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# Supplementary Information

## Influence of the Structure on the Antioxidant Activity of Tetradentate Schiff Bases and their Copper(II) Complexes: Possible Mechanisms

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**Table S1.** Pearson's correlation matrix for Schiff bases

| | TEAC | Dipole moment | HOMO | LUMO | Delta | Charge N7[a] | Charge N10[a] | Charge O16[a] | Charge O3[a] | Charge H N7[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Dipole moment | –0.971 | | | | | | | | | |
| HOMO | 0.668 | –0.737 | | | | | | | | |
| LUMO | 0.075 | –0.125 | 0.607 | | | | | | | |
| Delta | –0.029 | 0.075 | –0.558 | –0.998 | | | | | | |
| Charge N7[a] | –0.180 | 0.251 | –0.756 | –0.372 | 0.331 | | | | | |
| Charge N10[a] | –0.068 | 0.118 | –0.533 | –0.988 | 0.992 | 0.234 | | | | |
| Charge O16[a] | –0.828 | 0.843 | –0.404 | 0.412 | –0.460 | 0.143 | –0.428 | | | |
| Charge O3[a] | –0.765 | 0.780 | –0.350 | –0.180 | 0.162 | –0.333 | 0.267 | 0.542 | | |
| Charge H N7[a] | –0.795 | 0.852 | –0.950 | –0.332 | 0.275 | 0.719 | 0.254 | 0.657 | 0.391 | |
| Charge H N10[a] | –0.839 | 0.890 | –0.896 | –0.564 | 0.521 | 0.388 | 0.552 | 0.514 | 0.727 | 0.866 |

[a]Charge obtained by NBO analysis.

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**Table S2.** Pearson's correlation matrix for copper(II) complexes

| | TEAC | Spin density Cu | Spin density N2 | Spin density N3 | Spin density O4 | Spin density O5 | Sum Spin density | Alfa HOMO | Alfa LUMO | Beta HOMO | Beta LUMO | Delta alfa | Delta beta | Dipole moment | Chelate plane angle | Charge Cu[a] | Charge N2[a] | Charge N3[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Spin density Cu | –0.414 | | | | | | | | | | | | | | | | | |
| Spin density N2 | -0.700 | 0.915 | | | | | | | | | | | | | | | | |
| Spin density N3 | –0.702 | 0.915 | 0.985 | | | | | | | | | | | | | | | |
| Spin density O4 | –0.287 | –0.589 | –0.377 | –0.278 | | | | | | | | | | | | | | |
| Spin density O5 | 0.582 | –0.937 | –0.916 | –0.964 | 0.273 | | | | | | | | | | | | | |
| Sum spin density | –0.887 | 0.734 | 0.930 | 0.942 | –0.018 | –0.850 | | | | | | | | | | | | |
| Alfa HOMO | –0.056 | –0.867 | –0.632 | –0.599 | 0.880 | 0.662 | –0.313 | | | | | | | | | | | |
| Alfa LUMO | –0.023 | –0.867 | –0.594 | –0.619 | 0.677 | 0.756 | –0.329 | 0.935 | | | | | | | | | | |
| Beta HOMO | –0.109 | –0.841 | –0.585 | –0.557 | 0.878 | 0.635 | –0.259 | 0.998 | 0.945 | | | | | | | | | |
| Beta LUMO | –0.550 | –0.491 | –0.131 | –0.103 | 0.862 | 0.233 | 0.229 | 0.850 | 0.801 | 0.880 | | | | | | | | |
| Delta alfa | 0.021 | 0.864 | 0.590 | 0.618 | –0.663 | –0.758 | 0.329 | –0.928 | –1.000 | –0.939 | –0.795 | | | | | | | |
| Delta beta | 0.698 | 0.306 | –0.072 | –0.098 | –0.793 | -0.046 | –0.420 | –0.727 | –0.682 | –0.767 | –0.979 | 0.677 | | | | | | |
| Dipole moment | –0.345 | –0.657 | –0.385 | –0.326 | 0.966 | 0.380 | –0.021 | 0.941 | 0.811 | 0.948 | 0.940 | –0.801 | –0.869 | | | | | |
| Chelate plane angle | 0.906 | –0.468 | –0.761 | –0.784 | –0.265 | 0.656 | –0.937 | –0.010 | 0.011 | –0.068 | –0.527 | –0.012 | 0.684 | –0.278 | | | | |
| Charge Cu[a] | –0.121 | 0.948 | 0.745 | 0.742 | –0.741 | –0.818 | 0.481 | –0.969 | –0.970 | –0.963 | –0.738 | 0.966 | 0.590 | –0.831 | –0.167 | | | |
| Charge N2[a] | 0.546 | –0.314 | –0.336 | –0.476 | –0.518 | 0.599 | –0.518 | –0.057 | 0.256 | –0.055 | –0.285 | –0.273 | 0.363 | –0.356 | 0.510 | –0.181 | | |
| Charge N3[a] | 0.440 | –0.255 | –0.236 | –0.384 | –0.523 | 0.535 | –0.407 | –0.070 | 0.263 | –0.058 | –0.233 | –0.281 | 0.290 | –0.347 | 0.395 | –0.159 | 0.991 | |
| Charge O4[a] | –0.350 | 0.230 | 0.175 | 0.329 | 0.505 | –0.500 | 0.330 | 0.056 | –0.288 | 0.038 | 0.173 | 0.306 | –0.218 | 0.314 | –0.310 | 0.163 | –0.974 | –0.995 |

