

COMMUNICATION

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

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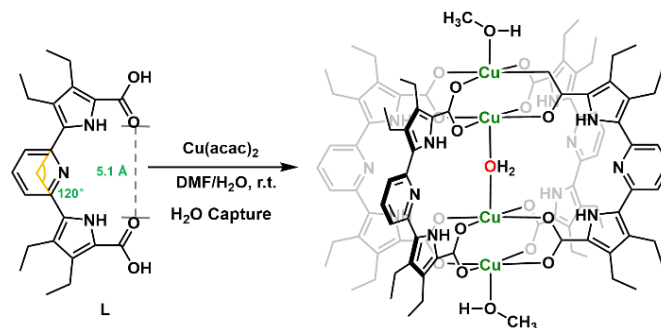
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The first oligopyrrolic Cu(II)-based metallocage featuring two antiferromagnetically coupled dimeric cupric tetracarboxylate units linked by a single molecule of water was assembled successfully using a nonlinear pyridine-pyrrolic ligand. Broken symmetry density functional theory (BS-DFT) calculations show that the exchange couplings between Cu(II) ions in Cu₂ unit and over the water bridge are -298 and -0.13 cm⁻¹, respectively.

Since the known paddle-wheel structure of cupric acetate dehydrate was reported in 1953,^{1, 2} copper(II) carboxylates with general formula [Cu₂(COOR)₄] have gained considerable attentions of a wide cross-section of the chemistry community as they not only can be used as a rigid secondary building unit (SBU) to prepare coordination polymers (CPs),³ metal-organic frameworks (MOFs)⁴ and metal-supported cages⁵ but also exhibit fascinating magnetic properties,^{6, 7} showing promising applications in gas storage,^{8, 9} catalyst,¹⁰ and biology. In particular, the studies on the magnetic coupling of copper acetate provided the starting point for the entire research field of molecular magnetism,^{11, 12} a vibrant field aiming at developing magnetic molecules for high-density data storage applications, mainly including molecular permanent magnets,¹³ single-molecule magnets,¹⁴ and single-chain magnets (SCMs).¹⁵ In addition, attention was drawn early to the possibility of a Cu-Cu bond in cupric acetate dimer. According to the Cu(II)-Cu(II) distance of 2.64 Å¹ and the covalent atom radius of Cu of 1.32 Å,¹⁶ the Cotton's formal shortness ratio (FSR) value of Cu(II) acetate dimer can be calculated to be 1.0,¹⁷ implying the presence of Cu(II)-Cu(II) single bond. However, such bonding interaction is rather weak described as a δ bond rather than σ

bond arising from overlap between the two copper d orbitals.¹⁸ The mechanism of spin-spin coupling in [Cu(OAc)₂·H₂O]₂ is predominantly dominated by the super-exchange interaction through the bridging carboxylate ligands rather than by metal-metal interaction. Consequently, its magnetic properties can be modified by regulating the ligand field, i.e. using different bridging and axial ligands.¹⁹ Although various types of polymeric chains²⁰⁻²² and MOFs²³⁻²⁷ assemblies of dicopper-tetracarboxylate motif have been reported, the precise structure construction implemented at the true molecular level is rare. In general, such discrete assemblies of paddlewheel-type Cu₂ unit require bridging ligands with suitable bend angles.^{8, 28, 29} Recently, oligopyrrolic cages have attracted intense attentions in the area of molecular recognition as the slightly polar pyrrole subunits can bind with various polarized species by hydrogen-bonding. In 2016, the first oligopyrrolic metallocage was prepared via metal-directed self-assembly between a pyridine-fused oligopyrrolic dicarboxylic acid linker (2,6-bis(3,4-diethyl-5-carboxy-1H-pyrrol-2-yl)pyridine, **L**, Scheme 1) and Zn(acac)₂ (acac = acetylacetonate).³⁰ Subsequently, its morphology and multidimensional ensemble was finely tuned by using different counter cation sources.³¹ We notice that such a ligand is inherently nonlinear exhibiting a bend angle close to 120° between the two pyrrole subunits. In addition, the two pyrroles are almost coplanar and the inter-carboxylic-acid distance is about 5.1 Å (Scheme 1).³⁰



Scheme 1. Synthetic protocol for **1**.

Inspired by the proper geometry and size of **L** in constructing discrete assemblies of Cu₂ unit, here, the first

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oligopyrrolic metallocage $[\text{Cu}_4\text{L}_4(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})]\cdot 2\text{DMF}$ (**1**) with two coupling Cu_2 units by a single molecule of water was successfully prepared. Magnetic investigations revealed the exchange coupling between $\text{Cu}(\text{II})$ ions in Cu_2 unit and over the water bridge of -298 and -0.13 cm^{-1} , respectively.

