

Supporting Information

Design and programmable self-assembly of eight-coordinate Cu(II) heterometallic structure via dipalladium corner as building block

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Instruments and Methods

Instruments and Methods: NMR experiments of all compounds were recorded at 400 MHz on a Bruker Avance III HD 400 spectrometer using tetramethylsilane. ESI-MS measurements were performed with an JEOL Accu-TOF-4G LC-plus mass spectrometer. The FT-IR spectra were recorded as KBr pellets on a Shimadzu IR Prestige-21 spectrometer. The elemental analysis was performed on a Thermo Electron SPA Flash EA1112 analyzer. Thermal gravimetric and differential thermal gravimetric (TG-DTG) was carried out by heating in N₂ from room temperature to 800 °C at rate of 10 °C/min using a Perkin-Elmer Pyris1.

Experimental Section

All chemicals and solvents were of reagent grade and were purified according to conventional methods. Ligand 4-(4-carboxylatophenyl)pyrazolate (H₂L) was synthesized according to a reported procedure with spectroscopic data consistent with the literature.^[1] The metal complexes (bpy)Pd(NO₃)₂ was prepared according to literature procedures.^[2]

Synthesis of [(bpy)₂Pd₂(HL)₂](NO₃)₂ (**C1**): H₂L (11.3 mg, 0.06 mmol) was added to a suspension of (bpy)Pd(NO₃)₂ (23.2 mg, 0.06 mmol) in H₂O (1.0 mL) and acetone (0.5 mL), and the mixture was stirred for 8 h at room temperature. The mixture was stirred at 60 °C for 12 h and then the clear solution was dried under vacuum to obtain yellow crystalline material (28.4 mg, 0.024 mmol, 92.5% yield). ¹H NMR confirmed the quantitative formation of **C1**. ¹H NMR (400 MHz, D₂O, 298 K, ppm) : 8.81 (d, 4H, bpy-Ha) , 8.72 (d,4H, bpy-Hc) , 8.48 (d, 4H, bpy-Hb) , 8.37 (s, 4H, pz-H1) , 8.26 (d, 4H, ph-H2) , 8.07 (d, 4H, ph-H3) , 8.00 (t, 4H, bpy-Hd). ESI-MS (CH₃COCH₃): m/z Calcd for [**C1**·NO₃]⁺ 961.58, [**C1**]²⁺ 449.79; Found 449.95, 961.89. Elemental analyses calcd (%)

for $C_{40}H_{28}N_8O_4Pd_2$: C, 53.53; H, 3.14; N, 12.48; Found: C, 53.39; H, 3.16; N, 12.51. IR: (KBr, cm^{-1}): 3400 (O-H), 1700 (C=O) 1608, 1540, 1500, 1470, 1450, 1425 (C=C), 1385 (C-N), 1100 (C-O).

Synthesis of $[(bpy)_4Pd_4CuL_2](NO_3)_2$ (**1**): A solution of **C1** (11.79 mg, 0.01 mmol) in methanol (1 mL) and NaOH solution (0.2 mM in water) was carefully layered on top of a solution of $Cu(NO_3)_2$ (2.415 mg, 0.01 mmol) in water/methanol (1:1 v/v, 1 mL) solvent separated by a layer of water/methanol (1:2 v/v, 2 mL) mixed solvent. After one month, the green crystals were obtained (21.20mg, 85.2 % yield). Elemental analyses calcd (%) for $C_{80}H_{56}CuN_{18}O_{14}Pd_4$: C, 48.46; H, 2.85; N, 12.72; Found: C, 48.43; H, 2.83; N, 12.70. IR (KBr, cm^{-1}): 3400 (O-H), 1610, 1540, 1500, 1470, 1450, 1425 (C=C), 1385 (C-N), 1100 (C-O).

