



## Synthesis and Characterization of Nickel(II) and Copper(II) Complexes with 3-(*p*-Chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one

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In the paper, the nickel(II) and copper (II) complexes of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one have been synthesized and characterized by elemental analyses, IR, UV-vis, <sup>1</sup>H NMR spectra.

**Key Words:** Ni(II) and Cu(II) complexes, 3-(*p*-Chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one.

### INTRODUCTION

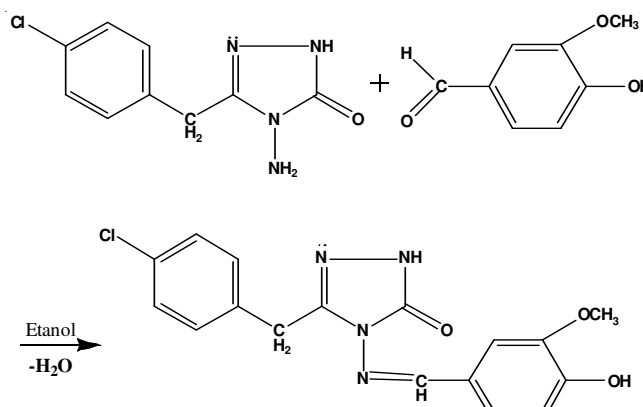
Schiff bases perform very important role in bioinorganic chemistry since they have significant biological activities. Some metal complexes of Schiff bases can cause to DNA damage, cleavage<sup>1-4</sup>. Schiff bases the dependence of their mode of binding with transition metal ions in the living system have been of remarkable interest<sup>5-9</sup>. The transition metal compounds of Schiff bases have been reported to behave for enzyme inhibitors<sup>10</sup> and are beneficial because of their pharmacological applications<sup>11-13</sup>. The Schiff base 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one shows remarkable antibacterial, antioxidant and analgesic activity<sup>14</sup>, but no metal complexes of this Schiff base have been reported in the past which can have better pharmaceutical potentials. Therefore, study of the metal complex of this schiff base is important to discover the potential new drug.

In the present study, 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one was synthesized and characterized and its nickel(II) and copper(II) complexes were synthesized.

### EXPERIMENTAL

All the solvents and reagents were provided commercially and used without further purification. Infrared spectra (4000-400 cm<sup>-1</sup>) were determined with KBr disks on Thermo Mattson FTIR spectrometer. The UV-visible spectra were recorded on a PG Instruments Ltd. T80 UV/vis spectrometer. <sup>1</sup>H NMR spectra were measured on a Bruker 300 Mhz Ultrashield TM NMR.

**Preparation of the ligand of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one:** The ligand (Fig. 1) was prepared according to the literature (Scheme-I)<sup>14</sup>. 1 g of 4-amino-3-(*p*-chlorobenzyl)-1*H*-1,2,4-triazole-5-one with 1.05 g hydroxy-3-methoxybenzaldehyde were boiled in 30 mL ethanol under condenser for 2 h. The solvent was evaporated on water bath. The solid yield was crystallized in the alcohol, as white solid (m.p. 205 °C), <sup>1</sup>H NMR (300 MHz, DMSO) (ppm): 3.5 (-OCH<sub>3</sub>), 4.01 (-CH<sub>2</sub>-), 7.01-7.34 (Ar-H), 9.75 (N=CH), 9.75 (OH) and 11.33 (NH). Anal. calcd. (%) for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O: C, 62.95; H, 4.97; N, 17.27. Found (%): C, 62.83; H, 4.80; N, 17.29. IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): (C=O): 1625, (C=N): 1584, (N-H): 3216, (O-H): 3339.



