

# SUPPORTING INFORMATION

For

## **Solid-state and solution characterizations of [(TMPA)Cu(II)(SO<sub>3</sub>)] and [(TMPA)Cu(II)(S<sub>2</sub>O<sub>3</sub>)] complexes: application to sulfite and thiosulfate fast detection.**

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**Table S1.** Crystal data, data collection, and structure refinement for **1** and **2**.

| ID  | <b>1</b>  | <b>2</b> , 2H <sub>2</sub> O   |
|---|---|--|
| formula   | C <sub>18</sub> H <sub>18</sub> CuN <sub>4</sub> O <sub>3</sub> S | C <sub>18</sub> H <sub>18</sub> CuN <sub>4</sub> O <sub>3</sub> S <sub>2</sub> , 2(H <sub>2</sub> O) |
| <i>M<sub>r</sub></i>  | 433.97  | 502.07   |
| crystal system  | orthorhombic  | monoclinic   |
| space group   | <i>Pcca</i>   | <i>C 2/c</i>   |
| <i>a</i> (Å)  | 17.086(4)   | 13.1003(12)  |
| <i>b</i> (Å)  | 14.960(3)   | 12.1622(11)  |
| <i>c</i> (Å)  | 17.372(4)   | 25.323(2)  |
| $\alpha$ (°)  | 90  | 90   |
| $\beta$ (°)   | 90  | 90.589(3)  |
| $\gamma$ (°)  | 90  | 90   |
| <i>V</i> (Å <sup>3</sup> )  | 4440.4(17)  | 4034.5(6)  |
| <i>Z</i>  | 8   | 8  |
| $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )                              | 1.298   | 1.653  |
| $\mu$ (mm <sup>-1</sup> )   | 1.100   | 1.33   |
| <i>F</i> (000)  | 1784  | 2072   |
| crystal size (mm <sup>3</sup> )   | 0.20 x 0.16 x 0.04  | 0.20 x 0.08 x 0.08   |
| <i>T</i> /K   | 273(2)  | 110(2)   |
| measd reflns  | 67459   | 88088  |
| Unique reflns (Rint)  | 4025 (0.0739)   | 7397 (0.0466)  |
| Data/restraints/parameters  | 4025/0/244  | 7397/0/287   |
| GOF on <i>F</i> <sup>2</sup>  | 1.062   | 1.111  |
| <i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] | 0.0927  | 0.0244   |
| w <i>R</i> <sub>2</sub> <sup>b</sup> [all data]                         | 0.2797  | 0.0624   |