NMR spectrum

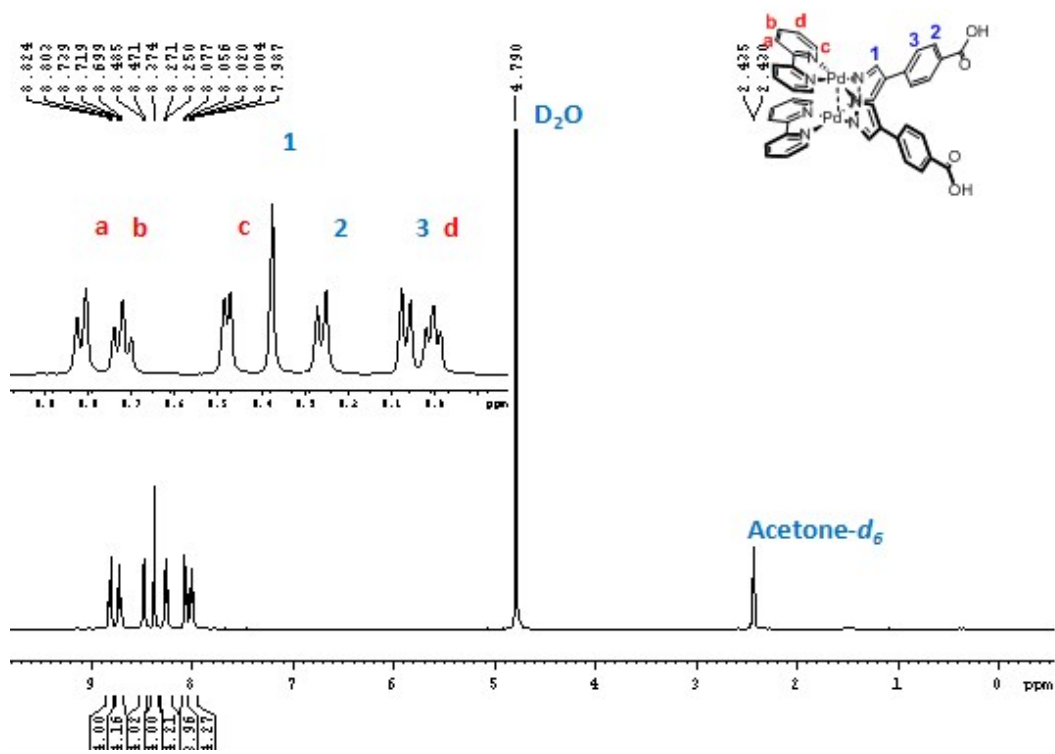


Figure S1 ^1H NMR (400 MHz, 298 K) spectrum of C1 in D_2O .

