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Two copper(II) coordination polymers constructed by bis(4-(1*H*-imidazol-1-yl)phenyl)methanone and dicarboxylate ligands

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Abstract: Two new copper(II) complexes, $\{[Cu(bipmo)(npa)]\}_n$ (**1**) and $\{[Cu(bipmo)(pa)]\}_n$ (**2**) (bipmo = bis(4-(1*H*-imidazol-1-yl)phenyl)methanone), were synthesized by solvothermal methods and structurally characterized by elemental analyses, infrared spectroscopy, and single-crystal X-ray diffraction. The results from single-crystal X-ray diffraction data indicate that the solid state structures of **1** and **2** consist of neutral metal aromatic carboxylate layers, which are pillared by the weak interactions to generate 3D architectures. The topological structures of **1** and **2** are uninodal nets based on 4-connected nodes with the Schläfli symbol of $(6^5{\cdot}8)$.

Keywords: benzophenone; carboxylate ligand; copper(II); imidazole; semirigid ligand; topology.

1 Introduction

Coordination polymers (CPs) have attracted much interest due to their structural diversity and potential applications in areas such as gas adsorption and separation, ion exchange, magnetism, and catalysis [1–8]. There are many factors governing the final structure, such as the ligands, the metal-to-ligand ratio, the pH value, and the counterions. Any subtle alteration of these factors can lead to the formation of new structures or extended frameworks.

Polycarboxylic acids are often chosen as an essential tool to develop CPs due to the fact that the carboxylate ligand has a rich diversity of coordination modes and connectivities. The structural complexity can be further enhanced through the design of N-donor ligands which can pillar the metal-carboxylate motifs into higher dimensionality to generate an extended structural topology [9–13].

As part of our research on the synthesis of imidazole based complexes [14–18], we report here the synthesis and characterization of two copper complexes, $\{[Cu(bipmo)(npa)]\}_n$ (**1**) and $\{[Cu(bipmo)(pa)]\}_n$ (**2**), constructed from $Cu(OH)_2$, bipmo, and H_2npa (H_2pa), in which the dicarboxylate groups in **1** and **2** present μ_1-η^1:η^0 monodentate and μ_1-η^1:η^1 chelate coordination modes (Scheme 1). The topological structures of **1** and **2** are uninodal net based on 4-connected nodes with the Schläfli symbol of $(6^5{\cdot}8)$.

2 Results and discussion

2.1 Preparation and characterization of the complexes

The two new copper(II)-based coordination polymers were synthesized by solvothermal reactions of $Cu(OH)_2$ with H_2npa (H_2pa) and bipmo in good yields. The complexes were characterized by elemental analyses and FT-IR spectroscopy. The asymmetric stretching vibrations $\upsilon_{as}(COO^-)$ were observed in the range of 1680–1665 cm^{-1} and the symmetric stretching vibrations $\upsilon_s(COO^-)$ with 1338–1364 cm^{-1}. The above stretching vibrations are shifted to lower values, compared to the carboxyl frequencies of free H_2npa (H_2pa). The peaks for **1** and **2** from 3057 to 3171 cm^{-1} are attributed to C–H stretching vibrations.

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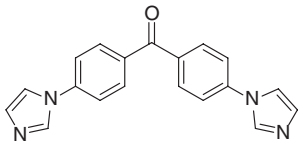

Scheme 1: Molecular formula of the ligand bis(4-(1*H*-imidazol-1-yl) phenyl)methanone (bipmo).