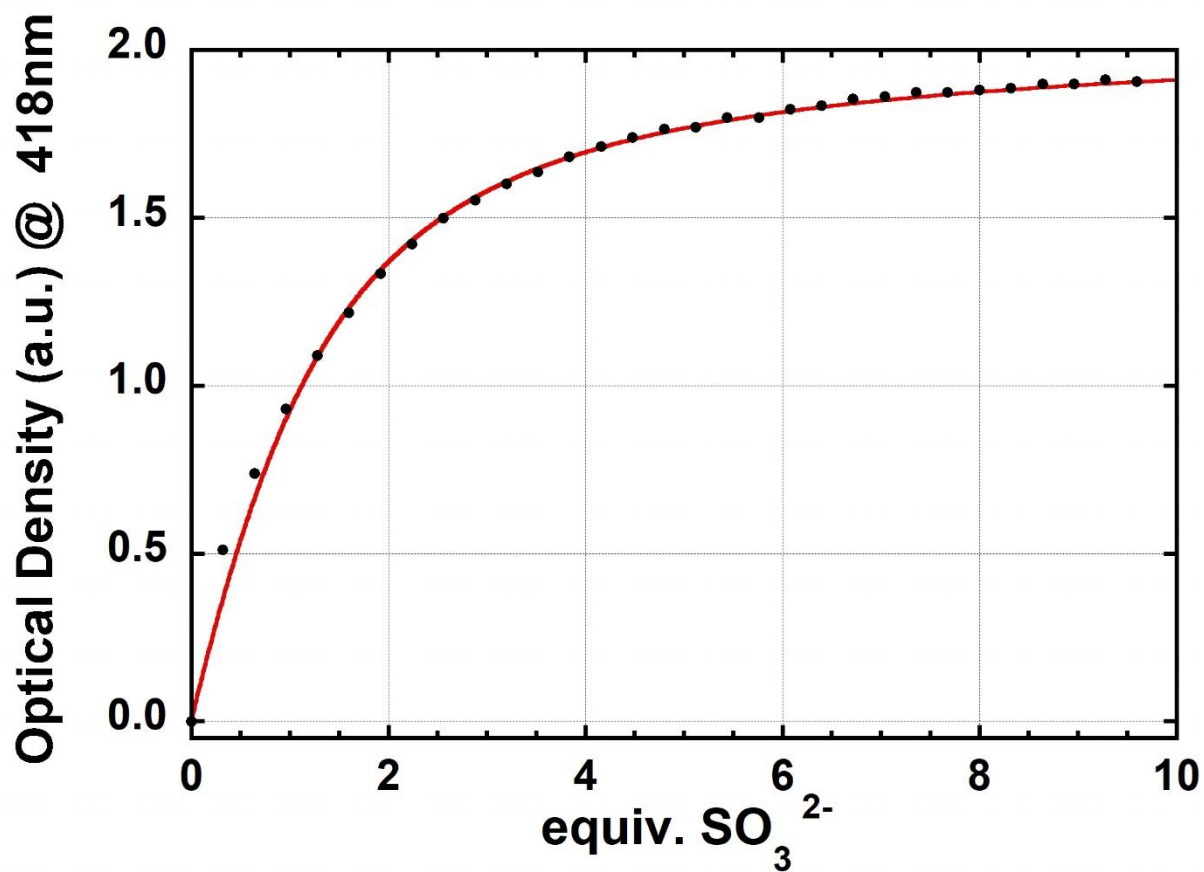
<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

