**Crystal Structure of an 8-Shaped Discrete Porous Complex, [Cu₂L₂(DMF)₂]
2DMF, H₂L = 2,4-bis[(2'-carboxyphenoxy)methyl]-1,3,5-trimethylbenzene**

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The crystal structure of [Cu₂L₂(DMF)₂]₂DMF (H₂L = 2,4-bis[(2'-carboxyphenoxy)methyl]-1,3,5-trimethylbenzene) was determined by an X-ray diffraction method. This complex crystallized in the monoclinic space group *P*2₁/*n*, with, *a* = 15.528(5), *b* = 10.052(3), *c* = 21.035(6) Å, β = 103.697(4)°, *Z* = 2, *V* = 3091.3(16) Å³, and *R* = 0.0621. Each Cu(II) ion is coordinated by four carboxylate O donor atoms from two ligands and by O donor atoms from the solvent molecule, DMF. The whole molecule looks like an Arabic number, '8'. A 2-D porous sheet was constructed by intermolecular hydrogen bonds between neighboring 8-shaped units.

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The design and synthesis of supramolecular architectures with open channel structures that contain pores of well-defined sizes, shapes, and chemical environments have attracted considerable attention from chemists, physicists, and materials scientist due to their potential applications in the areas of molecular sieves, sensors, gas absorption, ion exchange, size-selective separation, and heterogeneous catalysis.¹ In this field, extensive research in past decades has been devoted to the synthesis and characterization of metal-organic polygons and polyhedra (MOPs), such as squares, hexagons, cubes, tetrahedral, and

Table 2 Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for the title complex

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu(1)	4659(1)	6197(1)	4842(1)	38(1)
N(1)	2670(4)	9184(6)	4237(3)	67(2)
N(2)	3631(5)	58(8)	6090(4)	99(2)
O(1)	3650(3)	5271(4)	4151(2)	45(1)
O(2)	4255(3)	3242(4)	4417(2)	53(1)
O(3)	1785(3)	4541(5)	3532(2)	53(1)
O(4)	4072(3)	5917(4)	5528(2)	47(1)
O(5)	4669(3)	3886(4)	5802(2)	54(1)
O(6)	2525(3)	5839(5)	5933(2)	55(1)
O(7)	4022(3)	8098(4)	4556(2)	55(1)
O(8)	2179(10)	810(20)	5908(10)	172(7)
O(8')	2303(10)	-790(20)	6063(10)	158(6)
C(1)	3696(4)	4056(7)	4037(3)	42(2)
C(2)	3063(4)	3501(6)	3389(3)	44(2)
C(3)	2119(4)	3723(6)	3150(3)	46(2)
C(4)	1587(5)	3111(8)	2562(3)	66(2)
C(5)	1969(7)	2341(8)	2202(4)	78(3)
C(6)	2895(6)	2165(8)	2407(4)	78(2)
C(7)	3429(5)	2724(7)	3011(4)	64(2)
C(8)	4245(4)	4891(7)	5892(3)	43(2)
C(9)	3956(4)	4859(7)	6505(3)	48(2)
C(10)	3117(4)	5324(7)	6517(3)	49(2)
C(11)	2917(5)	5249(9)	7113(4)	71(2)
C(12)	3531(7)	4733(10)	7685(4)	93(3)
C(13)	4362(7)	4299(10)	7684(4)	88(3)
C(14)	4567(6)	4351(9)	7098(4)	74(2)
C(15)	658(4)	5369(8)	3952(4)	56(2)
C(16)	1135(4)	5161(7)	4642(3)	52(2)
C(17)	1018(4)	6059(7)	5115(3)	52(2)
C(18)	405(5)	7101(8)	4915(4)	64(2)
C(19)	-93(5)	7244(8)	4230(5)	71(2)
C(20)	35(5)	6413(9)	3751(4)	64(2)
C(21)	828(4)	4473(8)	3441(4)	62(2)
C(22)	1758(5)	3967(7)	4867(4)	62(2)
C(23)	1562(4)	5878(8)	5851(3)	64(2)
C(24)	261(5)	8107(9)	5410(5)	85(3)
C(25)	-511(6)	6669(10)	3019(4)	94(3)
C(26)	3173(5)	8152(8)	4441(4)	64(2)
C(27)	1694(6)	9177(12)	4092(6)	136(4)
C(28)	3061(7)	10376(10)	4098(6)	138(4)
C(29)	3145(10)	1230(13)	6087(9)	184(4)
C(30)	3159(9)	-1086(11)	6095(6)	140(4)
C(29')	3159(9)	-1086(11)	6095(6)	140(4)
C(30')	3145(10)	1230(13)	6087(9)	184(4)
C(31)	4521(7)	50(14)	6067(7)	165(5)

