Supporting Information for:

Oligopyrrolic Cu(II)-based tetragonal cage: synthesis, structure, spectral and magnetic properties

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1. General information

Unless otherwise noted, all oxygen or moisture sensitive reactions were conducted in flame-dried glassware under nitrogen atmosphere. Dry tetrahydrofuran (THF) was obtained according to standard method prior to use, other reagents were purchased from commercial source and used without further purification.

Reactions were monitored by thin layer chromatography (TLC) carried out on Shanghai Shengya Chemicals (China) plates (GF254) using UV light as the visualizing agent. Column chromatographic purification of products was accomplished using forced-flow chromatography on Tsingdao Haiyang silica gel (200-300 mesh). ¹H-NMR spectra were recorded on Bruker AV400 MHz instrument and calibrated using TMS as an internal reference. FT-IR was recorded on a Nicolet 6700 Flex FTIR spectrometer. X-ray crystallographic analysis was performed on a Bruker D8 Venture CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) at 180 K. The structures were solved by intrinsic phasing methods and refined by full-matrix least-squares methods on F² with anisotropic thermal parameters for all non-hydrogen atoms by using the SHELXT¹ (intrinsic phasing methods) and refined by SHELXL² (full matrix least-squares techniques) in the Olex2³ package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms.

2. Preparation of ligand L and compound 1



Scheme S1. Synthetic route of ligand L.

4-nitrohexan-3-yl acetate (S2): To a mixture of 1-nitropropane (20.0 mL, 224 mmol) and propionaldehyde (19.0 mL, 263 mmol) at 0 °C was added DMAP (1.35 g, 11.2 mmol) slowly. The mixture was allowed to stir at room temperature for 72 h. The reaction mixture was diluted with DCM (135 mL) and then acetic anhydride (33.0 mL) was added. The solution was stirred at room temperature for 24 h before MeOH (25.0 mL) was added. The mixture was allowed to stir at room temperature for additional 6 h then diluted with EtOAc (1.5 L). The mixture was washed with H₂O, dried over anhydrous Na₂SO₄, then filtered and concentrated under reduced pressure to give **S2** as a pale-yellow liquid (45 g, yield: quantitative). The pale-yellow liquid can be used without further purification to the next step.

Ethyl 3,4-diethyl-5-iodo-1H-pyrrole-2-carboxylate (S4): To a mixture of S2 (34.8 g, 185 mmol) and ethyl 2-isocyanoacetate (21.0 g, 185 mmol) in dry THF (100 mL) at 0 °C was added DBU (54 mL, 360 mmol) dropwise. After stirring at room temperature overnight, acetic acid was added until the pH of the mixture turn to be neutral. The mixture was diluted with H₂O (60 mL) and extracted with EtOAc (100 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to obtain S3 as a dark red liquid. To a mixture of S3 and I₂ (117.7 g, 464 mmol) in DCM (1 L) was added aqueous solution (500 mL) of KI (153.7 g, 926 mmol) and NaHCO₃ (119.4 g, 1.42 mol). After the reaction mixture was allowed to stir at room temperature for 72 h, an aqueous solution (450 mL) of Na₂S₂O₃ (230 g, 1.46 mol) was added. The organic layers were washed with H₂O and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to obtain S3 as added. The organic phase was separated, and the aqueous layer was extracted with DCM (100 mL × 2). The combined organic layers were washed with H₂O and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product S4 as a pale-yellow solid (31.3 g, yield: 53% over 2 steps). ¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H).

Ethyl 3,4-diethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carboxylate (S5): Pinacolborane (2.7 mL, 18.5 mmol) and Et₃N (5.0 mL, 39 mmol) were added slowly to a mixture of S4 (5.0 g, 15.57 mmol) and Pd(PPh₃)Cl₂ (0.11 g, 0.16 mmol, 0.01 equiv) in dry THF (50 mL). The mixture was stirred at 60 °C for 3 h and diluted with hexane (125 mL), filtered, and the filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product S5 as an orange oil (4.6 g, yield: 91%). ¹H NMR (400 MHz, CDCl₃) δ 9.11 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 12H), 1.18 – 1.09 (dt, 6H).