**Table S2.** Selected bond lengths (Å) of Cu(II) complexes with 4N tripodal ligands.

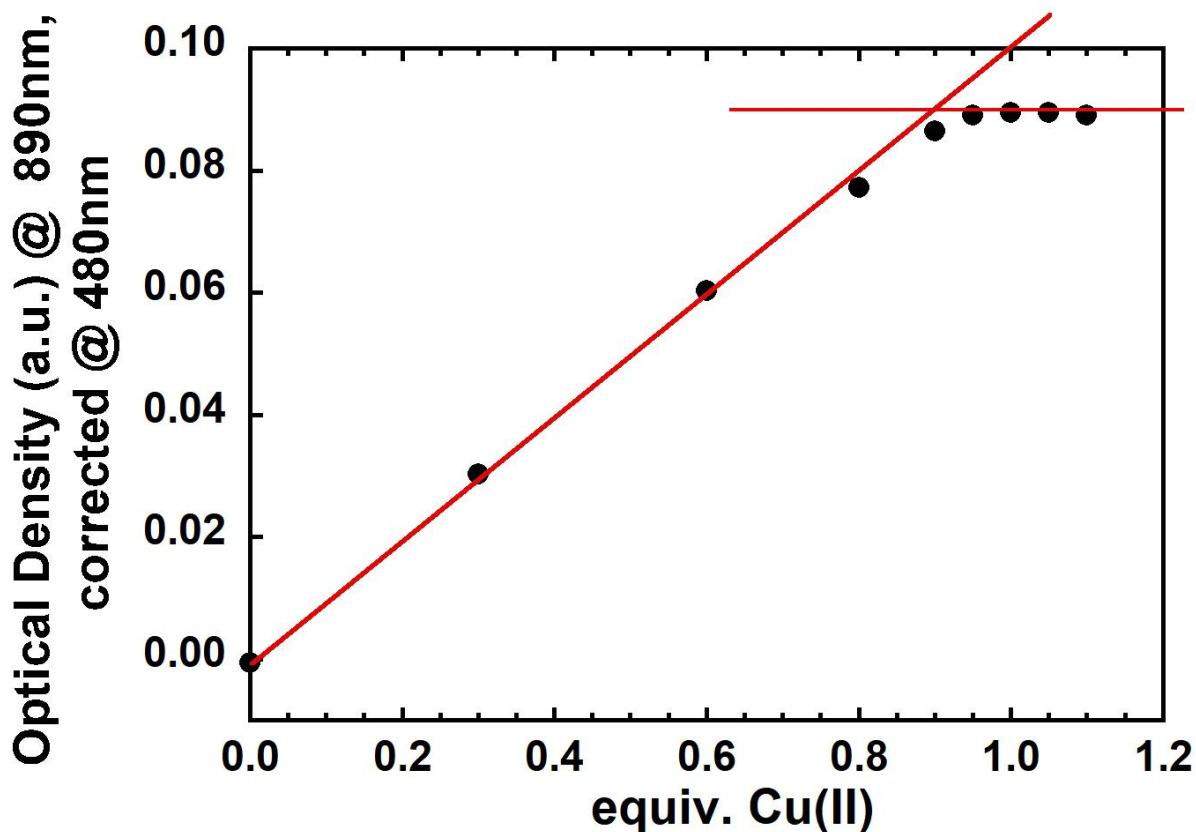
|   | <u>1</u> | <u>2</u> | [LCu(H <sub>2</sub> O)] <sup>2+</sup> 1 | [LCu(AcN)] <sup>2+</sup> 2 | [(Bz <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] <sup>3</sup> | [(tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] <sup>3</sup> | [(Me <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] (a) <sup>3</sup> | [(Me <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] (b) <sup>3</sup> |
|---|----------|----------|---|----------------------------|---|---|---|---|
| <b>Cu-N(1)</b>                            | 2.072(7) | 2.029(1) | 2.071(1)                                | 2.042(5)                   | 2.098(4)  | 2.112(2)  | 2.040(8)  | 2.10(1)   |
| <b>Cu-N(2)</b>                            | 2.087(7) | 2.062(1) | 2.006(1)                                | 2.021(4)                   | 2.064(3)  | 2.075(2)  | 2.05(1)   | 2.08(1)   |
| <b>Cu-N(3)</b>                            | 2.077(7) | 2.202(1) | 2.059(1)                                | 2.082(4)                   | 2.168(4)  | 2.047(2)  | 2.195(7)  | 2.08(1)   |
| <b>Cu-N(4)</b>                            | 2.085(7) | 2.042(1) | 2.061(1)                                | 2.025(5)                   | 2.100(4)  | 2.062(2)  | 2.103(8)  | 2.10(1)   |
| <b>Cu-S/O<sub>w</sub>/N<sub>AcN</sub></b> | 2.253(2) | 2.288(1) | 1.952(1)                                | 1.976(5)                   | 2.301(1)  | 2.3158(8)   | 2.329(3)  | 2.281(3)  |
| <b>Cu-O<sub>(S2O3)</sub></b>              | -        | 2.695(1) | -                                       |                            |   |   | 2.872(6)  |   |