ESI-MS spectrum

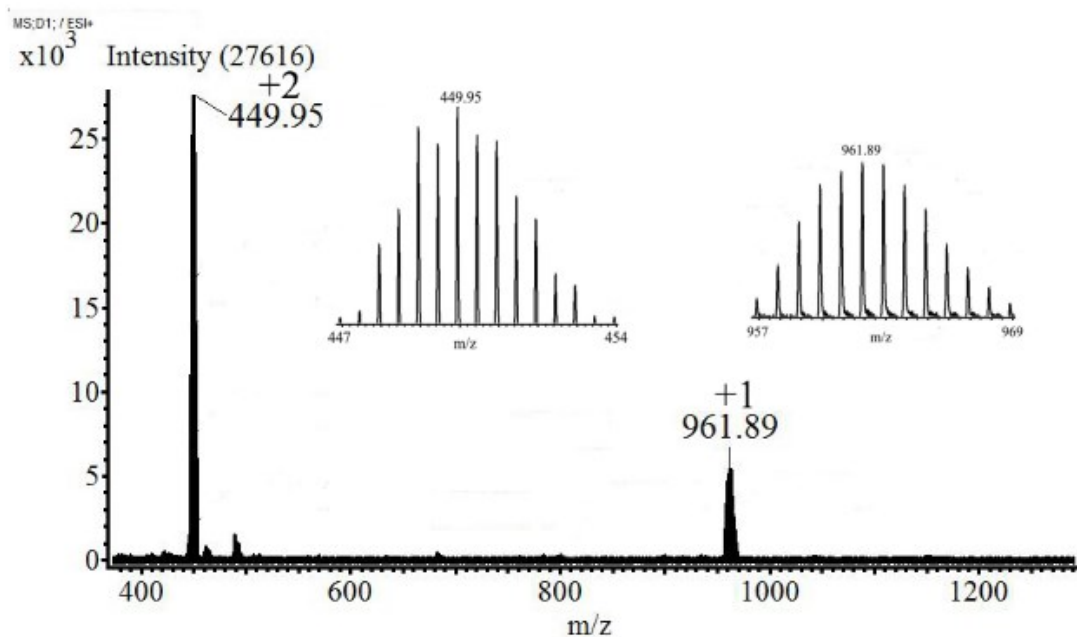


Figure S2 The ESI-MS spectrum of C1 in methanol

IR spectrum

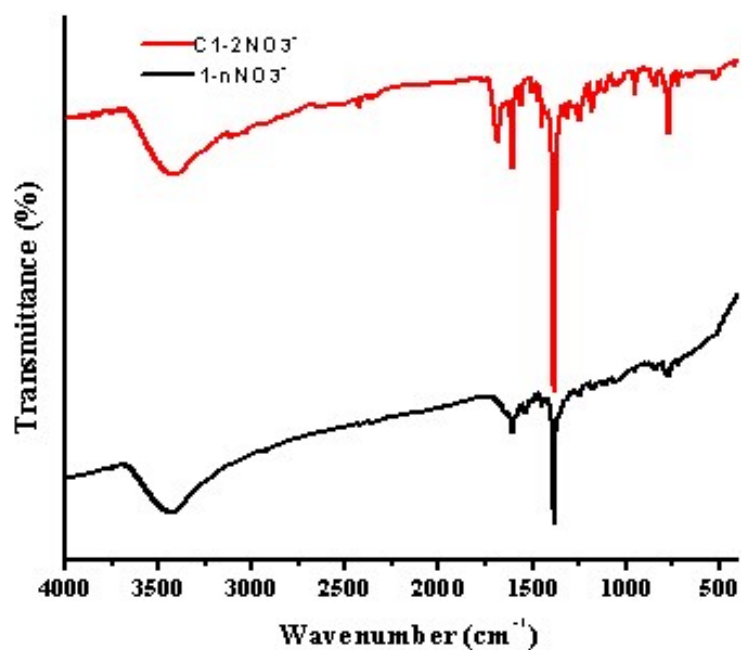


Figure S3 The IR spectrum of C1 and 1.

TGA data

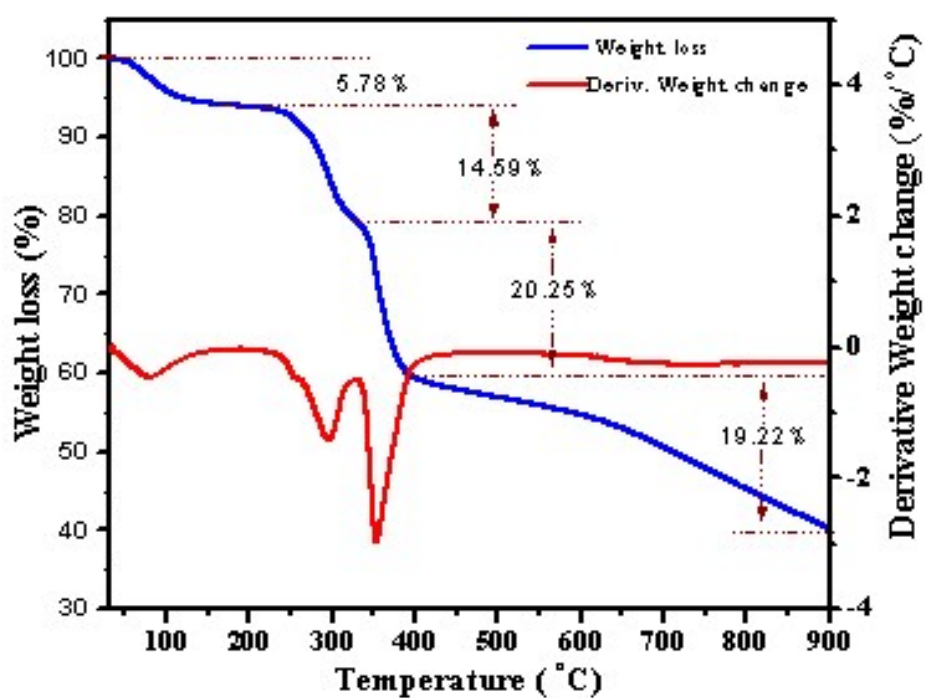


Figure S4 Thermogravimetric analysis (TGA) of 1 under N₂ atmosphere.