Diethyl 5,5'-(pyridine-2,6-diyl)bis(3,4-diethyl-1H-pyrrole-2-carboxylate) (S6): To a mixture of 2,6-dibromopyridine (0.24 g, 1.0 mmol), Pd(OAc)₂ (0.0224 g, 0.1 mmol), PPh₃ (0.0525 g, 0.2 mmol) and K₂CO₃ (0.46 g, 3.3 mmol) in DMF/H₂O (20 mL, 4/1) was added **S5** (0.77 g, 2.4 mmol). The mixture was stirred at 90 °C for 24 h and diluted with DCM (20 mL). Precipitates were removed by filtration through Celite. The filtrate was washed with H₂O and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (petroleum ether/Et₂O = 10/1) to yield the product **S6** as a white solid (0.4 g, yield: 86%). ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 2H), 7.76 (t, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 4H), 2.82 (p, *J* = 7.6 Hz, 8H), 1.39 (t, *J* = 7.1 Hz, 6H), 1.28 (t, *J* = 7.5 Hz, 6H), 1.21 (t, *J* = 7.5 Hz, 6H).

5,5'-(pyridine-2,6-diyl)bis(3,4-diethyl-1H-pyrrole-2-carboxylic acid) (L): An aqueous solution (50 mL) of NaOH (1.4 g, 35 mmol) was added to a mixture of **S6** (2.7 g, 5.9 mmol) in EtOH (100 mL). The reaction mixture was stirred at 90 °C overnight. Aqueous solution of HCl (1 M) was added to adjust pH of the system to acidic. The solid was collected by filtration, washed with H₂O and dried under vacuum to yield product L as white solid (2.3 g, yield: 94%). ¹H NMR (400 MHz, DMSO) δ 12.44 (s, 2H), 11.53 (s, 2H), 7.89 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 2.79 – 2.66 (m, 8H), 1.15 (dt, *J* = 22.8, 7.4 Hz, 12H).

 $[Cu_4L_4(CH_3OH)_2(H_2O)] \cdot 2DMF$ (1): Ligand L (0.1 mmol, 40.9 mg) was dissolved in a mixture of methanol (9 mL) and DMF (3 mL). When Cu(acac)_2 (0.1 mmol, 26.2 mg) was added to the mixture, the color immediately changed from blue to green. The resultant solution was stirred for 10 min at room temperature and then filtered. Cubic green crystals of 1 suitable for X-ray single-crystal diffraction were obtained by slow diffusion of pentane into the filtrate for a week at room temperature. Yield: 16% based on Cu.

Note: When $Cu(acac)_2$ (0.1 mmol, 26.2 mg) and various PF_6^- salts with different sizes of organic cations, including dimethylamine (DMA), tetraethylammonium (TEA) and tetrabutylammonium (TBA) (0.1 mmol) were added to the mixture, the same phenomenon was observed and still only 1 was obtained with almost unchanged yield.







Fig. S2 ¹H NMR of the compound S5 in CDCl₃.







Fig. S4 1 H NMR of the compound L in DMSO.



Fig. S5 Negative mode ESI-MS spectrum of L.

4. Single-crystal X-ray crystallography

Table S1.	Crystal	Data	and	Structure	Refinement	for 1

Compound reference	1
Chemical formula	$C_{100}H_{123}Cu_4N_{14}O_{21}$
Formula Mass	2110.87
Temperature (K)	180.0
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	12.4654(5)
<i>b</i> (Å)	14.3776(6)
<i>c</i> (Å)	16.9641(6)
α (°)	74.143(2)
eta (°)	72.291(2)
γ (°)	89.349(2)
Unit cell volume (Å ³)	2777.51(19)
Ζ	1
$ ho_{ m calc} ({ m g/cm^3})$	1.262
μ / mm ⁻¹	0.825
F (000)	1105
Radiation	MoKa ($\lambda = 0.71073$)
Reflections collected	42579
Independent reflections	9798
$R_{ m int}$	0.0856
GOF on F^2	1.019
$R_1(I \ge 2\sigma(I))$	0.0542
wR_2 (all data)	0.0131
CCDC number	2182868

Table 52. Selected bond distances and angles for complex I (A,).					
Cu1-O10	2.243(1)	Cu2-O1	1.969(3)		
Cu1-O4	1.928(4)	Cu2-O3	1.972(4)		
Cu1-O5	1.930(3)	Cu2-O7	1.983(3)		
Cu1-O6	1.932(4)	Cu2-O2	1.984(3)		
Cu1-O8	1.936(4)	Cu2-O9	2.127(4)		
O4-Cu1-O10	92.4(1)	O2-Cu2-O3	166.6(1)		
O6-Cu1-O10	93.5(1)	O7-Cu2-O1	168.0(1)		
O10-Cu1-O5	94.2(1)	O2-Cu2-O1	86.1(1)		
O10-Cu1-O8	94.5(1)	O7-Cu2-O3	88.4(1)		
O6-Cu1-O5	172.3(2)	O1-Cu2-O3	89.8(1)		
O4-Cu1-O8	173.0(2)	O2-Cu2-O7	93.0(1)		
O4-Cu1-O5	86.7(2)	O2-Cu2-O9	94.4(2)		
O6-Cu1-O8	87.3(2)	O7-Cu2-O9	94.6(2)		
O5-Cu1-O8	91.8(2)	O9-Cu2-O1	97.4(2)		
O4-Cu1-O6	93.2(2)	O9-Cu2-O3	98.8(2)		

Table S2. Selected bond distances and angles for complex 1 (Å, °).