**Scheme-I:** Synthesis of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one

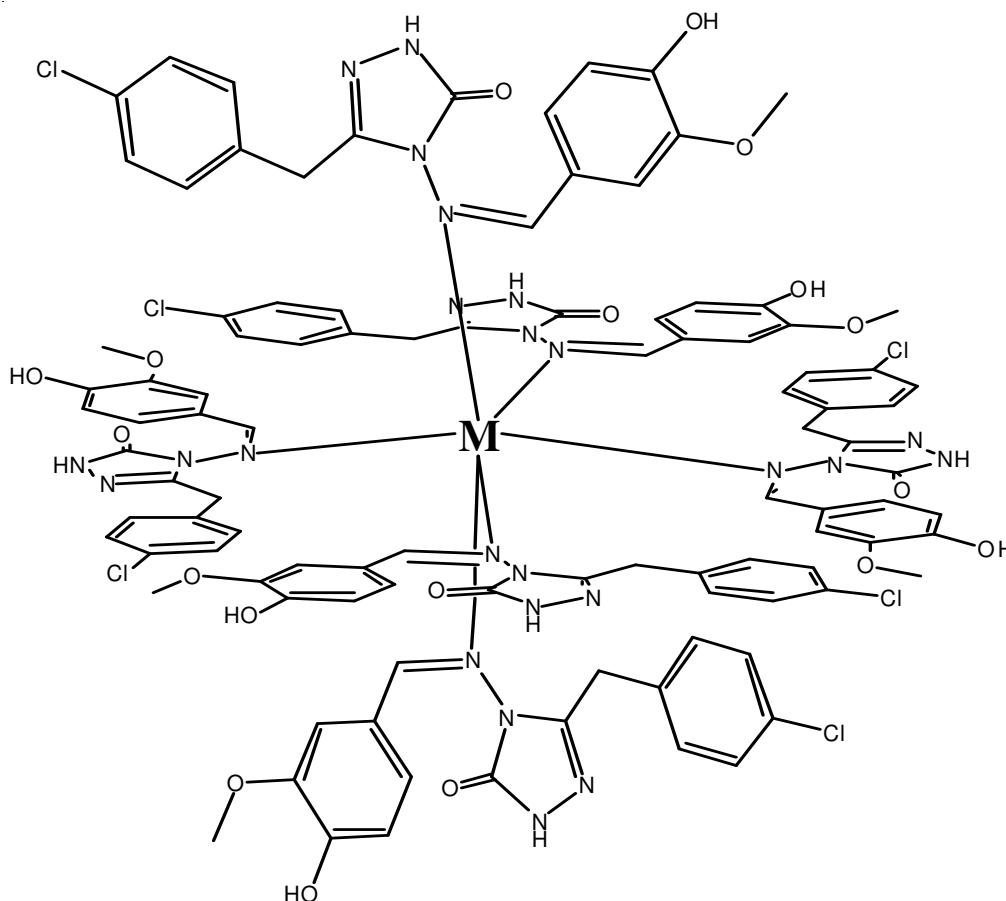


Fig. 1. Structure of (3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one) Ni(II) complex **1** (M= Ni)

**Preparation of (3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one) Ni(II) complex:** The ligand (3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one) (1.5 mmol, 0.541 g) and the NiCl<sub>2</sub>·6H<sub>2</sub>O (1.5 mmol, 0.541 g) were mixed in ethanol (150 mL). The colour of solution turned into light green. 20 mL of NH<sub>3</sub> was added in this solution. The blue green precipitate was formed at the bottom of the container. The mixture were stirred under the condenser for 3 h and the mixture was left at room temperature. After 24 h, jelly green precipitate was formed. The mixture were filtered to remove any insoluble residues and then stirring was continued for 24 h at room temperature. A green precipitate of the Ni(II) (complex **1**) (Fig. 1), was separated from the solution by suction filtration, purified by washing several times with ethanol and dried for 3 h under vacuum at 150 °C, yield 70 %. Anal. calcd. (found) (%) for the Ni(II) complex (**1**) C<sub>102</sub>H<sub>75</sub>N<sub>24</sub>O<sub>18</sub>Cl<sub>6</sub>Ni: C, 55.40 (55.16); H, 4.10 (4.19); N, 15.20 (14.60). <sup>1</sup>H NMR (300 MHz, DMSO) (ppm): 3.5 (-OCH<sub>3</sub>), 3.8 (-CH<sub>2</sub>-), 6.86-7.37 (Ar-H), 9.49 (N=CH), 9.8 (OH), 11.9 (NH). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): (C=O): 1707, (C=N): 1588, (N-H): 3216, (O-H): 3400, (Ni-N): 492.