The synthesis of **1** was improved giving the overall yield of 39% over 6 steps (details see Supporting Information, Scheme S1, Fig. S1-S3). **1** was characterized by ^1H NMR (Fig. S4) and electrospray ionization mass spectrometry (ESI-MS) (Fig. S5) and the results were consistent with the previous report.³⁰ Compound **1** was prepared by reacting **L** with $\text{Cu}(\text{acac})_2$ in $\text{DMF}/\text{CH}_3\text{OH}$ solution ($v/v = 1:4$) (Scheme 1). Distinguished from reacting **L** with $\text{Zn}(\text{acac})_2$,³¹ where the cage structures were modulated by different ancillary organic cations, here, only **1** was obtained in the presence of various PF_6^- salts with different sizes of organic cations, including dimethylamine (DMA), tetraethylammonium (TEA) and tetrabutylammonium (TBA), probably due to the highly stable arrangement of dimeric cupric tetracarboxylate units.³²

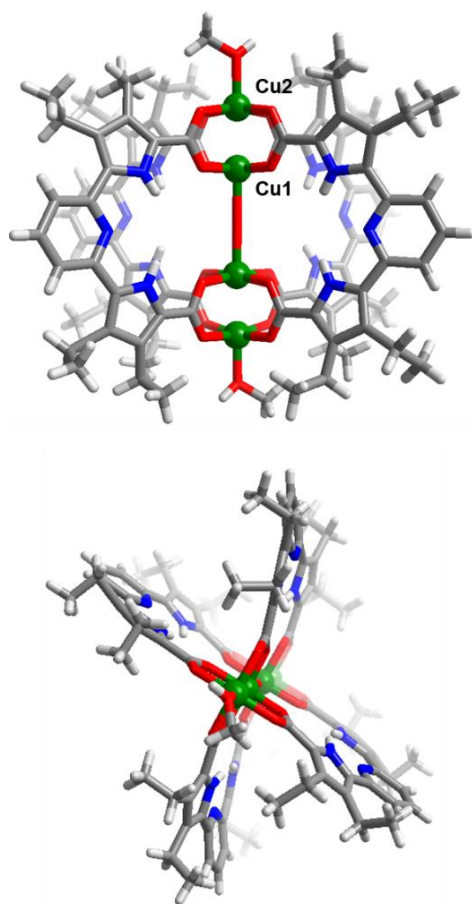


Fig. 1 X-ray structure of **1** viewed along the crystallographic a axis (upper) and c axis (bottom). Color code: Cu green, C gray, N blue, O red, H white.

The single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into above mixture solution. The complex crystallized in the triclinic $P\bar{1}$ space group with the asymmetric unit of a binuclear $\text{Cu}(\text{II})$ structure (Table S1). $\text{Cu}(\text{II})$ ions are surrounded by four **L** ligands in a *syn-syn* coordination mode to form a large paddlewheel-like

tetragonal cage (Fig. 1). Each $\text{Cu}(\text{II})$ ion was coordinated to five oxygen atoms, four of which from carboxylate-oxygen atoms of **L** at the equatorial positions and another one from CH_3OH or H_2O molecule at the axial position, leading to the square pyramidal coordination geometry with the angular structural parameter τ of 0.013 and 0.025 for $\text{Cu}1$ and $\text{Cu}2$, respectively.³³ The $\text{Cu}(\text{II})$ ions were displaced out of the basal plane by 0.123 ($\text{Cu}1$) and 0.216 Å ($\text{Cu}2$) toward axial ligand (Fig. S6). The basal $\text{Cu}-\text{O}$ distances range from 1.928(3) to 1.935(3) Å for $\text{Cu}1$ and 1.969(3) to 1.983(3) Å for $\text{Cu}2$ while the axial $\text{Cu}1-\text{O}_{\text{H}_2\text{O}}$ and $\text{Cu}2-\text{O}_{\text{MeOH}}$ bond lengths are respective 2.2431(5) and 2.127(3) Å (Table S2). The equatorial $\text{O}-\text{Cu}-\text{O}$ angles vary from 86.74(17) to 173.05(14)° for $\text{Cu}1$ and 86.14(14) to 168.04(13)° for $\text{Cu}2$ and the axial $\text{O}_{\text{MeOH}}-\text{Cu}2-\text{Cu}1$ and $\text{Cu}2-\text{Cu}1-\text{O}_{\text{H}_2\text{O}}$ arrangement are almost linear with angles of 176.46(13) and 179.33(3)°, respectively. A relatively short $\text{Cu}(\text{II})-\text{Cu}(\text{II})$ internuclear separation of 2.5825(8) Å was observed giving FSR value of 0.98. The dimensions and inner cavity sizes are 9.65 (outer $\text{Cu}-\text{Cu}$ height) \times 17.74 Å (C-C distance from opposite ligand) and 4.48 (inner $\text{Cu}-\text{Cu}$ height) \times 12.23 Å (N-N distance from opposite ligand), respectively. Such a molecular cavity is suitable to trap a H_2O molecule. Note that the outer axial sites were blocked by the intramolecular H-bonding between axial CH_3OH and non-coordinated DMF molecule in the lattice (Fig. S7) and no intermolecular noncovalent interactions were observed, both preventing the formation of extended frameworks.

