# **Electronic Supplementary Information**

### for

# Formation of a four-bladed waterwheel-type chloro-bridged dicopper(II) complex with dithiamacrocycle via double exo-coordination

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#### **Experimental Procedures**

**General.** All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 and 500 spectrometers (300 and 500 MHz). The Fourier transform infrared (FT-IR) spectra were measured with a Nicolet *i*S10 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.



Scheme S1. Synthesis of  $L^1$  and  $L^2$ .

Synthesis of L<sup>1</sup>. 1,2-Ethanedithiol (1.10 g, 11.68 mmol) and dichloride **5** (3.00 g, 8.45 mmol) were dissolved in DMF (50 mL) and added over one day to a suspension of Cs<sub>2</sub>CO<sub>3</sub> (4.10 g, 12.58 mmol) in DMF (750 mL) stirred at 55 °C. The reaction mixture was allowed to stand for a further 10 h. After it was cooled to room temperature, the reaction mixture was filtered, and the solvent was evaporated. Water (100 mL) was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and filtered, and the solvent was removed to give a yellow oil. Flash column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 8.5:1.5) afforded the final product L<sup>1</sup> as a colorless solid in 43% yield. mp 91-92 °C. IR (KBr, pellet): 3063, 2921, 2877, 1599, 1493, 1450, 1418, 1358, 1245, 1127, 1103, 949, 830, 757 cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub>: C, 63.80; H, 6.42; S, 17.03. Found: C, 63.98; H, 6.43; S, 17.36%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.85-7.35 (m, 8H, Ar*H*), 4.16 (t, 4H, ArOC*H*<sub>2</sub>), 3.99 (t, 4H, ArOCH<sub>2</sub>C*H*<sub>2</sub>), 3.83 (s, 4H, ArC*H*<sub>2</sub>), 2.75 (s, 4H, ArCH<sub>2</sub>SC*H*<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) 156.42, 130.89, 128.23, 127.58, 121.30, 111.38, 70.20, 68.03, 31.41, 29.43. Mass spectrum m/z (ESI): 377.2 [L<sup>1</sup>+H]<sup>+</sup>.

Synthesis of L<sup>2</sup>. 1,3-Propanedithiol (1.21 g, 11.09 mmol) and dichloride **5** (3.00 g, 8.45 mmol) were dissolved in DMF (50 mL) and added over one day, to a suspension of Cs<sub>2</sub>CO<sub>3</sub> (4.11 g, 12.58 mmol) in DMF (750 mL) stirred at 55 °C. The reaction mixture was allowed to stand for a further 10 h. After it was cooled to room temperature, the reaction mixture was filtered, and the solvent was evaporated. Water (100 mL) was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and filtered, and the solvent was removed to give a yellow oil. Flash column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate 8:2) afforded the final product L<sup>2</sup> as a colorless solid in 37% yield. mp 103-104 °C. IR (KBr, pellet): 3061, 3033, 2928, 2879, 1598, 1494, 1452, 1361, 1293, 1248, 1125, 1103, 1049, 956, 945, 751 cm<sup>-1</sup>. Anal. Calcd for C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>S<sub>2</sub>: C, 64.58; H, 6.71; S, 16.42. Found: C, 64.98; H, 6.67; S, 16.65%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.85-7.35 (m, 8H, Ar*H*), 4.19 (t, 4H, ArOCH<sub>2</sub>), 4.01 (t, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.79 (s, 4H, ArCH<sub>2</sub>), 2.61 (t, 4H, ArCH<sub>2</sub>SCH<sub>2</sub>), 1.94 (m, 2H, S CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) 156.45, 130.80, 128.16, 127.45, 121.12, 111.50, 70.38, 68.20, 30.69, 29.64, 29.13. Mass spectrum m/z (ESI): 391.5 [L<sup>2</sup>+H]<sup>+</sup>.