X-ray Structural Determination: X-Ray diffraction data of the crystals of complex **C1** were collected at 173 K on a Bruker Smart Apex CCD area detector equipped with a graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined employing full-matrix least-squares on F^2 by using SHELXTL (Bruker, 2008) program and expanded using Fourier techniques.[3-4] All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealized positions. In complexes **C1**, the unit cell includes a large region of disordered solvent methanol molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules, thereby, to produce a set of solvent-free.

Data for **1** were carried out at 173 K using synchrotron radiation ($\lambda = 0.720 \text{ \AA}$) via the 3W1A in the IHEP with the approval of the Beijing Synchrotron Radiation Facility (BSRF). The diffraction data reduction and integration were performed by the HKL2000 software. Most of the nonhydrogen atoms were found using the direct methods program in the Bruker SHELXTL software. In complexes **1**, the unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules, thereby, to produce a set of solvent-free.

CCDC 1980844 (**C1**), 1980845 (**1**) contains the supplementary crystallographic data for this paper. These data can be achieved via the Cambridge Crystallographic Data Centre deposit @ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk/deposit>.

The final residuals along with unit cell, space group, data collection, and refinement parameters are presented in Tables S1-S3.

X-ray diffraction measurement

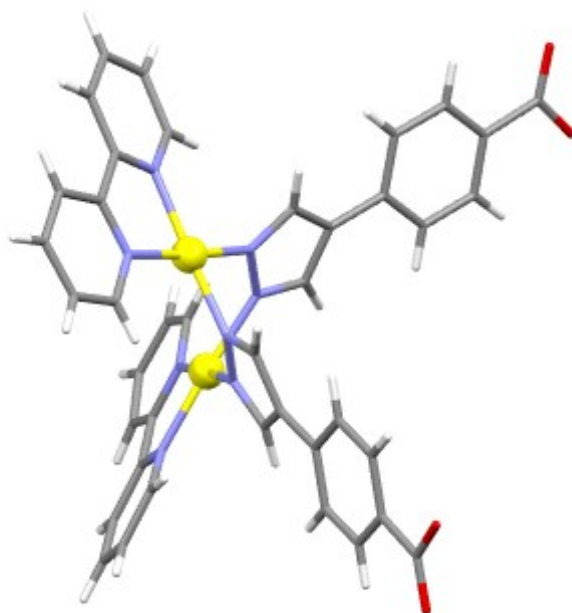


Figure S5 Crystal structure of **C1**.

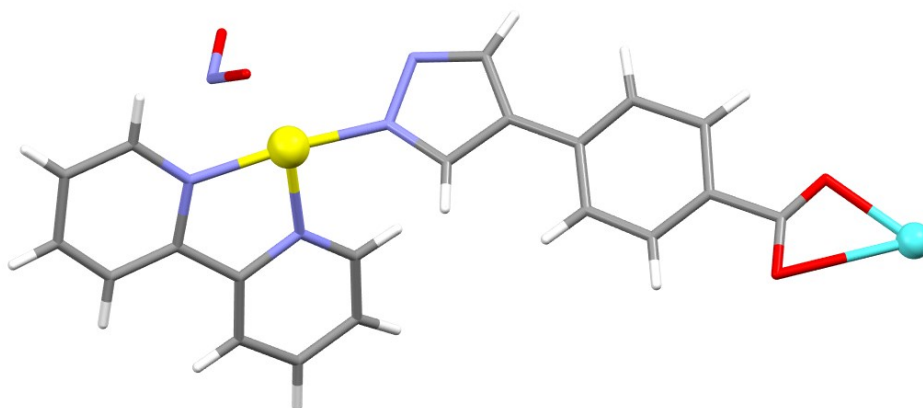


Figure S6 Asymmetric unit in the crystal structure of **1**.