**Preparation of (3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one) Cu(II) complex:** The ligand (3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one) (1.5 mmol, 0.541 g) was dissolved 300 mL of ethanol and the solution was taken into a flask. 5 mL of NaOH (0.05 g) was

added to the solution and the solution was stirred for 0.5 h at 60 °C. Afterward, the CuSO<sub>4</sub>·5H<sub>2</sub>O (0.34 g, 1.5 mmol g) were added to the solution. The mixture were stirred under the condenser for 3 h and the mixture was left for over night at room temperature. The reaction mixture was filtered to remove any insoluble residues and then stirring was continued for 24 h at room temperature (m.p. 233 °C, yield 48 % (Fig. 2). Anal. calcd (found) (%) for the Cu(II) (complex **2**) C<sub>34</sub>H<sub>37</sub>N<sub>8</sub>O<sub>10</sub>CuCl<sub>2</sub>: C, 44.98 (45.38); H, 5.26 (4.11); N, 13.16 (10.10). <sup>1</sup>H NMR (300 MHz, DMSO) (ppm): 3.5 (-OCH<sub>3</sub>), 3.8 (-CH<sub>2</sub>-), 6.86-7.37 (Ar-H), 9.50 (N=CH), 9.8 (OH), 11.9 (NH). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): (C=O): 1625, (C=N): 1588, (N-H): 3216, (O-H): 3400, (Cu-O): 571.

## RESULTS AND DISCUSSION

Analytical data for Ni(II) and Cu(II) complexes conform to C<sub>102</sub>H<sub>75</sub>N<sub>24</sub>O<sub>18</sub>Cl<sub>6</sub>Ni and C<sub>34</sub>H<sub>37</sub>N<sub>8</sub>O<sub>10</sub>Cl<sub>2</sub>Cu. The complexes are soluble in DMF, DMFSD, ethanol. The spectroscopic characterization of the novel synthesized compounds involved <sup>1</sup>H NMR, elemental analysis, IR and UV-vis spectral investigations and the results are matched the proposed structures.

3-(*p*-Chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one Ni(II) complex (Fig. 1) was obtained by the reaction of the ligand with NiCl<sub>2</sub>·6H<sub>2</sub>O in ethanol. 3-(*p*-Chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one Cu(II) complex **1** was obtained by the reaction compound with metal salts