Table 1 Crystal and experimental data

Formula: C ₆₂ H ₇₂ Cu ₂ N ₄ O ₁₆
Formula weight = 1256.32
Crystal system: monoclinic,
Space group: <i>P</i> 2 ₁ / <i>n</i> <i>Z</i> = 2
<i>a</i> = 15.528(5) Å
<i>b</i> = 10.052(3) Å β = 103.697(4)°
<i>c</i> = 21.035(6) Å
<i>V</i> = 3091.3(16) Å ³
<i>D</i> _x = 1.350 g/cm ³
No. of reflections used = 5431
2θ _{max} = 50.02° with Mo <i>K</i> _α
<i>R</i> = 0.0621
<i>wR</i> = 0.1490
Goodness-of-fit = 1.040
(Δσ) _{max} = 0.000
(Δρ) _{max} = 0.599 e Å ⁻³
(Δρ) _{min} = -0.595 e Å ⁻³
Measurement: Bruker SMART CCD
Program system: SHELXS-97
Structure determination: direct method
Refinement: full matrix
CCDC No. 619686

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Table 3 Selected bond lengths (Å) and angles (°)

Cu(1)-O(2)#1	1.955(4)	Cu(1)-O(5)#1	1.970(4)
Cu(1)-O(4)	1.971(4)	Cu(1)-O(1)	1.973(4)
Cu(1)-O(7)	2.142(4)	Cu(1)-Cu(1)#1	2.6235(15)
O(2)#1-Cu(1)-O(5)#1	92.60(19)	O(2)#1-Cu(1)-O(4)	86.81(18)
O(5)#1-Cu(1)-O(4)	168.68(18)	O(2)#1-Cu(1)-O(1)	168.63(18)
O(5)#1-Cu(1)-O(1)	87.00(18)	O(4)-Cu(1)-O(1)	91.36(17)
O(2)#1-Cu(1)-O(7)	99.16(18)	O(5)#1-Cu(1)-O(7)	98.39(18)
O(4)-Cu(1)-O(7)	92.86(17)	O(1)-Cu(1)-O(7)	92.14(17)
O(2)#1-Cu(1)-Cu(1)#1	84.02(14)	O(5)#1-Cu(1)-Cu(1)#1	82.74(13)
O(4)-Cu(1)-Cu(1)#1	85.96(13)	O(1)-Cu(1)-Cu(1)#1	84.66(13)
O(7)-Cu(1)-Cu(1)#1	176.56(13)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

Fig. 1 Chemical diagram of complex 1.

hexahedra.² MOPs have voids within their structures where guest solvent molecules or counterions reside. Their structures have been constructed from nodes of either single metal ions or metal carboxylate clusters that are joined by organic links.³ Here, we report an 8-shaped discrete porous Cu(II) supramolecule constructed by a derivative of salicylic acid and Cu(AcO)₂.

All chemicals used were of analytical reagent grade and were used directly without further purification. The ligand (42.0 mg, 0.1 mmol), 2,4-bis[(2'-carboxyphenoxy)methyl]-1,3,5-trimethylbenzene (H₂L), was reacted with Cu(AcO)₂·H₂O (20.0 mg, 0.1 mmol) in 5 mL DMF. Slow evaporation of the solvent gave pale blue crystals. The X-ray diffraction data for complex 1 were collected on a Bruker SMART CCD1000 diffractometer equipped with a monochromator in the Mo K α (λ = 0.71073 Å) incident beam. The crystal and experimental data are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond lengths and angles are given in Table 3. A chemical diagram is shown in Fig. 1, and the structure is shown in Fig. 2.

From the crystal structure, the copper carboxylate paddlewheel forms in this compound and joins two ligands to two rings.⁴ Thus, compound 1 looks like the number symbol '8'. Each Cu(II) ion is coordinated by four carboxylate O donor atoms from two ligands and by O donor atoms from the solvent molecule, DMF. The Cu-O distances range from 1.955(4) to 2.142(4) Å, with an average of 2.006 Å. The oxygen-copper-oxygen bond angles on each side of the

Fig. 2 Ortep drawing of 8-shaped complex 1 (20% probability ellipsoids; the free counter anions as well as the solvent molecules and hydrogen atoms have been removed for clarity).

Fig. 3 2-D porous sheet constructed by 8-shaped units with hydrogen bonds.

paddlewheel range from 86.81(18) to 92.60(19)°. The copper-copper bond length of 2.6235(15) Å is normal. There are two hydrogen bonds between a phenyl ring, and two oxygen atoms from another complex molecule (C(5)···O(1) 3.3924 Å, $\angle$ C(5)-H5···O(1) 152°; C(6)···O(3) 3.4306 Å, $\angle$ C(6)-H6···O(3) 150°). Thus, a 2-D porous sheet was constructed by intermolecular hydrogen bonds between neighboring 8-shaped units (Fig. 3).

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References

1. A. Stein, *Adv. Mater.*, **2003**, *15*, 763.
2. N. Takeda, K. Umemoto, K. Yamaguchi, and M. Fujita, *Nature*, **1999**, *398*, 794.
3. J. P. Bourgeois, M. Fujita, M. Kawano, S. Sakamoto, and K. Yamaguchi, *J. Am. Chem. Soc.*, **2003**, *125*, 9260.
4. N. Schultheiss, J. M. Ellsworth, E. Bosch, and C. L. Barnes, *Eur. J. Inorg. Chem.*, **2005**, 45.