[a]Charge obtained by NBO analysis.

**Table S3.** Descriptors for Schiff bases (L1 - L5)

| | | L1 | | L2 | | L3 | | L4 | | L5 |
|---|---|---|---|---|---|---|---|---|---|---|
| | Dipole moment | 5.1271 | | 5.041 | | 4.8587 | | 0.6573 | | 0.5303 |
| | BDE (calculated from Scheme 1) | 14.0 | | 13.2 | | 13.4 | | 14.5 | | 14.9 |
| | HOMO | –0.20147 | | –0.20152 | | –0.20248 | | -0.20033 | | –0.20116 |
| | LUMO | –0.02947 | | –0.0479 | | –0.04993 | | –0.02937 | | –0.04918 |
| | Delta | –0.172 | | –0.15362 | | –0.15255 | | –0.17096 | | –0.15198 |
| Atom No. | Charge NBO | | | | | | | | | |
| 1 | C | –0.75658 | C | –0.75806 | C | –0.11758 | C | –0.75561 | C | –0.11665 |
| 2 | C | 0.51915 | C | 0.52121 | C | 0.50227 | C | 0.51706 | C | 0.50105 |
| 3 | O | –0.64471 | O | –0.63812 | O | –0.64823 | O | –0.65183 | O | –0.65141 |
| 4 | C | –0.46628 | C | –0.46732 | C | –0.44816 | C | –0.46612 | C | –0.44934 |
| 5 | C | 0.28936 | C | 0.28641 | C | 0.29008 | C | 0.29523 | C | 0.29454 |
| 6 | C | –0.72627 | C | –0.72569 | C | –0.72605 | C | –0.72818 | C | –0.72771 |
| 7 | N | –0.61544 | N | –0.61787 | N | –0.61225 | N | –0.61736 | N | –0.6153 |
| 8 | C | –0.27632 | C | –0.27627 | C | –0.27686 | C | –0.06617 | C | –0.06623 |
| 9 | C | –0.27631 | C | –0.27676 | C | –0.27663 | C | –0.27162 | C | –0.27219 |
| 10 | N | –0.61546 | N | –0.61209 | N | –0.61251 | N | –0.61547 | N | –0.6122 |
| 16 | O | –0.64467 | O | –0.648 | O | –0.64761 | O | –0.64968 | O | –0.6521 |
| 17 | H | 0.23496 | C | –0.2392 | C | –0.23911 | C | –0.70039 | C | –0.23932 |
| 18 | H | 0.23496 | C | –0.22491 | C | –0.22483 | H | 0.23541 | C | –0.22534 |
| 19 | H | 0.23458 | C | –0.19465 | C | –0.19464 | H | 0.24417 | C | –0.1956 |
| 20 | H | 0.25437 | C | –0.24135 | C | –0.24126 | H | 0.23564 | C | –0.2409 |
| 21 | H | 0.25505 | C | –0.21204 | C | –0.21219 | H | 0.25488 | C | –0.21247 |
| 22 | H | 0.25322 | H | 0.23454 | C | –0.2118 | H | 0.23183 | C | –0.21221 |
| 23 | H | 0.25823 | H | 0.23271 | C | –0.24124 | H | 0.25446 | C | –0.24114 |
| 24 | H | 0.24453 | H | 0.24573 | C | –0.22483 | H | 0.25775 | C | –0.22549 |
| 25 | H | 0.46114 | H | 0.24672 | C | –0.19475 | H | 0.25396 | C | –0.19559 |
| 26 | H | 0.24826 | H | 0.25445 | C | –0.23919 | H | 0.2507 | C | –0.23951 |
| 27 | H | 0.23273 | H | 0.25304 | H | 0.23262 | H | 0.45766 | C | –0.70082 |
| 28 | H | 0.23273 | H | 0.258 | H | 0.23301 | H | 0.23793 | H | 0.23318 |
| 29 | H | 0.24826 | H | 0.244 | H | 0.25381 | H | 0.24066 | H | 0.24452 |
| 30 | H | 0.46114 | H | 0.46014 | H | 0.25806 | H | 0.45816 | H | 0.23396 |
| 31 | H | 0.24453 | H | 0.2484 | H | 0.24456 | H | 0.25207 | H | 0.25741 |
| 32 | H | 0.25322 | H | 0.23281 | H | 0.46269 | H | 0.2538 | H | 0.25413 |
| 33 | H | 0.25823 | H | 0.23274 | H | 0.24917 | H | 0.25752 | H | 0.25085 |
| 34 | H | 0.25435 | H | 0.24854 | H | 0.23319 | H | 0.25407 | H | 0.45869 |
| 35 | H | 0.25505 | H | 0.46251 | H | 0.23315 | H | 0.25441 | H | 0.23838 |
| 36 | H | 0.23462 | H | 0.24502 | H | 0.249 | H | 0.23462 | H | 0.24193 |
| 37 | | | H | 0.25354 | H | 0.46259 | H | 0.24974 | H | 0.45974 |
| 38 | | | H | 0.25783 | H | 0.24482 | H | 0.23271 | H | 0.25245 |
| 39 | | | H | 0.24065 | H | 0.25372 | H | 0.24972 | H | 0.25428 |
| 40 | | | H | 0.23927 | H | 0.25799 | | | H | 0.25728 |
| 41 | | | H | 0.26026 | H | 0.24073 | | | H | 0.24033 |
| 42 | | | H | 0.23933 | H | 0.23936 | | | H | 0.23929 |
| 43 | | | H | 0.23484 | H | 0.26015 | | | H | 0.25902 |
| 44 | | | | | H | 0.23942 | | | H | 0.23959 |
| 45 | | | | | H | 0.23501 | | | H | 0.23585 |
| 46 | | | | | H | 0.23494 | | | H | 0.23558 |
| 47 | | | | | H | 0.23945 | | | H | 0.23942 |
| 48 | | | | | H | 0.23932 | | | H | 0.2391 |
| 49 | | | | | H | 0.26012 | | | H | 0.25928 |
| 50 | | | | | H | 0.24063 | | | H | 0.24014 |
| 51 | | | | | | | | | H | 0.25044 |
| 52 | | | | | | | | | H | 0.23246 |
| 53 | | | | | | | | | H | 0.25022 |