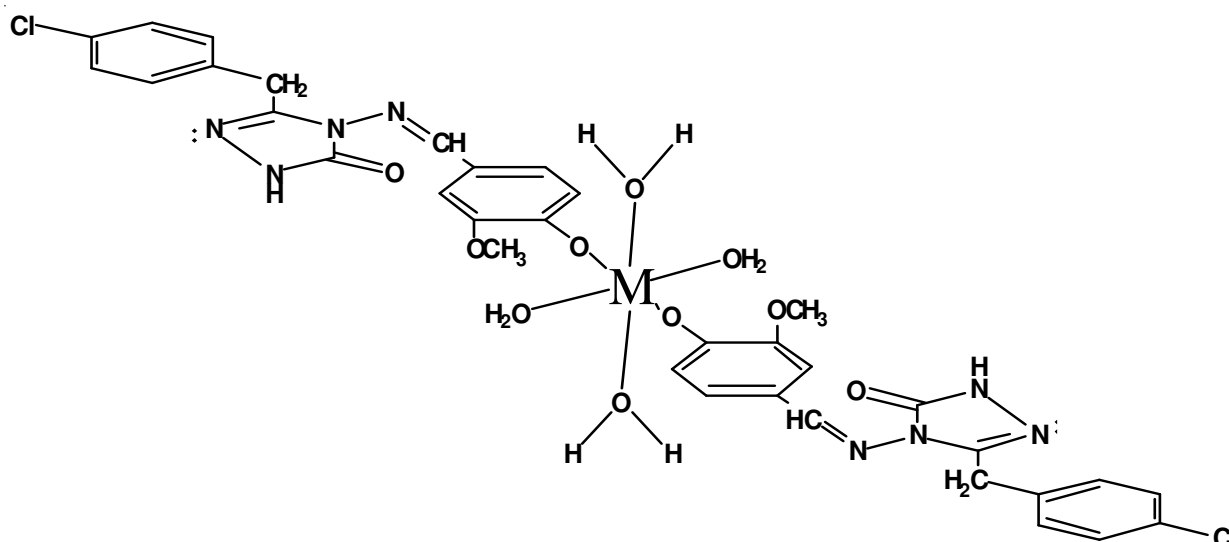


Fig. 2. Structure of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one Ni(II) compound (M=Cu)

(CuSO<sub>4</sub>·5H<sub>2</sub>O) at 60 °C (Fig. 2). While complex **1** was obtained in high yield in ethanol and complex **2** was obtained in low yield with CuSO<sub>4</sub>·5H<sub>2</sub>O in ethanol. Thus, best reaction conditions of each metal complexes could be changed by solvent. Therefore, high yield of complex **1** can be attributed to the solvent effect of ethanol. In this study, we tried the synthesis of metal complexes (Ni(II) and Cu(II)) of *p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one with solvent. Spectral data of new synthesized compounds are consistent with the suggested structures.

The IR spectrum of the free ligand show bands at 1588 cm<sup>-1</sup> and (N-H): 3216 cm<sup>-1</sup> (Fig. 3), which is assigned to C=N and N-H, respectively. In the complex **1**, the band for C=N is shifted by about 4 cm<sup>-1</sup>, indicating that the (=N-) of imidazole ring takes part in the coordination (Fig. 4). The band for (N-H) of imidazole ring is not shifted, which shows that the (=N-) of imidazole ring do not take part in the coordination. For the complex **1**, the band corresponding to at 492 cm<sup>-1</sup> is indication for formation of Ni-N bond. The band corresponding to (O-H) at 3400 cm<sup>-1</sup> indicates that the complex contains water molecules that is in accordance with the results of elemental analyses The IR spectrum peak of C=O is shifted to 1711 cm<sup>-1</sup>.

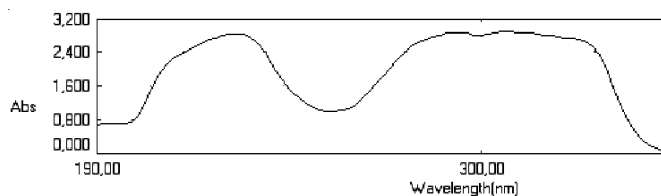


Fig. 3. Electronic spectra of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one

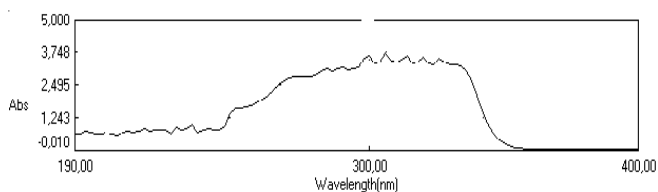


Fig. 4. Electronic spectra of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one Ni(II) complex

The band for (N-H) of imidazole ring is not shifted, which indicates that the (=N-) of imidazole ring do not take part in the coordination for the complex **2**. The band corresponding to at 571 cm<sup>-1</sup> is indication for formation of M-O bond (Fig. 5). The band corresponding to (O-H) at 3400 cm<sup>-1</sup> indicates that the complex contains water molecules that is in accordance with the results of elemental analyses. The IR spectrum peak of C=O is shifted to 1711 cm<sup>-1</sup>.