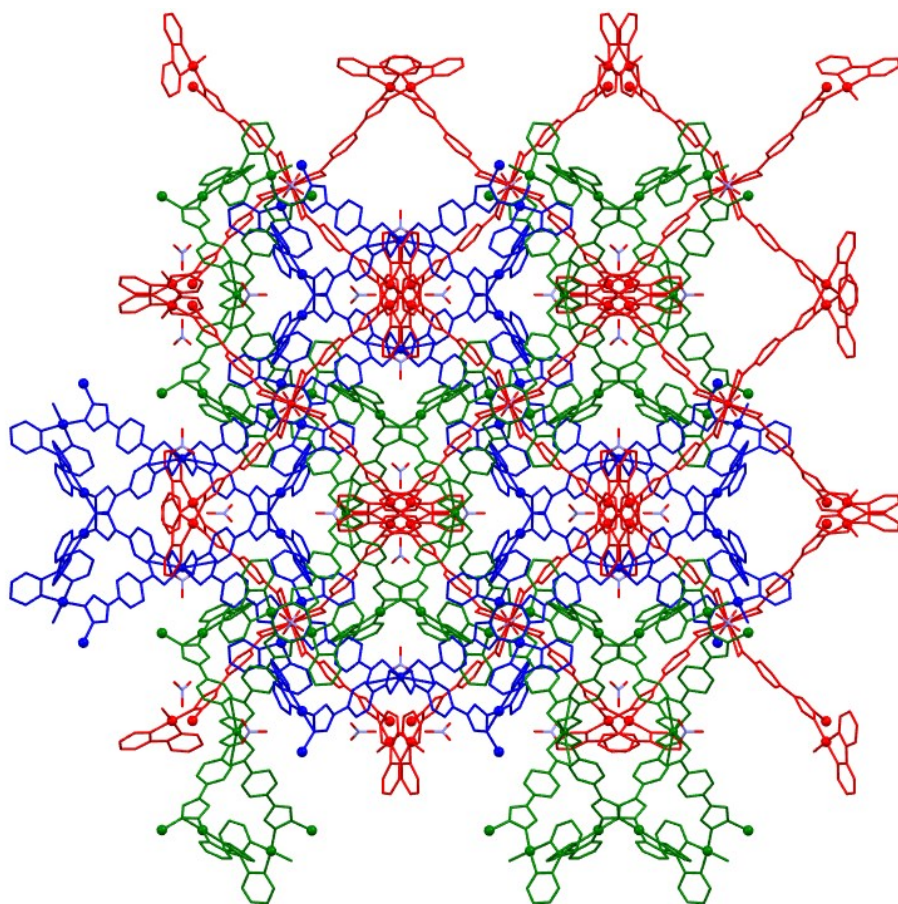


Figure S7 The 3D framework of **1** showing interpenetration.

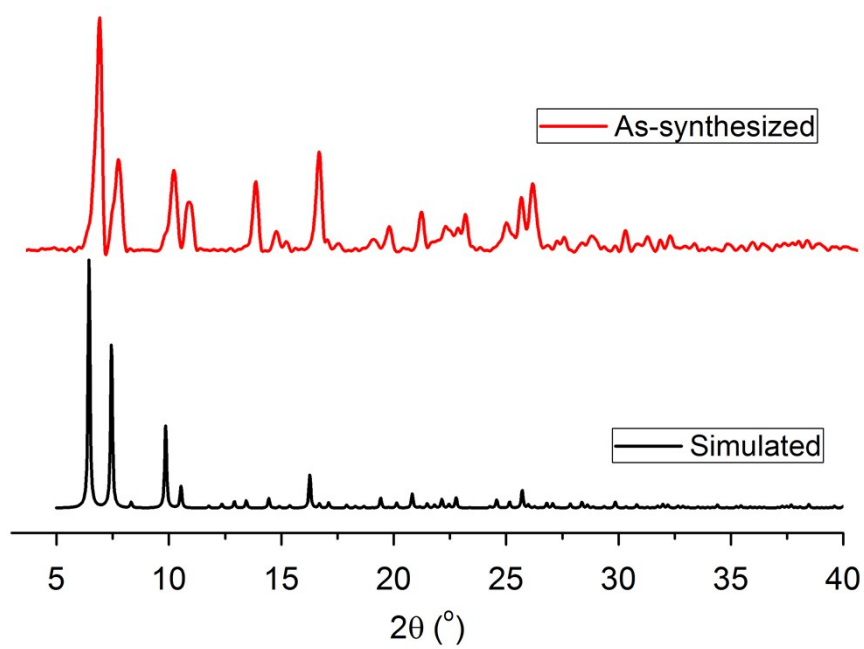


Figure S8 Powder XRD pattern for **1**.