**Preparation of**  $[Cu_2(L^1)(NO_3)_4]_n$  (1). Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (9.8 mg, 0.041 mmol) in acetonitrile (1.0 mL) was added to a solution of L<sup>1</sup> (10.0 mg, 0.027 mmol) in dichloromethane (1.0 mL). Slow evaporation of the solution at room temperature afforded a dark green crystalline product 1 suitable for X-ray analysis. mp 169-170 °C. IR (KBr, pellet): 2929, 2868, 1599, 1484 (NO<sub>3</sub><sup>-</sup>), 1452, 1384, 1305, 1283, 1256, 1124, 1069, 1027 (NO<sub>3</sub><sup>-</sup>), 1012, 955, 945, 760 cm<sup>-1</sup>. Anal. Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>9</sub>S<sub>2</sub>Cu: C, 42.59; H, 4.29; N, 4.97; S, 11.37. Found: C, 42.29; H, 4.23; N, 4.91; S, 11.74%.

**Preparation of**  $[Cu_2(\mu$ -Cl)( $L^2_{ox}$ )\_4]Cl(NO<sub>3</sub>)\_2 (2). A dichloromethane (1.0 mL) solution of  $L^2$  (10.0 mg, 0.026 mmol) was allowed to diffuse slowly into an acetonitrile (1.0 mL) solution of Cu(NO<sub>3</sub>)\_2·3H<sub>2</sub>O (18.6 mg, 0.078 mmol) in a capillary tube (i.d. 5 mm). Slow evaporation of the reaction mixture afforded a blue crystalline product 2. mp 178-179 °C. IR (KBr, pellet): 3019, 2928, 2868, 1601, 1496 (NO<sub>3</sub><sup>-</sup>), 1453, 1384, 1291, 1255, 1107, 1009 (S=O), 960, 761 cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.31-6.93 (m, 8H, Ar*H*), 4.21-3.90 (d, 4H, Ar*CH*<sub>2</sub>S), 4.17 (m, 4H, ArO*CH*<sub>2</sub>), 3.86 (m, 4H, ArO*CH*<sub>2</sub>*CH*<sub>2</sub>), 2.88-2.69 (m, 4H, Ar*CH*<sub>2</sub>S*CH*<sub>2</sub>), 2.03-1.86 (m, 2H, S*CH*<sub>2</sub>*CH*<sub>2</sub>). Due to the disordered lattice solvent molecules and the hygroscopic nature, the elemental analysis result was not included.

**X-Ray Crystallographic Analysis.** Crystal data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.<sup>S1</sup> All of the calculations for the structure determination were carried out using the SHELXTL package.<sup>S2</sup> Since the lattice acetonitrile molecule in **2** is highly disordered, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.<sup>S3</sup> Relevant crystal data collection and refinement data for the crystal structures are summarized in Table S1.

**Magnetic Studies.** A superconducting quantum interference device (SQUID) magnetometer MPMS was used for the magnetic characterization (see Fig. 5). Powder sample with a weight of 5-10 mg was sealed in a plastic capsule. Magnetic moment was measured in the temperature range of 2 K to 300 K. The empty plastic capsule exhibited diamagnetism and its magnetic moment was measured for correction. After correction for the diamagnetism of the plastic capsule and sample holder, the diamagnetism of monomer and paramagnetic contamination (for example free radical), the magnetic susceptibility was fitted using the PHI program<sup>S4</sup> by means of an isotropic spin Hamiltonian (SH) accounting for the exchange coupling (Heisenberg-Dirac-van Vleck Hamitonian) and zero-field splitting (ZFC).

$$H = H_{ex} + H_{Zee} + H_{CF}$$

$$H_{ex} = -2J_{12}\vec{S_1}\vec{S_2}$$

$$H_{Zee} = \mu_B \sum_{i=1}^{2} \vec{S_i} g_i \vec{B}$$

$$H_{CF} = \sum D_i [S_{z,i}^2 - \frac{1}{3}S_i(S_i + 1) + \frac{E_i}{D_i}(S_{z,i}^2 - S_{y,i}^2)]$$

D: axial ZFS parameter; F: rhombic ZFS parameter;  $\vec{s}$ : spin vector;  $\vec{B}$ : magnetic field vector; g: g-factor;  $\mu_B$ : Bohr magneton.

#### References

(S1) APEX2 Version 2009.1–0 Data Collection and Processing Software; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2008.

(S2) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8.