**Table S4.** Descriptors for copper(II) complexes (1-5)

| Atom No. | Spin density | 1 | | 2 | | 3 | | 4 | | 5 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Cu | 0.541488 | Cu | 0.544047 | Cu | 0.545634 | Cu | 0.539366 | Cu | 0.543073 |
| 2 | N | 0.122008 | N | 0.122716 | N | 0.124117 | N | 0.119456 | N | 0.121146 |
| 3 | N | 0.121994 | N | 0.123428 | N | 0.124122 | N | 0.11877 | N | 0.121038 |
| 4 | O | 0.093561 | O | 0.093655 | O | 0.090063 | O | 0.093211 | O | 0.090532 |
| 5 | O | 0.093547 | O | 0.089545 | O | 0.090066 | O | 0.097222 | O | 0.09319 |
| 6 | C | 0.001611 | C | 0.001803 | C | 0.001748 | C | 0.001755 | C | 0.001754 |
| 7 | C | 0.001611 | C | 0.001681 | C | 0.001748 | C | 0.003127 | C | 0.003152 |
| 8 | C | –0.009671 | C | –0.009705 | C | –0.00948 | C | –0.008069 | C | –0.008047 |
| 9 | C | –0.009668 | C | –0.009343 | C | –0.00948 | C | –0.009734 | C | –0.009619 |
| 10 | C | 0.011315 | C | 0.011052 | C | 0.011199 | C | 0.011139 | C | 0.011008 |
| 11 | C | 0.011313 | C | 0.011433 | C | 0.0112 | C | 0.010953 | C | 0.010912 |
| 12 | C | 0.004183 | C | 0.004144 | C | 0.00409 | C | 0.004372 | C | 0.004423 |
| 13 | C | –0.007624 | C | –0.007686 | C | –0.007565 | C | –0.006182 | C | –0.006384 |
| 14 | C | 0.004175 | C | 0.003972 | C | 0.00409 | C | 0.004419 | C | 0.004371 |
| 15 | C | –0.007618 | C | –0.007442 | C | –0.007566 | C | –0.007923 | C | –0.007912 |
| 28 | H | –0.000569 | H | –0.000796 | H | 0.000187 | H | –0.000606 | C | 0.000994 |
| 29 | H | –0.000568 | H | –0.00062 | H | 0.003646 | H | –0.000589 | H | 0.002092 |
| 30 | H | 0.00199 | H | –0.000804 | H | 0.000186 | H | –0.000296 | H | 0.000124 |
| 31 | H | –0.000548 | H | –0.00066 | H | 0.003647 | H | –0.000749 | H | 0.003916 |
| 32 | H | –0.000713 | H | 0.001015 | H | –0.000807 | H | 0.00192 | H | 0.000999 |
| 33 | H | –0.000712 | H | –0.000567 | H | –0.000639 | H | –0.000711 | H | –0.000743 |
| 34 | H | 0.00199 | H | –0.000537 | H | 0.001081 | H | 0.002059 | H | –0.000651 |
| 35 | H | –0.000549 | H | –0.000721 | H | –0.000639 | H | –0.000567 | H | –0.000516 |
| 36 | | | H | 0.001988 | H | 0.001081 | H | –0.000108 | H | 0.001288 |
| 37 | | | H | –0.000557 | H | –0.000807 | H | –0.000085 | H | –0.000984 |
| 38 | | | H | 0.000024 | H | –0.000544 | H | 0.000973 | H | –0.000601 |
| 39 | | | H | 0.000036 | H | –0.000544 | | | H | –0.000562 |
| | Energy of orbital | | | | | | | | | |
| | Alfa HOMO | –0.19058 | | –0.19108 | | –0.1917 | | –0.19051 | | –0.19153 |
| | Alfa LUMO | –0.02441 | | –0.04208 | | –0.04413 | | –0.02481 | | –0.0442 |