Table S1 Crystal data and structure refinement for **C1** and **1**.

	C1	1
Formula	C ₄₀ H ₂₈ N ₈ O ₄ Pd ₂	C ₈₀ H ₅₆ CuN ₁₈ O ₁₄ Pd ₄
Formula weight	897.50	1982.56
Temperature/K	173(2)	173(2)
Crystal system	monoclinic	cubic
Space group	<i>C2/c</i>	<i>I-43d</i>
a/Å	19.4170(19)	33.5608(19)
b/Å	28.8384(18)	33.5608(19)
c/Å	17.3860(15)	33.5608(19)
α /°	90	90
β /°	91.524	90
γ /°	90	90
Volume/Å ³	9731.9(14)	37800(6)
Z	8	12
ρ _{calc} /g/cm ³	1.225	1.045
μ /mm ⁻¹	0.780	0.793
F(000)	3584	11844
Crystal size/mm ³	0.260 × 0.240 × 0.220	0.24 × 0.22 × 0.18
2θ range for data collection/°	1.835 - 26.000	2.750 - 26.990
Index ranges	-19 ≤ h ≤ 23, -18 ≤ k ≤ 35, -21 ≤ l ≤ 21	-42 ≤ h ≤ 42, -42 ≤ k ≤ 42, -31 ≤ l ≤ 31
Reflections collected	20062	52138
Independent reflections [R _{int}]	9456 [0.0325]	5525 [0.0095]

Data/restraints/parameters	9456/1/487	5525/1/265
Goodness-of-fit on F^2 [a]	1.027	1.065
$R1, wR2$ ($I > 2(I)$) [b]	0.0394, 0.1005	0.0277, 0.0755
$R1, wR2$ (all data) [b]	0.0441, 0.1021	0.0310, 0.0760
resid. el. dens.[$e/\text{\AA}^3$]	1.195/-0.743	0.297/-0.248

[a] $GOF = [w(F_o^2 - F_c^2)] / (n - p)^{1/2}$, where n and p denote the number of data points and the number of parameters, respectively. [b] $R1 = (||F_o|| - ||F_c||) / ||F_o||$; $wR2 = [w(F_o^2 - F_c^2)] / [w(F_o^2)]^{1/2}$, Where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2) / 3$.

Table S2 Selected Bond Lengths (\AA) and Bond Angles ($^\circ$) for **C1**.

N1-Pd1	2.021(2)	N5-Pd1	2.028(2)
N2-Pd1	2.015(3)	N6-Pd2	2.022(3)
N3-Pd2	2.006(2)	N7-Pd2	2.011(2)
N4-Pd2	2.011(2)	N8-Pd1	2.015(3)
N3-Pd1-N4'	87.75(9)	N7-Pd2-N6	96.58(10)
N3-Pd1-N2	176.85(10)	N7-Pd2-N8'	86.44(10)
N4'-Pd1-N2	95.39(10)	N6-Pd2-N8'	176.64(10)
N3-Pd1-N1	96.44(10)	N7-Pd2-N5	174.75(11)
N4'-Pd1-N1	173.52(10)	N6-Pd2-N5	80.93(12)
N2-Pd1-N1	80.45(10)	N8'-Pd2-N5	95.94(11)

Table S3 Selected Bond Lengths (\AA) and Bond Angles ($^\circ$) for **1**.

N3-Pd1	1.950(3)	Pd1-Pd1'	3.501(8)
N4-Pd1'	1.970(4)	Cu-Cu ¹	18.761(12)
N2-Pd1	1.988(4)	Cu-O1	2.766(5)
N1-Pd1	2.008(4)	Cu-O2	2.052(4)
O1-Cu1-O2	50.34(16)	O2_c-Cu1-C20	95.78(17)
O1-Cu1-C20	25.14(17)	C20-Cu1-C20_c	92.97(18)
O1-Cu1-O1_a	91.85(14)	O1_a-Cu1-O2_a	50.34(16)
O1-Cu1-O2_a	92.80(15)	O1_a-Cu1-C20_a	25.14(17)
O1-Cu1-C20_a	96.25(16)	O1_a-Cu1-O1_b	91.85(14)
O1-Cu1-O1_b	159.30(16)	O1_a-Cu-O2_b	92.80(15)
O1-Cu1-O2_b	149.65(16)	O1_a-Cu1-C20_b	96.25(16)

