, S.W.; Liu. J.Z. Two cobalt(II) complexes based on 2-propyl-4,5-imidazoledicarboxylic acid: syntheses, crystal structures, and properties. *J. Coord. Chem*. **2011**, *64*, 1054–1062.
18. Zhang, F.W.; Li, Z.F.; Ge, T.Z.; Yao, H.C.; Li, G. Four novel frameworks built by imidazole-based dicarboxylate ligands: hydro(solvo)thermal synthesis, crystal structures and properties. *Inorg. Chem*. **2010**, *49*, 3776–3788.
19. Li, Z.F.; Guo, L.; Zhang, F.W.; Li, G.; Zhu, L. A novel 2D coordination polymer constructed from left- and right-handed helical chains and 4,4'-bipyridine bridges. *Synth. React. Inorg. Met.-Org. Chem.* **2010**, *40*, 734–738.
20. Wang, W.Y.; Niu, X.L.; Gao, Y.C.; Zhu, Y.Y.; Li, G.; Lu, H.J. One chiral and two achiral 3-D coordination polymers constructed by 2-phenyl imidazole dicarboxylate. *Cryst. Growth Des.* **2010**, *10*, 4050–4059.
21. Wang, W.Y.; Yang, Z.L.; Wang, C.J.; Lu, H.J.; Zang, S.Q.; Li, G. 2-Phenyl-4,5-imidazole dicarboxylate-based metal-organic frameworks assembled under hydro(solvo)thermal conditions. *CrystEngComm* **2011**, *13*(*15*), 4895–4902.
22. Li, Z.F.; Chen, C.J.; Yan, L.H.; Li, G.; Wu, C.J.; Lu, H.J. Three main group metal coordination polymers built by 2-propyl-1H-imidazole-4,5-dicarboxylate. *Inorg. Chim. Acta*, **2011**, *377*, 42–49.
23. Wang, S.; Zhang, L.R.; Li, G.H.; Huo, Q.S.; Liu, Y.L. Assembly of two 3-D metal-organic frameworks from Cd(II) and 4,5-imidazoledicarboxylic acid or 2-ethyl-4,5-imidazoledicarboxylic acid. *Cryst. Eng.* **2008**, *10*, 1662–1666.
24. Nie, X.L.; Wen, H.L.; Wu, Z.S.; Liu, D.B.; Liu, C.B. Diaquabis(5-carboxy-2-methyl-1H-imidazole-4-Carboxylato-k2N3,O4)cadmium(II). *Acta Cryst*. **2007**, *E63*, 753–755.
25. Wang, D.P.; Chen, Y.G.; Wang, H.Y.; Zhang, C.J.; Tang, Q. Syntheses, crystal structures, and properties of four new coordination compounds of transition metals and imidazoledicarboxylic acid derivatives. *J. Coord. Chem.* **2011**, *64*, 2824–2833.
26. Li, X.X.; Wang, N.; Yue, S.T.; Li, Z.Y.; Wu, H.Y.; Liu, Y.L. Supramolecular structures with the 2-propyl-4,5-dicarboxy-1H-imidazole ligand: hydrothermal synthesis, structures, and photoluminescence. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2648–2652.
27. He, L.Z.; He, L.Z.; Li, S.J.; Song, W.D.; Miao, D.L. Diaquabis(4-carboxy-2-propyl-1H-imidazole-5-carboxylato-k^{2}N^3,O^4)-copper(II) N,N-dimethylformamide disolvate. *Acta Cryst*. **2010**, *E66*, m896.
28. Fun, H.K.; Raj, S.S. S.; Xiong, R.G.; Zuo, J.L.; Yu, Z.; You, X.Z. A three-dimensional network coordination polymer, (terephthalato)(pyridine)cadmium, with blue fluorescent emission. *J. Chem. Soc., Dalton Trans.* **1999**, 1915–1916.
29. Grimmett, M.R. Product class 3: imidazoles. *Org. Chem.*, **2002**, *12*, 325–528.
30. Shelddrick, G.M. *SHELX-97, Program for the Solution and Refinement of Crystal Structures*; Germany, University of Göttingen **1997**.