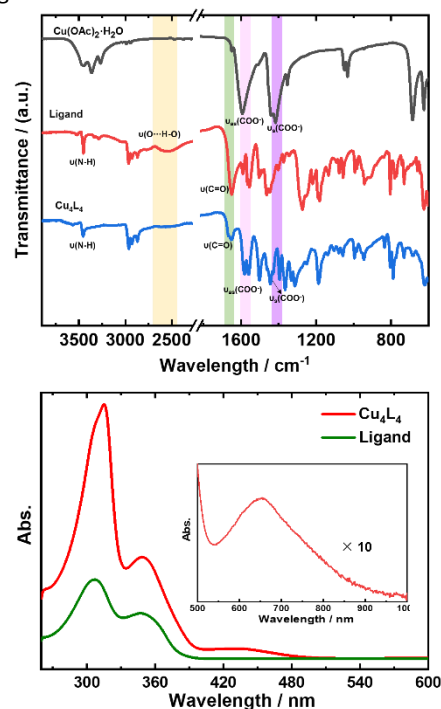


Fig. 2 FT-IR spectra of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$, **L** and **1** (upper). UV-visible spectra of **L** and **1** ($c = 10^{-5}$ $\text{mol}\cdot\text{L}^{-1}$ in DMF) (bottom). Inset: amplified spectrum in the range of 500-1000 nm.

The compound was characterized by FT-IR spectrum, UV-Vis absorption spectrum and UV-Vis-NIR reflectance spectrum. Fig. 2 shows the FT-IR spectra of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$, ligand **L** and compound **1**. Compared to the free ligand **L**, the depletion of a broad band at ~ 2700 cm^{-1} ascribed to the stretching vibrations of hydrogen-bonded O-H groups and a strong peak at 1650 cm^{-1}

¹ assignable to the $\nu(\text{C}=\text{O})$ stretching vibrations of $-\text{COOH}$ group confirmed the coordination of $\text{Cu}(\text{II})$ ions to carboxylate groups. A weak $\nu(\text{C}=\text{O})$ band at 1657 cm^{-1} from DMF molecule in the lattice was observed. Additionally, the coordination mode of the carboxylate groups to $\text{Cu}(\text{II})$ ions was inferred from the difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ vibrations. For **1**, the difference is estimated to be $\sim 160\text{ cm}^{-1}$ comparable to that in $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$, suggesting the *syn-syn* bidentate bridging coordination of carboxylates.³⁴ As the compound is almost insoluble in MeOH, the UV-Vis spectra were recorded in DMF at room temperature. A broad absorption band with maximum at 656 nm corresponding to the typical d-d transition for five-coordinate $\text{Cu}(\text{II})$ ions with square pyramidal geometry was clearly observed.³⁵ In addition, the spectrum shows a typical ligand to metal charge transfer (LMCT) band at $405\text{--}490\text{ nm}$, which is common for copper(II) carboxylates,³⁶ and a red-shift of intra-ligand $\pi\text{--}\pi^*$ transition from 306 nm in **L** to 315 nm in **1**. The reflectance spectra of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ and **1** resemble each other in shape (Fig. S8), exhibiting two significant bands, Band I and Band II, corresponding to the ligand-field transition and the LMCT process, respectively. All spectral data clearly support the structure of **1** as determined by the X-ray diffraction method.

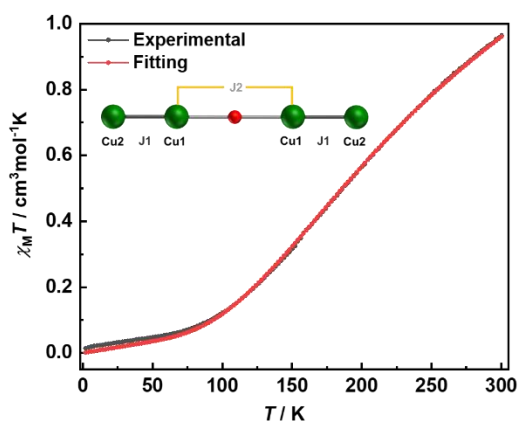


Fig. 3 The static magnetic susceptibility of **1** in a field of 1000 Oe along with the best fit by *PHI* package. Inset: *J*-coupling model employed for the elucidation of the magnetic exchange interactions in **1**.