2.2 Molecular structures of 1 and 2

Numerical details of the crystal structure determinations of **1** and **2** are given in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2. Compound **1**, $\{[Cu(bipmo)(npa)]\}_n$, features a porous 2D metal organic frameworks, with the asymmetric unit comprising one Cu^{2+} center, one npa^{2-}, and one bipmo ligand. As shown in Fig. 1, the Cu1 center is surrounded by three carboxylate oxygen atoms from two crystallographically equivalent npa^{2-} ligands in which the dicarboxylate groups of npa^{2-} present μ_1-η^1:η^0 monodentate and μ_1-η^1:η^1 chelate coordination modes, and two imidazole nitrogen atoms from two crystallographically equivalent bipmo ligands. It displays a coordination geometry that resembles a distorted square pyramid [$\tau = 0.224$; $\tau = (\beta - \alpha)/60$, where α and β are the two largest bond angles around the Cu(II) center; $\tau = 0$ for an ideal square pyramid; and $\tau = 1$ for an ideal trigonal bipyramid [19]: O2, O3#1, N1, and N4#2 are in the equatorial positions [Cu1–O = 2.013(3), 1.931(3) Å; and Cu1–N = 1.984(4), 1.986(3) Å, symmetry code: #1 = 1 − *x*, 1 − *y*, 1/2 + *z*; #2 = 1 + *x*, *y*, −1 + *z*] and O1 is in the axial position [Cu1–O1 = 2.445(3) Å] (Table 2). These values lie within the normal range for Cu–N and Cu–O bond lengths in similar complexes [20–22].

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

1		**2**	
Cu(1)–O(3)$^{\#1}$	1.931(3)	Cu(1)–O(3)$^{\#1}$	1.9386(17)
Cu(1)–N(1)	1.984(4)	Cu(1)–O(1)	1.9626(18)
Cu(1)–N(4)$^{\#2}$	1.986(3)	Cu(1)–N(4)	1.975(2)
Cu(1)–O(2)	2.013(3)	Cu(1)–N(1)	1.990(2)
Cu(1)–O(1)	2.445(3)		
O(3)$^{\#1}$–Cu(1)–N(1)	93.50(14)	O(3)$^{\#1}$–Cu(1)–O(1)	161.04(8)
O(3)$^{\#1}$–Cu(1)–N(4)$^{\#2}$	86.69(13)	O(3)$^{\#1}$–Cu(1)–N(4)	93.07(8)
N(1)–Cu(1)–N(4)$^{\#2}$	162.81(14)	O(1)–Cu(1)–N(4)	87.98(8)
O(3)$^{\#1}$–Cu(1)–O(2)	176.23(12)	O(3)$^{\#1}$–Cu(1)–N(1)	94.50(8)
N(1)–Cu(1)–O(2)	88.36(12)	O(1)–Cu(1)–N(1)	90.87(8)
N(4)$^{\#2}$–Cu(1)–O(2)	92.50(13)	N(4)–Cu(1)–N(1)	159.79(9)

[a]Symmetry operations for **1**: $^{\#1}$ 1 − *x*, 1 − *y*, 1/2 + *z*2; $^{\#2}$ 1 + *x*, *y*, *z* − 1; symmetry operations for **2**: $^{\#1}$ − *x*, 1/2 + *y*, − 1/2–*z*.

Table 1: Summary of crystallographic data for complex $\{[Cu(bipmo)(npa)]\}_n$ (**1**) and $\{[Cu(bipmo)(pa)]\}_n$ (**2**).

Compound	**1**	**2**
Empirical formula	$Cu(C_{19}H_{14}N_4O)(C_8H_3NO_6)$	$Cu(C_{19}H_{14}N_4O)(C_8H_4O_4)$
Formula weight	587.00	542.00
T, K	293(2)	293(2)
Crystal system, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$
a, Å	13.41067(20)	13.7593(8)
b, Å	15.7008(3)	11.3375(7)
c, Å	11.7254(2)	17.9277(15)
β, °	90	122.087(5)
V, Å^{-3}	1856.17(13)	2369.4(3)
Z	4	4
$D_{calc.}$, g cm^{-3}	1.58	1.52
μ, mm^{-1}	0.9	1.0
F(000), *e*	1196	1108
θ range, deg	3.01–25.34	2.91–25.50
h_{min}, h_{max}	− 14, 16	− 16, 16
k_{min}, k_{max}	− 17, 18	− 13, 12
l_{min}, l_{max}	− 10, 14	− 18, 21
Refl. collected/unique/	7796/3612/0.0226	9412/4416/0.0200
Data/restraints/parameters	3612/1/362	4416/0/334
Goodness-of-fit on F^2	1.059	1.016
R_1/R_2 [$I > 2\sigma(I)$]	0.0353/0.0904	0.0352/0.0859
R_1/R_2 (all data)	0.0400/0.0943	0.0438/0.089
x(Flack)	0.446(17)	–
Largest peak/hole, e Å^{-3}	0.82/− 0.32	1.11/− 0.36