**Table S3.** Selected bond angles ( $^{\circ}$ ) of Cu(II) complexes with 4N tripodal ligands.

|  | <u>1</u> | <u>2</u>  | [LCu(H <sub>2</sub> O)] <sup>2+</sup> 1 | [LCu(AcN)] <sup>2+</sup> 2 | [(Bz <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] <sup>3</sup> | [(tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] <sup>3</sup> | [(Me <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] (a) <sup>3</sup> | [(Me <sub>3</sub> tren)<br>Cu(S <sub>2</sub> O <sub>3</sub> )] (b) <sup>3</sup> |
|--|----------|-----------|---|----------------------------|---|---|---|---|
| <b>N(1)-Cu-N(2)</b>                            | 80.9(3)  | 82.47(4)  | 82.31(5)                                | 82.2(2)                    | 84.1(1)   | 83.67(7)  | 85.3(4)   | 81.7(4)   |
| <b>N(1)-Cu-N(3)</b>                            | 118.5(3) | 93.95(4)  | 117.66(5)                               | 113.9(2)                   | 113.7(1)  | 117.01(8)   | 111.1(3)  | 120.1(5)  |
| <b>N(1)-Cu-N(4)</b>                            | 116.1(3) | 161.62(4) | 117.04(5)                               | 127.2(2)                   | 128.9(1)  | 112.97(8)   | 139.2(3)  | 112.9(4)  |
| <b>N(2)-Cu-N(3)</b>                            | 80.4(3)  | 82.49(3)  | 82.00(5)                                | 82.4(2)                    | 83.8(1)   | 84.77(7)  | 83.8(3)   | 84.9(5)   |
| <b>N(2)-Cu-N(4)</b>                            | 80.0(3)  | 81.49(4)  | 82.38(5)                                | 83.3(2)                    | 83.8(1)   | 83.75(7)  | 84.3(4)   | 83.2(4)   |
| <b>N(3)-Cu-N(4)</b>                            | 117.2(3) | 92.80(4)  | 119.9(5)                                | 114.1(2)                   | 114.0(1)  | 126.85(8)   | 106.8(3)  | 123.0(5)  |
| <b>S/O<sub>w</sub>/N<sub>AcN</sub>-Cu-N(1)</b> | 100.1(2) | 98.19(3)  | 99.91(5)                                | 95.6(2)                    | 94.3(1)   | 96.85(6)  | 90.6(2)   | 101.5(3)  |
| <b>S/O<sub>w</sub>/N<sub>AcN</sub>-Cu-N(2)</b> | 178.9(2) | 168.09(3) | 176.54(5)                               | 177.7(2)                   | 178.3(1)  | 175.72(5)   | 173.1(3)  | 174.6(3)  |
| <b>S/O<sub>w</sub>/N<sub>AcN</sub>-Cu-N(3)</b> | 98.7(2)  | 109.26(3) | 94.60(5)                                | 99.2(2)                    | 97.1(1)   | 91.22(6)  | 102.8(2)  | 89.7(4)   |
| <b>S/O<sub>w</sub>/N<sub>AcN</sub>-Cu-N(4)</b> | 99.9(2)  | 95.67(3)  | 98.84(5)                                | 97.5(2)                    | 97.0(1)   | 99.90(6)  | 95.3(2)   | 99.4(3)   |
| <b>O<sub>(S2O3)</sub>-Cu-N(1)</b>              |          | 92.32(4)  |   |                            |   |   | 75.3(3)   |   |
| <b>O<sub>(S2O3)</sub>-Cu-N(2)</b>              |          | 98.45(3)  |   |                            |   |   | 108.4(3)  |   |
| <b>O<sub>(S2O3)</sub>-Cu-N(3)</b>              |          | 173.72(3) |   |                            |   |   | 167.0(3)  |   |
| <b>O<sub>(S2O3)</sub>-Cu-N(4)</b>              |          | 81.23(4)  |   |                            |   |   | 70.9(3)   |   |



**Figure S1.** SO<sub>3</sub><sup>2-</sup> titrations into [LCu(OH<sub>2</sub>)]<sup>2+</sup>. Variations of the absorbance measured on the MLCT (plain circles) 0.25 mM concentration in [LCu(OH<sub>2</sub>)]<sup>2+</sup> and corresponding fittings. Hepes (pH 6.5) 100mM;  $\ell = 1\text{cm}$ . T = 25°C.



**Figure S2.** TMPA (L) titration with Cu(II) stock solution. Phosphate buffer (pH 7.7) 100mM;  $\ell = 1\text{cm}$ .  $T = 25^\circ\text{C}$ .

## References

1. Bazley, I. J.; Erie, E. A.; Feiereisel, G. M.; LeWarne, C. J.; Peterson, J. M.; Sandquist, K. L.; Oshin, K. D.; Zeller, M., X-ray Crystallography Analysis of Complexes Synthesized with Tris(2-pyridylmethyl)amine: A Laboratory Experiment for Undergraduate Students Integrating Interdisciplinary Concepts and Techniques. *Journal of Chemical Education* **2018**, *95* (5), 876-881.
2. Fujii, T.; Naito, A.; Yamaguchi, S.; Wada, A.; Funahashi, Y.; Jitsukawa, K.; Nagatomo, S.; Kitagawa, T.; Masuda, H., Construction of a square-planar hydroperoxo-copper(ii) complex inducing a higher catalytic reactivity. *Chemical Communications* **2003**, (21), 2700-2701.
3. Fischmann, A. J.; Warden, A. C.; Black, J.; Spiccia, L., Synthesis, Characterization, and Structures of Copper(II)-Thiosulfate Complexes Incorporating Tripodal Tetraamine Ligands. *Inorganic Chemistry* **2004**, *43* (21), 6568-6578.