Before magnetic characterization, the phase purity and thermal stability of **1** were rigorously verified by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA), respectively (Fig. S9 and S10). Examination of TGA curve disclosed that the entire molecule is relatively stable up to $70\text{ }^\circ\text{C}$. The magnetic susceptibility data of **1** were collected in the temperature range of $1.9\text{--}300\text{ K}$ under a dc field of 1000 Oe using SQUID magnetometry on polycrystalline samples and were shown in χT vs. T plot in Fig. 3. At 300 K , the χT value is $0.965\text{ cm}^3\text{ mol}^{-1}\text{ K}$, obviously smaller than the expected value of $1.5\text{ cm}^3\text{ mol}^{-1}\text{ K}$ for four magnetically isolated $\text{Cu}(\text{II})$ ions. Upon cooling, a dramatic decrease of χT values were observed. This behavior is characteristic of the strong antiferromagnetic $\text{Cu}(\text{II})\cdots\text{Cu}(\text{II})$ interaction in paddle-wheels dimers, leading to an $S = 0$ ground state.³⁷ Note that a true plateau was not reached at low temperature regime, which may be caused by the residual $\text{Cu}(\text{II})$ ions on the surface of the sample. To confirm this,

variable-temperature X-band powder EPR spectra were collected, where only peaks of $\text{Cu}(\text{II})$ ion were observed at 11 and 7.7 K , indicating the ground state of $S = 0$ (Fig. S11). When increasing the temperature, the signals of typical $\text{Cu}(\text{II})$ dimeric compounds with carboxylate bridges occurred which can be well reproduced by the parameters $S = 1$, $g = 1.99$, $D = 0.28\text{ cm}^{-1}$. A satisfactory fit of the susceptibility data was obtained with *PHI* by including a temperature-independent paramagnetism (TIP), with $g = 2.00$, $J_1 = -332\text{ cm}^{-1}$ and $J_2 = -0.12\text{ cm}^{-1}$ ($R^2 = 99.95\%$) (Fig. 3).³⁸ Note that such near-perfect agreement with the experiment is based on the assumption that the TIP contribution is the source of all deviations. In order to further elucidate intramolecular magnetic couplings in the present compound, broken symmetry density functional theory (BS-DFT) calculations were performed.^{39–44} The asymmetric unit of **1** consist of two nearest neighbor copper complexes with exchange coupling described by the parameter J_1 . Once hydrogen atoms are included on the oxygen bridge, the symmetry of the complex is somewhat lowered, and the exchange coupling constants in the two asymmetric units connected by the water bridge are no longer fully equivalent. Thus, two different exchange couplings were determined, but the values differed by less than half a wave number, which falls into the error margin of the BS-DFT calculations. The calculated value is $J_1 = -298\text{ cm}^{-1}$, which is very close to the exchange coupling -286 cm^{-1} of the copper acetate cartwheel dimer.¹¹ The exchange coupling over the water bridge was calculated as $J_2 = -0.13\text{ cm}^{-1}$. The magnetic susceptibility was simulated based on the calculated exchange coupling constants. The resulting χT plot is shown in Fig. S12 along with the measured magnetic susceptibility. The qualitative features of the susceptibility are well-reproduced by the calculations. Both the high-temperature and low-temperature susceptibility is somewhat underestimated. This most likely results from the residual $\text{Cu}(\text{II})$ ions and overestimation of the exchange coupling constants, which leads to higher spin states lying too high in energy.

In summary, an oligopyrrolic paddlewheel-like metallocage has been designed and prepared by coordination-directed self-assembly strategy and using a nonlinear pyridine dipyrrolic ligand. Structural analysis showed that it contains two dicopper-tetracarboxylate units bridged by a single molecule of water, which was also corroborated by optical spectra. Experimental and theoretical investigations revealed the strong anti-ferromagnetic super-exchange in the Cu_2 unit, attributed to the short $\text{Cu}(\text{II})\cdots\text{Cu}(\text{II})$ distance and the near-perfect square pyramidal coordination geometry of $\text{Cu}(\text{II})$ ions. Given that the coordinated solvent molecules can be removed to leave open metal sites,⁸ this cage is expected to have promising applications in gas separation and purification. Furthermore, this work encourages us to construct oligopyrrolic lanthanide self-assembled systems to study their luminescent and magnetic properties.

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Conflicts of interest

The authors declare no conflict of interest.

Notes and references

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Graphical Abstract

Oligopyrrolic Cu(II)-based metallocage was constructed featuring two antiferromagnetically coupled dimeric cupric tetracarboxylate units bridged by a single molecule of water.

Oligopyrrolic [Cu₄L₄] Cage