**Supporting Information**

Investigation of syntheses, structures, theoretical calculations and fluorescence properties of two N3O-donor half-salamo-type Cu(II) complexes

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Table S1. Selected bond distances (Å) and angles (deg) for complexes **1** and **2**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex **1** |  |  |  |  |  |
| Bond | Distances | Bond | Distances | Bond | Distances |
| Cu1-N1 | 2.251(2) | Cu1-N2 | 2.030(2) | Cu1-N3 | 1.950(2) |
| Cu1-O3 | 1.890(18) | Cu1-O4 | 2.071(18) |  |  |
| Bond  | Angles  | Bond  | Angles  | Bond  | Angles |
| N2-Cu1-N1 | 75.47(8) | N2-Cu1-O4 | 89.98(8) | N3-Cu1-N1 | 130.38(8) |
| N3-Cu1-N2 | 91.44(8) | N3-Cu1-O4 | 145.36(8) | O3-Cu1-N1 | 98.56(8) |
| O3-Cu1-N2 | 172.84(9) | O3-Cu1-N3 | 89.53(8) | O3-Cu1-O4 | 93.26(8) |
| O4-Cu1-N1 | 83.31(7) |  |  |  |  |
| Complex **2** |  |  |  |  |  |
| Bond | Distances | Bond | Distances | Bond | Distances  |
| Cu1-O1 | 1.889(8) | Cu1-O3 | 1.910(8) | Cu1-O6 | 1.932(8) |
| Cu1-N1 | 1.918(10) | Cu2-O3 | 1.929(9) | Cu2-O4 | 1.891(9) |
| Cu2-O6 | 1.903(9) | Cu2-N2 | 1.922(10) |  |  |
| Bond  | Angles  | Bond  | Angles  | Bond  | Angles |
| O1-Cu1-O3 | 172.5(4) | O1-Cu1-O6 | 95.9(4) | O1-Cu1-N1 | 92.6(4) |
| O3-Cu1-O6 | 76.9(3) | O3-Cu1-N1 | 94.8(4) | N1-Cu1-O6 | 169.3(4) |
| O4-Cu2-O3 | 95.9(4) | O4-Cu2-O6 | 173.0(4) | O4-Cu2-N2 | 92.1(4) |
| O6-Cu2-O3 | 77.1(3) | O6-Cu2-N2 | 94.9(4) | N2-Cu2-O3 | 170.4(4) |

Table S2. Geometrical parameters (Å, °) for C-H···π (aryl) and π···π (aryl-aryl) interactions in complex **1** andC-H···π (chelate) in complex **2**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex **1** |  |  |  |  |  |
| X-H···Cg | H···Cg | X···Cg | X-H···Cg | H-Perp | Symmetry |
| C4-H4···Cg4 | 2.92 | 3.696(4) | 140 | -2.77 | x,1-y,1/2+z |
| C11-H11B···Cg3 | 2.97 | 3.709(3) | 132 | 2.81 | 3/2-x,3/2-y,1-z |
| CgI···CgJ | *R*ca | *R*1vb | *R*2vc | α | Symmetry |
| Cg1···Cg1 | 3.493(13) | 3.484(9) | 3.484(9) | 7.80(11) | 1-x,y,3/2-z |
| Cg1···Cg2 | 3.485(14) | -3.277(9) | -3.216(10) | 4.26(11) | 1-x,1-y,1-z |
| Cg2···Cg1 | 3.485(14) | -3.216(10) | -3.277(9) | 4.26(11) | 1-x,1-y,1-z |
| Cg2···Cg2 | 3.544(15) | -3.205(10) | -3.205(10) | 0.00(11) | 1-x,1-y,1-z |
| Complex **2** |  |  |  |  |  |
| X-H···Cg | H···Cg | X···Cg | X-H···Cg | H-Perp | Symmetry |
| C13-H13B···Cg6 | 2.97 | 3.629(14) | 125 | -2.72 | -1+x,y,z |

a Centroid distance between CgI and CgJ; b Vertical distance from ring centroid I to ring J; cVertical distance from ring centroid J to ring I; α = dihedral angle between planes I and J. Ring for complex **1**:Cg1: N1/C1/C6-C9; Ring Cg2: C1-C6; Ring Cg3: C14-C18/C23; Ring Cg4: C18-C23, for complex **2**: Cg6: Cu(1)/O(1)/C(1)/C(10)/C(11)/N(1).