| | Beta HOMO | –0.1878 | | –0.18845 | | –0.18912 | | –0.1878 | | –0.18901 |
| | Beta LUMO | –0.07368 | | –0.07557 | | –0.07732 | | –0.0753 | | –0.07893 |
| | Delta alfa | –0.16617 | | –0.149 | | –0.14757 | | –0.1657 | | –0.14733 |
| | Delta beta | –0.11412 | | –0.11288 | | –0.1118 | | –0.1125 | | –0.11008 |
| | Dipole moment | 3.9769 | | 3.9655 | | 3.9226 | | 3.9735 | | 3.917 |
| | Chelate plane angle | 8.994 | | 10.86 | | 11.711 | | 22.634 | | 22.868 |
| | Charge by NBO | 1 | | 2 | | 3 | | 4 | | 5 |
| 1 | Cu | 1.24399 | Cu | 1.24968 | Cu | 1.25275 | Cu | 1.24248 | Cu | 1.25059 |
| 2 | N | –0.67401 | N | –0.71144 | N | –0.67133 | N | –0.6687 | N | –0.66584 |
| 3 | N | –0.67403 | N | –0.71367 | N | –0.67133 | N | –0.6735 | N | –0.67092 |
| 4 | O | –0.73414 | O | –0.71272 | O | –0.73562 | O | –0.73323 | O | –0.73351 |
| 5 | O | –0.73416 | O | –0.70973 | O | –0.73561 | O | –0.73113 | O | –0.7329 |
| 28 | H | 0.2328 | H | 0.25037 | H | 0.23062 | H | 0.23235 | C | -0.69605 |
| 29 | H | 0.23279 | H | 0.24874 | H | 0.22783 | H | 0.2328 | H | 0.23148 |
| 33 | H | 0.25374 | H | 0.22982 | H | 0.25043 | H | 0.2535 | H | 0.24814 |
| 34 | H | 0.23273 | H | 0.22632 | H | 0.25099 | H | 0.23281 | H | 0.25128 |
| 38 | | | H | 0.24117 | H | 0.23303 | H | 0.23592 | H | 0.2336 |
| 39 | | | H | 0.239 | H | 0.23303 | | | H | 0.23278 |

### Experimental details for determination of the antioxidant activity[1]

Antioxidant activities were determined *in vitro* by DPPH free radical scavenging assay. Trolox, in concentration range of 0-280 ng spot$^{-1}$, was used as a standard (r = 0.9993). The spots of 1 μL of compound solution (0.6 mg mL$^{-1}$) in appropriate solvents were applied by autosampler (Linomat 5, Camag) on RP18 silica plate (Merck, Germany) as well as series of standard solutions in methanol followed by applying 1 μL of methanolic solution of DPPH ($0.15 \times 10^{-3}$ mol L$^{-1}$) at the same spots. No development was carried out. This plate was left in the dark. After 30 min of incubation, the plate was scanned. Camag TLC Scanner with CATS evaluation software was used with the following settings: wavelength 515 nm, scanning speed 20 mm s$^{-1}$, multi level calibration via peak area. The values of antioxidant activity of the compounds are expressed as Trolox equivalent antioxidant capacity (TEAC).

## Reference

1. Aburas, N.; Lolić, A.; Stevanović, N.; Tripković, T.; Nikolić-Mandić, S.; Baošić, R.; *J. Iran. Chem. Soc.* **2012**, *9*, 859.