O1-Cu1-C20_b	170.77(16)	O1_a-Cu1-O1_c	159.30(16)
N2-Pd1-N1	82.74(16)	C1-N1-Pd1	130.7(4)
N3-Pd1-N4'	89.20(15)	C5-N1-Pd1	110.8(3)
N3-Pd1-N1	92.70(15)	C10-N2-Pd1	126.6(3)
N4'-Pd1-N2	95.39(16)	C6-N2-Pd1	115.4(3)
C5-N1-Pd1	110.8(3)	N4-N3-Pd1	123.4(3)
C6-N2-Pd1	115.4(3)	C11-N3-Pd1	128.6(3)
N3-N4-Pd1'	121.6(3)	N3-N4-Pd1'	121.6(3)
N4-N3-Pd1	123.4(3)	C13-N4-Pd1'	130.2(3)
C10-N2-Pd1	126.6(3)	N3-Pd1-N4'	89.20(15)
C11-N3-Pd1	128.6(3)	N3-Pd1-N2	174.58(15)
C13-N4-Pd1'	130.2(3)	N4'-Pd1-N2	95.39(16)
C1-N1-Pd1	130.7(4)	N3-Pd1-N1	92.70(15)
N3-Pd1-N2	174.58(15)	N4'-Pd1-N1	178.05(15)
O1-Cu1-O2	50.34(16)	O2_c-Cu1-C20	95.78(17)
O1-Cu1-C20	25.14(17)	C20-Cu1-C20_c	92.97(18)
O1-Cu1-O1_a	91.85(14)	O1_a-Cu1-O2_a	50.34(16)
O1-Cu1-O2_a	92.80(15)	O1_a-Cu1-C20_a	25.14(17)
O1-Cu1-C20_a	96.25(16)	O1_a-Cu1-O1_b	91.85(14)
O1-Cu1-O1_b	159.30(16)	O1_a-Cu-O2_b	92.80(15)
O1-Cu1-O2_b	149.65(16)	O1_a-Cu1-C20_b	96.25(16)
O1-Cu1-C20_b	170.77(16)	O1_a-Cu1-O1_c	159.30(16)
O1-Cu1-O1_c	91.85(14)	O1_a-Cu1-O2_c	149.65(16)
O1-Cu1-O2_c	74.12(15)	O1_a-Cu1-C20_c	170.77(16)
O1-Cu1-C20_c	79.02(16)	O2_a-Cu1-C20_a	25.71(18)
O2-Cu1-C20	25.71(18)	O1_b-Cu1-O2_a	74.12(15)
O1_a-Cu1-O2	74.12(15)	O2_a-Cu1-O2_b	113.01(16)
O2-Cu1-O2_a	113.01(16)	O2_a-Cu1-C20_b	95.78(17)
O2-Cu1-C20_a	95.78(17)	O1_c-Cu1-O2_a	149.65(16)
O1_b-Cu1-O2	149.65(16)	O2_a-Cu1-O2_c	102.60(17)
O2-Cu1-O2_b	102.60(17)	O2_a-Cu1-C20_c	128.07(18)
O2-Cu1-C20_b	128.07(18)	O1_b-Cu1-C20_a	79.02(16)
O1_c-Cu1-O2	92.80(15)	O2_b-Cu1-C20_a	100.59(17)
O2-Cu1-O2_c	113.01(16)	C20_a-Cu1-C20_b	92.97(18)
O2-Cu1-C20_c	100.59(17)	O1_c-Cu1-C20_a	170.77(16)
O1_b-Cu1-C20_b	25.14(17)	O1_c-Cu1-O2_c	50.34(16)
O1_b-Cu1-O2_b	50.34(16)	C20_b-Cu1-C20_c	92.97(18)
O1_b-Cu1-C20_c	96.25(16)	O1_c-Cu1-C20_b	79.02(16)

O2_b-Cu1-C20_b	25.71(18)	O2_b-Cu1-C20_c	95.78(17)
O1_c-Cu1-O2_b	74.12(15)	O2_b-Cu1-O2_c	113.01(16)

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