In **1**, the five-coordinated Cu ions connected npa^{2-} and bipmo ligands forming a layer (Fig. 2). In order to better understand the complicated framework, the network topology of the complex was analyzed by the freely available computer program Topos [23]. As depicted in Figs. 1–3, each Cu1 center acts as a 4-connected node to connect two npa ligands and two bipmo ligands. Each npa^{2-} and bipmo unit serves as a bridging linker for the Cu^{2+} ions. From a topological point of view, the framework of **1** can be classified as a 4-connected 2D network with the Schläfli symbol of $\{6^5{\cdot}8\}$ (Fig. 3).

Compound **2** displays a similar layer structure. As shown in Fig. 4, the asymmetric unit **2** consists of one Cu^{2+} cation, one pa^{2-}, and one bipmo ligand. Cu1 is four-coordinated by two oxygen atoms from two different pa^{2-} dianions and two nitrogen atoms from two different bipmo ligands, showing a square-planar coordination geometry. The Cu–N and Cu–O bond lengths lie in the ranges of 1.990(2)–1.975(2) and 1.9386(17)–1.9626(18) Å, respectively.

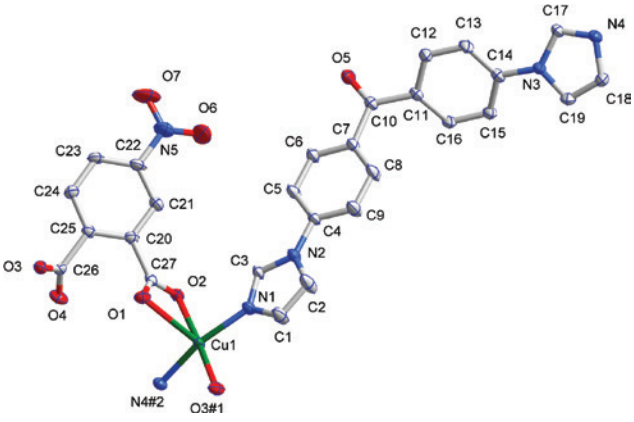

Fig. 1: Coordination environments of complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 $1-x, 1-y, 1/2+z$; #2 $1+x, y, z-1$.

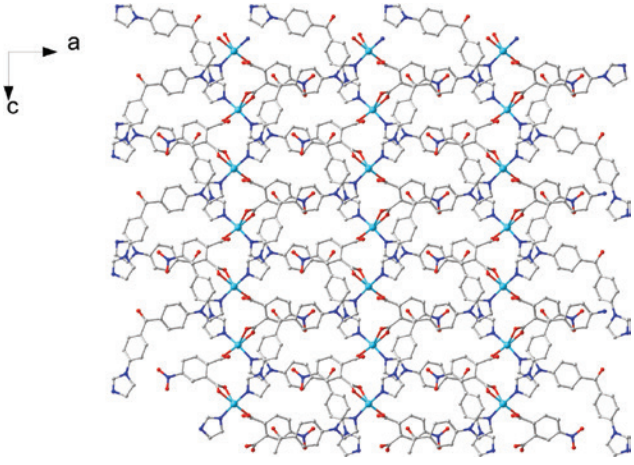

Fig. 2: A view of the layers in complex **1**.