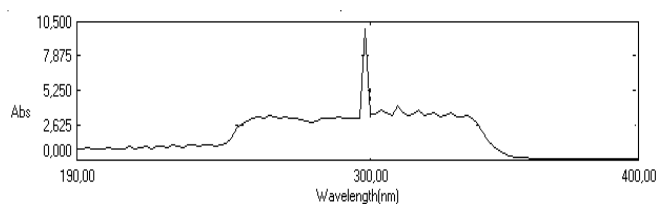


Fig. 5. Electronic spectra of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one Cu(II) complex

Comparison of the IR spectral data evidently showed that the formation of complex **1** and **2**, the appearance of new absorption bands at (C=O): 1707 cm<sup>-1</sup>, (C=N): 1588 cm<sup>-1</sup>, (N-H): 3216 cm<sup>-1</sup>, (O-H): 3400, (M-N): 492 and (C=O): 1625 cm<sup>-1</sup>, (C=N): 1588 cm<sup>-1</sup>, (N-H): 3216 cm<sup>-1</sup>, (O-H): 3400, (M-O): 571, respectively. After conversion of 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylideneamino)-1*H*-1,2,4-triazole-5-one into the metal complex **1** and **2**, the peak for the M-N and M-O vibration around differed. The <sup>1</sup>H NMR spectrum of complex **1** exhibited 3.5 (-OCH<sub>3</sub>), 3.8 (-CH<sub>2</sub>-), 6.86-7.37 (Ar-H), 9.49 (N=CH), 9.8 (OH), 11.9 (NH) and the <sup>1</sup>H NMR spectrum of complex **2** exhibited 3.5 (-OCH<sub>3</sub>), 3.8 (-CH<sub>2</sub>-), 6.86-7.37 (Ar-H), 9.50 (N=CH), 9.8 (OH), 11.9 (NH).

The <sup>1</sup>H NMR spectra of compound was almost identical except for small shift and in good correlation with the structures of the synthesized compounds. The complex **1** show typical electronic spectra with two strong absorption regions (Fig. 4), one of them in the UV region at about 286-310 nm. The UV-vis spectra of the complex **2** (Fig. 5) indicated band absorptions between 206-318 nm.

## Conclusion

3-(*p*-Chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzyliden amino)-1*H*-1,2,4-triazole-5-one was synthesized and used as a key ligand for the preparation and characterization of novel metal complexes (Ni, Cu). Some metal complexes of Schiff bases could cause to DNA damage, cleavage. Schiff bases the dependence of their mode of binding with transition metal ions in the living system have been of remarkable interest. These metal compounds of schiff bases could behave for enzyme inhibitors that are beneficial because of their pharmacological applications.

## REFERENCES

1. R. Rajaram, B.U. Nair and T. Ramasami, *Biochem. Biophys. Res. Commun.*, **210**, 434 (1995).
2. R. Vijavalakshmi, M. Kanthimathi, V. Subramanian and B.U. Nair, *Biochim. Biophys. Acta*, **1475**, 157 (2000).
3. H.Y. Shrivastava and B.U. Nair, *Biochem. Biophys. Res. Commun.*, **285**, 915 (2001).
4. H.Y. Shrivastava and B.U. Nair, *Biochem. Biophys. Res. Commun.*, **270**, 749 (2000).
5. L. Savanini, L. Chiasserini, A. Gaeta and C. Pellerano, *Bioorg. Med. Chem.*, **10**, 2193 (2002).
6. E. Ochiai, *Bioinorganic Chemistry An Introduction*, Allyn and Bacon, Inc., Boston (1977).
7. J.A. Anten, D. Nicholis, J.M. Markopoulos and O. Markopoulou, *Polyhedron*, **6**, 1075 (1987).
8. I.A. Tossadis, C.A. Bolos, P.N. Aslanidis and G.A. Katsoulos, *Inorg. Chim. Acta*, **133**, 275 (1987).
9. J.C. Craliz, J.C. Rub, D. Willis and J. Edger, *Nature*, **34**, 176 (1955).
10. J.R. Dilworth, *Coord. Chem. Rev.*, **21**, 29 (1976).
11. J.R. Merchant and D.S. Clothia, *J. Med. Chem.*, **13**, 335 (1970).
12. N.S. Biradar and B.R. Havinale, *Inorg. Chim. Acta*, **17**, 157 (1976).
13. H.N. Fox, *Science*, **116**, 129 (1952).
14. S. Manap, Master of Sciences Thesis, Kafkas Üniversitesi Fen Bilimleri Enstitüsü, Kars, Turkey (2009).