Table S3. Hydrogen bond parameters (Å, °) for complex **1**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠D-H···A | Symmetry |
| C2-H2···O3 | 0.95 | 2.31 | 3.088(3) | 139 |  |
| C11-H11A···O6 | 0.99 | 2.59 | 3.579(4) | 178 |  |
| C10-H10···O4 | 0.95 | 2.55 | 3.118(3) | 119 | 1-x,y,3/2-z |
| C10-H10···O5 | 0.95 | 2.55 | 3.465(4) | 163 | 1-x,y,3/2-z |
| C12-H12A···O5 | 0.99 | 2.40 | 3.314(4) | 153 | -1/2+x,3/2-y,-1/2+z |
| C13-H13···O6 | 0.95 | 2.55 | 3.065(3) | 114 | 3/2-x,3/2-y,1-z |

Table S4. Comparison of selected bond distances (Å) and angles (deg) for complex **2** in this work and similar complex reported by Ren *et al*.

|  |  |
| --- | --- |
| This work | Reported by Ren *et al.* |
| Bond | Distances | Bond | Distances |
| Cu1-O1 | 1.889(8) | Cu1-O1 | 1.884(5) |
| Cu1-N1 | 1.918(10) | Cu1-N1 | 1.947(6) |
| Cu1-O6 | 1.932(8) | Cu1-O6 | 1.918(5) |
| Cu1-O3 | 1.910(8) | Cu1-O5 | 1.908(4) |
| Cu2-N2 | 1.922(10) | Cu2-N2 | 1.928(6) |
| Cu2-O4 | 1.891(9) | Cu2-O3 | 1.890(5) |
| Cu2-O6 | 1.903(9) | Cu2-O6 | 1.902(5) |
| Cu2-O3 | 1.929(9) | Cu2-O3 | 1.890(5) |
| Bond  | Angles  | Bond  | Angles |
| O1-Cu1-O3 | 172.5(4) | O1-Cu1-O5 | 173.6(2) |
| O1-Cu1-O6 | 95.9(4) | O1-Cu1-O6 | 96.4(2) |
| O1-Cu1-N1 | 92.6(4) | O1-Cu1-N1 | 91.7(2) |
| O3-Cu1-O6 | 76.9(3) | O5-Cu1-O6 | 77.32(19) |
| O3-Cu1-N1 | 94.8(4) | O5-Cu1-N1 | 94.7(2) |
| N1-Cu1-O6 | 169.3(4) | N1-Cu1-O6 | 169.9(2) |
| O4-Cu2-O3 | 95.9(4) | O3-Cu2-O5 | 95.6(2) |
| O4-Cu2-O6 | 173.0(4) | O3-Cu2-O6 | 172.7(2) |
| O4-Cu2-N2 | 92.1(4) | O3-Cu2-N2 | 92.1(2) |
| O6-Cu2-O3 | 77.1(3) | O6-Cu2-O5 | 77.08(18) |
| O6-Cu2-N2 | 94.9(4) | O6-Cu2-N2 | 95.2(2) |
| N2- Cu2-O3 | 170.4(4) | N2- Cu2-O5 | 170.7(2) |

Table S5. The absorption transitions for HL1 and its complexes **1** and **2** in DMF solution by TD-DFT method.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| λcal (nm) | Oscillator strength (f) | Transitions | λexpt (nm) | Assignments |
| **HL1** |  |  |  |  |
| 305 | 0.5584 | HOMO – 1 → LUMO | 300 | π-π\* |
| 331 | 0.3077 | HOMO → LUMO + 1 | 340 | n-π\* |
| 358 | 0.0139 | HOMO → LUMO | 356 | n-π\*, π-π\* |
| Complex **1** |  |  |  |  |
| 321 | 0.0977 | HOMOb – 6 → LUMOb | 320 | LMCT |
|  |  | HOMOa – 2 → LUMOa + 1 |  |  |
| 406 | 0.0004 | HOMOb – 4 → LUMOb | 400 | LMCT |
| Complex **2** |  |  |  |  |
| 397 | 0.0119 | HOMOb → LUMOb + 1 | 400 | LMCT |



Figure S1. 1H NMR spectrum of HL1 in CDCl3.



Figure S2. FT-IR spectra of HL1 and the complexes **1** and **2**.



Figure S3. UV-Vis absorption spectral of (a) complex **1** and (b) complex **2** at different times (0, 1 and 3 days).



Scheme S1. Plausible mechanism for copper-catalyzed N-O bond cleavage of HL1.