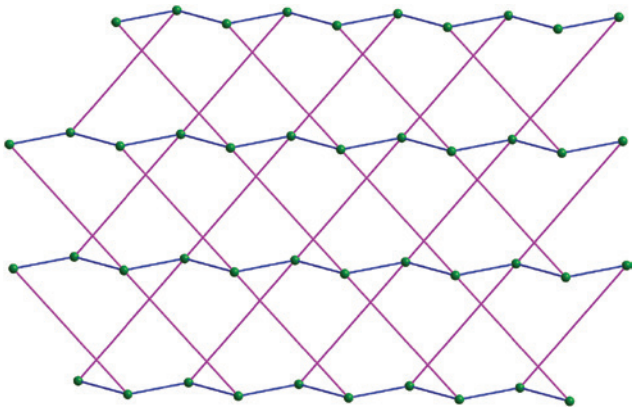

Fig. 3: View of the 2D simplified framework of **1** and **2**.

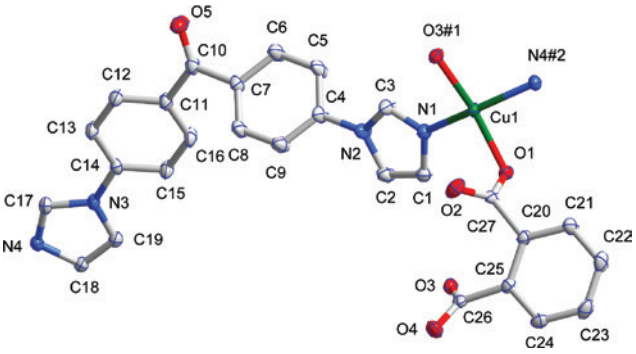

Fig. 4: Coordination environments of complex **2**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 $-x, 1/2+y, -1/2-z$; #2 $x+1, y+1, z$.

In compound **2**, two pa^{2-} dianions connect two Cu^{2+} cations via the carboxylate groups (μ_1-η^1:η^0 monodentate mode) to afford a [Cupa] unit. Neighboring [Cupa] units are linked by two bipmo ligands to furnish a 2D network (Fig. 5). The bipmo and pa^{2-} ligands, like in **1**, connect the Cu^{2+} ions to generate a similar 2D network with the Schläfli symbol of $\{6^5{\cdot}8\}$ (Fig. 3).

It is observed that in the crystals of **1** and **2** a large number of hydrogen bonds are formed between the hydrogen atoms at the nitrogen atoms and the oxygen atoms of the imidazole rings, carbonyl groups, and carboxylate units. The lengths of these bonds are very different, varying from 2.816(5) to 3.785(6) Å, reflecting the difference in strength of these bonds. Obviously, these hydrogen bonds sustain the stability of the three-dimensional structure of the crystals. In addition, C–H···π and π···π interactions are present in the structures.

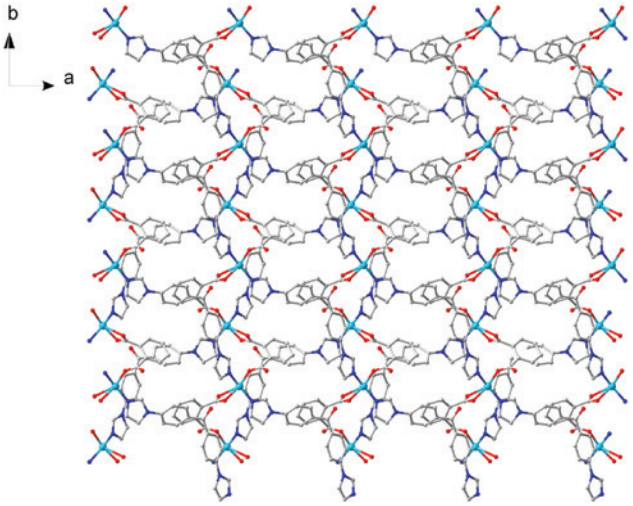

Fig. 5: A view of the layers in complex **2**.

