SUPPLEMENTARY MATERIAL TO

**(E)-4-(((2-amino-5-chlorophenyl)imino)methyl)-5-(hydroxymethyl)-2-methylpyridin-3-ol and its Cu(II) complex: Synthesis, DFT calculations and AIM analysis**

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**Figure S1.** The M062X optimized geometry of the TSEnol-Keto of the *meta* isomer.

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**Figure S2.** Optimized geometry and the isosurface Fukui map of the **L-**.



**Figure S3.** The 1H- and 13C-NMR spectra of the **HL** Schiff base.

 

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| sphere |  |  |  |  |  |  |
| Atom | H | C | N | O | Cl | Cu |

**Figure S4.** The QTAIM molecular graphs of the **HL** Schiff base and [Cu(**L**)Cl] complex (small green and red spheres correspond to the BCPs and RCPs, respectively).

**Table S1.** The elemental analysis of the investigated compounds.

|  |  |  |  |
| --- | --- | --- | --- |
| Chemical formula | Experimental (%) | Calculated (%) | Species |
| Metal | N | H | C | Metal | N | H | C |
| C14H14ClN3O2 | - | 15.01 | 4.76 | 57.34 | - | 14.40 | 4.84 | 57.64 | **HL** |
| C14H13Cl2CuN3O2 | 17.02 | 10.46 | 3.48 | 43.52 | 16.31 | 10.78 | 3.36 | 43.15 | [Cu(**L**)Cl] |

**Table S2.** Relative electronic energies (E+ZPE) for the investigated species of the **HL** Schiff base (in term of kJ.mol-1).

|  |  |  |
| --- | --- | --- |
| ΔG(Methanol solution) | E+ZPE | **Species** |
| Gas phase | Methanol solution |
| 0 | 0 | 0 | Enol tautomer of the *meta* isomer |
| 24.59 | 35.07 | 28.85 | Keto tautomer of the *meta* isomer |
| 20.94 | 21.06 | 19.02 | Enol tautomer of the *para* isomer |
| 28.63 | 31.92 | 25.14 | Keto tautomer of the *para* isomer |
| 131.02 | 160.54 | 163.01 | TSEnol-Keto |

**Table S3.** Important experimental and the DFT-computed IR vibrational frequencies (cm-1) of the **HL** Schiff base (Enol tautomer of the *meta* isomer) and [Cu(**L**)Cl] complex.

|  |  |  |
| --- | --- | --- |
| Experimental frequencies | Calculated frequencies | Vibrational assignment |
| **HL** | [Cu(**L**)Cl] | **HL** | [Cu(**L**)Cl] |
| Frequency | Intensity(km.mol-1) | Frequency | Intensity(km.mol-1) |
| - | 547 (m) | - | - | 540 | 29 | υasym(Cu-N, Cu-O) |
| - | 640 (w) | - | - | 625 | 5 | υsym(Cu-N, Cu-O) |
| 765 (m) | 767 (m) | 750 | 12 | 727 | 11 | Breathing of the aromatic rings |
| 809 (m) | - | 802 | 54 | - | - | δop(H12) |
| 846 (w) | 851 (w) | 846 | 20 | 851 | 27 | δop(aromatic hydrogens) |
| 912 (w) | 915 (w) | 885 | 56 | 907 | 86 | υ(C13-Cl1) |
| 1032 (vs) | 1027 (s) | 1060 | 68 | 1149 | 271 | υ(C7-O2) |
| 1208 (m) | 1188 (m) | 1174 | 85 | 1171 | 186 | υ(C9-N2) |
| 1298 (m) | 1262 (m) | 1278 | 94 | 1256 | 139 | υ(C10-N3)+ υ(Ar-C) |
| 1380 (vs) | 1416 (vs) | 1389 | 218 | 1378 | 156 | υ(C1-O1) |
| 1471 (m) |  | 1457 | 127 | 1450 | 234 | υ(C9-N2) |
| 1521 (m) | 1507 (m) | 1578 | 154 | 1484 | 191 | υasym(C=C) of the benzene ring |
| 1559 | 117 | 1532 | 192 | υsym(C=C) of the benzene ring |
|  |  | 1572 | 100 | 1554 | 91 | υ(C=N, C=C) of the pyridine ring + υ(C4-N2) |
| 1617 (vs) | 1605 (vs) | 1594 | 140 | 1595 | 28 | υ(C=N, C=C) of the pyridine ring  |
| 1604 | 16 | 1602 | 331 | υ(C4=N2) |
| 2746 (m) | 2741 (s) | 2853 | 40 | 2882 | 47 | υsym(C-H) of -CH2- groups |
| 2840 (s) | 2838 (s) | 2876 | 30 | 2911 | 27 | υasym(C-H) of -CH2- groups |
| 2919 (s) | 2918 (s) | 2914 | 19 | 2953 | 7 | υsym(C-H) of the methyl groups |
| 3110 (vs, br) | 3096 (vs, br) | 2956 | 33 | 3039 | 10 | υ(C4-H1) |
| 2959 | 14 | 3061 | 9 | υasym(C-H) of the methyl groups |
| 3088-3046 | 3 | 3125-3087 | 2 | υasym(C-H) of the aromatic hydrogens |
|  | 3129 | 467 | - | - | υ(O1-H12) |
| 3463 (m, br) | 3362 (s) | 3439 | 26 | 3368 | 58 | υsym(H-N-H) of the -NH2 amine group |
| 3444 (s) | 3541 | 35 | 3427 | 57 | υasym(H-N-H) of the -NH2 amine group |
| 3708 | 59 | 3773 | 79 | υ(O2-H5) |