(S3) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; University of Ultrecht: Ultrecht, The Netherlands, 2003.

(S4) N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* 2013, **34**, 1164-1175.



**Fig. S1** <sup>1</sup>H-NMR spectrum of  $L^1$  in CDCl<sub>3</sub>.



**Fig. S2**  $^{13}$ C-NMR spectrum of L<sup>1</sup> in CDCl<sub>3</sub>.



**Fig. S3** <sup>1</sup>H-NMR spectrum of L<sup>2</sup> in CDCl<sub>3</sub>



Fig. S4 <sup>13</sup>C-NMR spectrum of L<sup>2</sup> in CDCl<sub>3</sub>



**Fig. S5** Crystal structure of  $[Cu_2(\mu-Cl)(L^2_{ox})_4]Cl(NO_3)_2$  (2): (a) side view (two nitrate ions in the lattices are disordered.) and (b) top view (space-filling representation, noncoordinated anions are omitted).



**Fig. S6** IR spectra of (a)  $L^2$  and (b) **2**.



**Fig. S7** Comparison of PXRD patterns for (a) **1** and (b) **2**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data.



**Fig. S8** Supramolecular interactions in 2: (a) octahedral environment of the chloride ion in 2 showing the CH···Cl<sup>-</sup> H-bonds (dashed lines; the outer parts of the  $L^2_{ox}$  ligands are omitted for clarity) and (b) the interligand C-H···O H-bonds (dashed lines) in 2.



**Fig. S9** <sup>1</sup>H-NMR spectral comparisons of (a)  $L^2$  and (b) 2 in DMSO- $d_6$ 

The <sup>1</sup>H-NMR spectrum of **2** using DMSO- $d_6$  was observed to occur in the normal (diamagnetic) region and the nonequivalent proton peaks (axial: "*ax*" and equatorial: "*eq*") for each methylene group of H<sub>3</sub>-H<sub>5</sub> are somewhat broadened (but still well resolved), presumably reflecting the restricted conformation of the 10-memberd metallacyclic part of the structure. Considering the similar spectral pattern and chemical shifts of the expected <sup>1</sup>H-NMR spectrum of  $L^2_{ox}$  with that of  $L^2$  (Fig. S10a), the larger complexationinduced downfield shifts of H<sub>3eq</sub> and H<sub>4eq</sub> (adjacent to the sulfoxide) in **2** (Fig. S10b) relative to those of H<sub>1</sub>, H<sub>2</sub>, and H<sub>5</sub> in  $L^2$  (Fig. S10a) indicates that **2** remains intact in DMSO- $d_6$  and is in keeping with complexation occurring through both sulfoxides of  $L^2_{ox}$ .

|  | $L^1$                     | L <sup>2</sup>            | 1                         | 2                                   |
|--|---------------------------|---------------------------|---------------------------|-------------------------------------|
| Formula                                  | $C_{20}H_{24}O_3S_2$      | $C_{21}H_{26}O_3S_2$      | $C_{20}H_{24}CuN_2O_9S_2$ | $C_{84}H_{112}Cl_2Cu_2N_2O_{26}S_8$ |
| Formula weight                           | 376.51                    | 390.54                    | 564.07                    | 2020.21                             |
| Temperature (K)                          | 173(2)                    | 173(2)                    | 173(2)                    | 173(2)                              |
| Crystal system                           | Monoclinic                | Orthorhombic              | Monoclinic                | Tetragonal                          |
| Space group                              | $P2_{1}/n$                | $P2_{1}2_{1}2_{1}$        | C2/c                      | I4/m                                |
| Ζ  | 4                         | 4                         | 8                         | 2                                   |
| <i>a</i> (Å)                             | 14.7867(2)                | 7.9980(2)                 | 17.2239(2)                | 16.627(9)                           |
| <i>b</i> (Å)                             | 4.62090(10)               | 13.8621(3)                | 13.0421(2)                | 16.627(9)                           |
| <i>c</i> (Å)                             | 27.4643(3)                | 17.8754(4)                | 20.8189(3)                | 19.050(10)                          |
| α (°)                                    | 90                        | 90                        | 90                        | 90                                  |
| eta (°)                                  | 94.3620(10)               | 90                        | 90.6790(10)               | 90                                  |
| γ (°)                                    | 90                        | 90                        | 90                        | 90                                  |
| $V(Å^3)$                                 | 1871.14(5)                | 1981.83(8)                | 4676.34(11)               | 5267(6)                             |
| $D_{\text{calc}}(g/\text{cm}^3)$         | 1.337                     | 1.309                     | 1.602                     | 1.274                               |
| $2\theta_{\max}(^{\circ})$               | 52.00                     | 52.00                     | 52.00                     | 52.00                               |
| $R_1, wR_2 \left[I > 2\sigma(I)\right]$  | 0.0332, 0.0828            | 0.0306, 0.0621            | 0.0423, 0.0816            | 0.0696, 0.1995                      |
| $R_1, wR_2$ [all data]                   | 0.0394, 0.0862            | 0.0357, 0.0642            | 0.0737, 0.0915            | 0.1124, 0.2234                      |
| Goodness-of-fit on $F^2$                 | 1.025                     | 1.033                     | 1.034                     | 1.045                               |
| No. of reflection used [> $2\sigma(I)$ ] | $3586 [R_{int} = 0.0244]$ | $3880 [R_{int} = 0.0357]$ | $4532 [R_{int} = 0.0594]$ | 2677 [ $R_{\rm int} = 0.0757$ ]     |