3 Conclusions

In this paper, we have reported the syntheses, crystal structures, and characterization of two new Cu(II) coordination polymers with the semirigid bipmo ligand. The dicarboxylate groups in **1** and **2** present μ_1-η^1:η^0 monodentate and μ_1-η^1:η^1 chelate coordination modes. The topological structures of **1** and **2** are uninodal nets based on 4-connected nodes with the Schläfli symbol of (6^5·8). In addition, the crystal contains a large quantity of weak interactions which link the layers to form 3D supramolecular structures.

4 Experimental section

4.1 Materials and measurements

Reagents and solvents were purchased from Aladdin Industrial Corporation of Shanghai, China, and used as received. Bipmo was prepared according to the literature method [14]. Elemental analyses were performed on an Elementar Vario ELIII elemental analyzer. The infrared (IR) spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region.

4.1.1 Synthesis of {[Cu(bipmo)(npa)]}$_n$ (1)

A mixture of $Cu(OH)_2$ (0.1 mmol), bipmo (0.1 mmol), and H_2npa (0.1 mmol) and H_2O-EtOH (5 mL/2 mL) was added to a 25 mL Teflon-lined stainless steel reactor and heated at 105°C for 7 days, and then slowly cooled to room temperature. Blue block single crystals suitable for X-ray data collection were obtained by filtration, washed with H_2O–MeOH (4:1), and air-dried. Yield: 95% (based on bipmo). – Anal. for $C_{27}H_{17}CuN_5O_7$: calcd. C 55.25, H 2.92, N 11.93; found C 55.14, H 2.79, N 11.96%. –IR (cm^{-1}): 3171, 3142, 3117, 1660, 1631, 1603, 1522, 1418, 1386, 1371, 1338, 1307, 1254, 1186, 1121, 1063, 963, 930, 866, 835, 788, 767, 749, 727, 672, 645, 621, 519, 480.

H_2npa: IR (cm^{-1}): 3116, 3094, 3000–2595, 1730, 1637, 1609, 1529, 1496, 1439, 1423, 1356, 1310, 1268, 1236, 1148, 1119, 1063, 905, 862, 812, 738, 696, 654, 590, 521.

4.1.2 Synthesis of {[Cu(bipmo)(pa)]}$_n$ (2)

Blue block crystals of **2** were obtained in moderate yields (42% based on bipmo) by a similar method as described for **1** except that H_2pa were used instead of H_2npa. – Anal. for $C_{27}H_{18}CuN_4O_5$: calcd. C 59.83, H 3.35, N 10.34; found C 59.66, H 3.19, N 10.48%. – IR (cm^{-1}): 3136, 3111, 3057, 1680, 1607, 1583, 1524, 1491, 1391, 1364, 1313, 1257, 1209, 1115, 1061, 959, 924, 858, 829, 754, 698, 650, 532, 473.

H_2pa: IR (cm^{-1}): 3080, 3300–2500, 2650, 2525, 1684, 1585, 1495, 1404, 1281, 1148, 1070, 1005, 906, 798, 739, 673, 555.

4.2 X-ray crystallography

All measurements were made on an Agilent Technology SuperNova Eos Dual system with a micro focus source (MoK_α, $\lambda = 0.71073$ Å) and focusing multilayer mirror optics. The data were collected at a temperature of 293 K and processed using CrysAlis^{Pro} [24]. Absorption corrections were applied using the SADABS program [25]. The structures were solved by Direct Methods [26] with the program Shelxtl (version 6.10) [26, 27] and refined by full matrix least-squares techniques on F^2 with Shelxtl [26, 27]. All non-hydrogen atoms were refined anisotropically. The ligand hydrogen atoms were localized in their calculated positions and refined using a riding model.