**Table S4.** Important topological parameters of the investigated species (energies in term of kJ.mol-1 and electron density in term of e-/a03).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Bond | ρ(r) | ∇2ρ | Vb | Gb | Hb | -Gb/Vb |
| **HL** Schiff base |  |  |  |  |  |
| C1-O1 | 0.296455 | -0.29584 | -2069.64 | 937.82 | -1131.82 | 0.45 |
| O1-H12 | 0.328394 | -2.3074 | -1861.35 | 174.14 | -1687.21 | 0.09 |
| N2…H12 | 0.048682 | 0.117582 | -123.01 | 100.06 | -22.95 | 0.81 |
| C4-N2 | 0.360837 | -0.74918 | -2447.96 | 978.35 | -1469.62 | 0.40 |
| C9-N2 | 0.288529 | -0.79631 | -1405.12 | 441.47 | -963.65 | 0.31 |
| C10-N3 | 0.300363 | -0.85216 | -1520.38 | 480.79 | -1039.59 | 0.32 |
| C7-O2 | 0.253926 | -0.44675 | -1481.29 | 594.16 | -887.12 | 0.40 |
| O2-H5 | 0.36575 | -2.53727 | -2045.54 | 190.86 | -1854.68 | 0.09 |
| O2…H2 | 0.015016 | 0.075301 | -31.9744 | 40.69 | 8.72 | 1.31 |
| C13-Cl1 | 0.189228 | -0.26237 | -505.52 | 166.74 | -338.78 | 0.33 |
| [Cu(**L**)Cl] complex |  |  |  |  |  |
| C1-O1 | 0.344817 | 0.072805 | -2945.70 | 1496.72 | -1448.98 | 0.51 |
| C4-N2 | 0.35068 | -0.58679 | -2706.94 | 1161.08 | -1545.86 | 0.43 |
| C9-N2 | 0.292404 | -0.91341 | -1479.89 | 440.46 | -1039.43 | 0.30 |
| C10-N3 | 0.271821 | -0.80724 | -1285.78 | 378.22 | -907.56 | 0.29 |
| C7-O2 | 0.261951 | -0.45338 | -1703.82 | 703.26 | -1000.56 | 0.41 |
| O2-H5 | 0.353374 | -1.87394 | -1576.75 | 173.96 | -1402.79 | 0.11 |
| C13-Cl1 | 0.199477 | -0.29389 | -545.37 | 176.33 | -369.04 | 0.32 |
| Cu-O1 | 0.084756 | 0.630332 | -409.91 | 411.63 | 1.72 | 1.00 |
| Cu-N2 | 0.076368 | 0.468496 | -316.97 | 312.09 | -4.88 | 0.98 |
| Cu-N3 | 0.068587 | 0.403737 | -264.16 | 264.45 | 0.29 | 1.00 |
| Cu-Cl2 | 0.065415 | 0.292258 | -217.09 | 204.37 | -12.72 | 0.94 |
| O2…H2 | 0.015985 | 0.076722 | -35.07 | 42.69 | 7.62 | 1.22 |