Fig. S6 The distance between Cu(II) ion and basal plane.



Fig. S7 The intramolecular H-bonding between DMF in the lattice and axial CH₃OH.

5. Optical properties



Fig. S8 UV-Vis-NIR reflectance spectra of Cu(OAc)₂·H₂O and Cu₄L₄ (1).



Fig. S9 Powder XRD analyses of 1. The black line is simulated data from single crystal data.



Fig. S10 TGA curve of **1**. Note: A slight weight increase occurred at ca. 500 °C, possibly from a part of the explosive solid dropping into the crucible.



Fig. S11 Variable-temperature EPR data for **1** in solid state (upper). Experimental and the simulated spectra at 171 K (bottom).



Fig. S12 The static magnetic susceptibility of 1 along with the susceptibility simulated from the calculated exchange coupling constants.

6. Computational details

The geometry of **1** used in the calculations was extracted from the crystal structure. The positions of the hydrogen atoms were optimized using density functional theory (DFT), while the positions of heavier atoms were frozen to their crystal-structure coordinates. Four different broken symmetry (BS) states were optimized in the BS-DFT calculations.⁴ The states are listed in Table 1. Following the usual practice, the BS states were interpreted as energy expectation values of the Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian⁵

$$\hat{H}_{\rm HDvV} = -J_1 \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B - J_1' \hat{\mathbf{S}}_C \cdot \hat{\mathbf{S}}_D - J_2 \hat{\mathbf{S}}_B \cdot \hat{\mathbf{S}}_C$$
(1)

acting on the states and are, therefore, equivalent to the eigenstates of the Ising Hamiltonian

$$\hat{H}_{\text{Ising}} = -J_1 \hat{S}_{z,A} \hat{S}_{z,B} - J_1' \hat{S}_{z,C} \hat{S}_{z,D} - J_2 \hat{S}_{z,B} \hat{S}_{z,C}$$
⁽²⁾

where the exchange coupling constants J_1 and J_1 ' describe the two nearest-neighbor Cu–Cu exchange interactions between ions A and B, and C and D, respectively, and J_2 describes the exchange interaction between ions B and C mediated by the water molecule. The operators \hat{S}_A and $\hat{S}_{z,A}$ are an effective spin operator and an effective spin projection operator, respectively, acting on spin site A. The exchange coupling constants can be evaluated from the energies of the spin configurations as

$$J_{1} = -2E_{1} + 2E_{2} - 2E_{3} + 2E_{4}$$

$$J'_{1} = -2E_{1} + 2E_{4}$$

$$J_{2} = 2E_{3} - 2E_{4}$$
(3)

All calculations were carried out using the *Gaussian* 16 quantum chemistry code revision C.01.⁶ The rangeseparated hybrid exchange-correlation functional LC- ω PBE⁷ was used along with def2-SVP basis sets for the geometry optimization and def2-TZVP basis sets for the energy evaluations.⁸ Dispersion effects were treated in the geometry optimizations with the empirical DFT-D3 dispersion correction⁹ along with the Becke– Johnson damping function.¹⁰ The LC- ω PBE functional was chosen due to its ability to produce a good estimate of the exchange coupling constant in the related copper acetate cartwheel complex.¹¹ The geometry optimization was carried out using the $M_S = 0$ BS spin state. No spatial or spin symmetry restrictions were enforced and stability analyses¹² were carried out on all optimized wave function to ensure that they represent true minima in the molecular orbital coefficient space.

The magnetic susceptibility was simulated based on the calculated exchange coupling parameters using the *PHI* program version 3.1.5.¹³

Spin configuration	Spins	of the C	u(II) ioi	ns	E(absolute) / Hartree	$E(\text{relative}) / \text{cm}^{-1}$
1	↑	1	↑	↑	-12294.6987859	0.000
2	↑	\downarrow	↑	↑	-12294.6994641	-148.848
3	↑	1	\downarrow	1	-12294.6994649	-149.023
4	1	1	1	\downarrow	-12294.6994646	-148.957

Table S3. The different spin configurations and their energies used in the BS-DFT calculations

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