## Table S1Crystal and Experimental Data

|            | 0         | с ( <u>с</u> , |            |
|------------|-----------|----------------|------------|
| Cu1-S1     | 2.3339(8) | Cu1-S2         | 2.3507(8)  |
| Cu1-O4     | 2.408(2)  | Cu2-O5         | 1.9603(19) |
| Cu2-O7     | 1.952(2)  |                |            |
|            |           |                |            |
| S1-Cu1-S1A | 180.0     | S1-Cu1-S2      | 87.47(3)   |
| S1-Cu1-S2A | 92.53(3)  | S2-Cu1-S2A     | 180.00(4)  |
| S1-Cu1-O4A | 88.38(6)  | S1A-Cu1-O4A    | 91.63(6)   |
| S1-Cu1-O4  | 91.62(6)  | S2-Cu1-O4      | 82.58(5)   |
| S1A-Cu1-O4 | 88.38(6)  | S2-Cu1-O4A     | 97.43(5)   |
| O4A-Cu1-O4 | 180.0     | O7B-Cu2-O7     | 180.0      |
| O7B-Cu2-O5 | 89.28(9)  | O7-Cu2-O5      | 90.72(9)   |
| O7-Cu2-O5B | 89.28(9)  | O5-Cu2-O5B     | 180.0      |
|            |           |                |            |

 Table S2
 Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Symmetry operations: (A) -x,-y+1,-z (B) -x-1/2,-y+3/2,-z

|  | Table S3 | Selected Bond | Lengths (Å) | ) and Bond Angles | (deg) for 2 |
|--|----------|---------------|-------------|-------------------|-------------|
|--|----------|---------------|-------------|-------------------|-------------|

| Cu1-O3             | 1.945(3)       | Cu1-Cl1       | 2.4699(17) |  |
|--------------------|----------------|---------------|------------|--|
| O3-Cu1-O3C         | 89.37(2)       | O3-Cu1-O3G    | 167.93(19) |  |
| O3-Cu1-Cl1         | 96.04(9)       | Cl-Cu-Cl      | 180        |  |
| Symmetry operation | s: (C) x,y+1,z | (G) x+1,y+1,z |            |  |

#### Table S4The H-bond Parameters of 2

| D-H        | d(D-H) | d(HA)      | <dha< th=""><th>d(DA)</th><th>А</th></dha<> | d(DA)      | А  |
|------------|--------|------------|---|------------|----|
| C-H12a…Cl1 | 0.99   | 2.9684(15) | 150.039(30)                                 | 3.8579(21) | Cl |
| C-H12b…O1  | 0.99   | 2.464(1)   | 173.441(39)                                 | 3.4494(14) | 01 |
| C-H11b…O2  | 0.99   | 2.7433(14) | 146.229(38)                                 | 3.6085(17) | O2 |