CCDC 1504730 and 1504734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
[2] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev*. **2009**, *38*, 1477.
[3] S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan, H.-C. Zhou, *J. Am. Chem. Soc*. **2008**, *130*, 1012.
[4] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105.
[5] Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815.
[6] M. P. Suh, Y. E. Cheon, E. Y. Lee, *Coord. Chem. Rev*. **2008**, *252*, 1007.
[7] M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev*. **2009**, *38*, 1330.
[8] L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev*. **2009**, *38*, 1248.
[9] Q.-Y. Liu, Z.-J. Xiahou, Y.-L. Wang, L.-Q. Li, L.-L. Chen, Y. Fu, *CrystEngComm* **2013**, *15*, 4930.
[10] Z. Zhang, J.-F. Ma, Y.-Y. Liu, W.-Q. Kan, J. Yang, *CrystEngComm* **2013**, *15*, 2009.
[11] Y. Zhang, J. Yang, Y. Yang, J. Guo, J.-F. Ma, *Cryst. Growth Des*. **2012**, *12*, 4060.
[12] S.-S. Chen, Z.-H. Chen, J. Fan, T. Okamura, Z.-S. Bai, M.-F. Lv, W.-Y. Sun, *Cryst. Growth Des*. **2012**, *12*, 2315.
[13] J. Cui, Q. Yang, Y. Li, Z. Guo, H. Zheng, *Cryst. Growth Des*. **2013**, *13*, 1694.
[14] G.-F. Wang, X. Zhang, S.-W. Sun, H. Sun, X. Yang, H. Li, C.-Z. Yao, S.-G. Sun, Y.-P. Tang, L.-X. Meng, *Z. Naturforsch.* **2016**, *71b*, 869.
[15] G.-F. Wang, X. Zhang, S.-W. Sun, Q.-P. Han, X. Yang, H. Li, H.-X. Ma, C.-Z. Yao, H. Sun, H.-B. Dong, *Crystallogr. Rep*. **2015**, *60*, 1038.
[16] G.-F. Wang, S.-W. Sun, K. Qian, H.-X. Ma, X. Yang, Z.-R. Liu, *Z. Kristallogr. NCS* **2015**, *230*, 101.
[17] G.-F. Wang, *Z. Naturforsch.* **2015**, *70b*, 165.
[18] G.-F. Wang, S.-W. Sun, Q.-P. Han, W.-C. Zhang, H. Sun, S.-F. Song, G.-H. Cui, *Crystallogr. Rep*. **2014**, *59*, 994.
[19] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijin, G. C. Verschoor, *J. Chem. Soc., Dalton Trans*. **1984**, 1349.
[20] L. Qin, Y. Gu, G. Y. Li, S. L. Xiao, G. H. Cui, *Transition Met. Chem*. **2013**, *38*, 407.
[21] M.-S. Chen, Z.-S. Bai, T. Okamura, Z. Su, S.-S. Chen, W.-Y. Sun, N. Ueyama, *CrystEngComm* **2010**, *12*, 1935.
[22] S.-Y. Zhang, M.-X. Yu, L.-G. Zhu, *J. Mol. Struct.* **2004**, *699*, 101.
[23] V. A. Blatov, Multipurpose crystallochemical analysis with the program package TOPOS; *IUCr Comput. Commission Newsl.* **2006**, *7*, 4. Available at http://www.iucr.org/resources/commissions/crystallographic-computing/newsletters/7 (accessed January 2017).
[24] CrysAlis^{Pro} (version 1.171.35.19), Agilent Technologies Inc., Santa Clara, CA (USA) **2011**.
[25] G. M. Sheldrick, Sadabs, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.
[26] G. M. Sheldrick, Shelxtl (version 6.1), Software Reference Manual, Bruker AXS Inc., Madison, WI (USA) **2000**.
[27] G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112.