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NOTE

Synthesis and Characterization of 2-{[(6-{[(2-Hydroxyphenyl)-methylidene]amino}-2-pyridyl)imino]methyl}phenol and Its Zn(II) Complex

FAHMIDEH SHABANI†, KHAYROALLAH MEHRANI†, SHAHRIAR GHAMMAMY*, MOHAMMAD. R. REZAKHANI, SEYED ABOLFAZL SEYED SADJADI‡, RAHMATTOLLAH RAHIMI§, SINA ASILI¶ and ALIREZA HEMATIMOGHADAM#

Department of Chemistry, Faculty of Science,
Imam Khomeini International University, Qazvin, Iran
Fax: (98)(281)3780040; Tel: (98)(281)3780040
E-mail: shghamami@yahoo.com; shghamami@ikiu.ac.ir; fafachem@yahoo.com

2-{[(6-{[(2-Hydroxyphenyl)methylidene]amino}-2-pyridyl)imino]-methyl}phenol (HMA) were synthesized and characterized. Zn(II) metal complex of this ligand prepared by reaction of Zn(II) acetate with HMA in dry acetonitrle. Characterization of the ligand and its zinc(II) complex was made by microanalyses, FT-IR, ^{1}H NMR, ^{13}C NMR and UV-visible spectroscopy. In the light of these results, it was suggested that one ligand coordinate to each metal atom to form octahedral complex of Zn(II). The zinc(II) complex was characterized by elemental analysis (C, H, N), FT-IR, electronic spectra and molar conductance measurements. The elemental analysis data suggest the stoichiometry to be 1:1 [M:L] ratio formation. The molar conductance measurements reveal the presence of 1:1 electrolytic nature complex.

Key Words: 2-{[(6-{[(2-Hydroxyphenyl)methylidene]amino}-2-pyridyl)imino]methyl}phenol, Zn(II) complex, Synthesis.

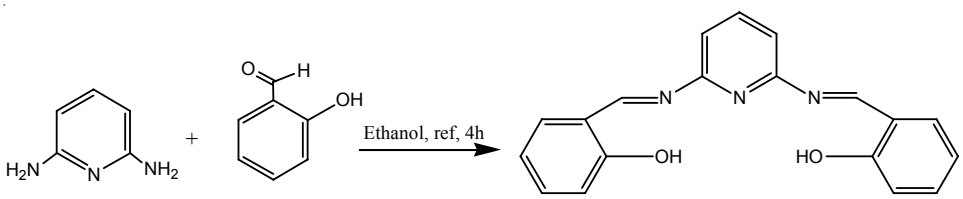
In the last few years a renewed interest in metal-based therapy has been developed. In fact, on coordination, bioactive ligands might improve their bioactivity profiles, while inactive ligands may acquire pharmacological properties[1-6]. In addition, metal-coordination is one of the most efficient strategies in the design of repository, slow-release or long-acting drugs[7]. Furthermore, metal complexes have gained importance as enzyme inhibitor. They can either strongly attach to enzymes (through covalent and ionic bonds) preventing substrate interaction or perturbing the active site or else disturb metals that are essential for enzymatic action[8].

†Department of Chemistry, Islamic Azad University, Ardabil Branch, Ardabil, Iran.
‡Faculty of Chemistry, Industry and Science University, Tehran, Iran.
§Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran.
¶Babasafari Student Research Center, Ardabil Branch, Ardabil, Iran.
#Department of Food Industries, Islamic Azad University, Tabriz Branch, Tabriz, Iran.

Metal complexes of biologically important ligands are sometimes more effective than the free ligands[9]. Zinc(II) plays critical role in liver enzyme function and synthesis. In 1980, Coulston and Dandona[10] found that Zn(II) is one of the essential elements in animals and humans, stimulates lip genesis in rat adipocytes similar to the action of insulin. Over expression of these zinc-containing enzymes is associated with several diseases including arthritis and cancer, so inhibition of the zinc active site is a reasonable drug development strategy. Indeed, enzymatic is an attractive target because of the diversity of structural and catalytic roles in enzymes[11]. Metal-mediated assembly has been widely used for the construction of supramolecular arrays with metal ions as connects and various ligands as linkers[12].

From these points of view, the present study deals with the preparation of 2-{[(6-{[(2-hydroxyphenyl)methylidene]amino}-2-pyridyl)imino]methyl}phenol (HMA) and its Zn(II) complex. The solid complex has been synthesized and studied by elemental analyses, IR and ^{1}H NMR, ^{13}C NMR and UV-visible spectroscopy.

Synthesis of the ligand: To a stirred solution of 4 mmol of the appropriate substituted salicylaldehyde in absolute ethanol (50 mL) was added drop wise an ethanolic solution (10 mL) of 2 mmol 1,6-diaminopyridine. This mixture was then refluxed for 4 h. After wards the mixture was cooled to room temperature, the cooled for 24 h at 5 °C. The solid was filtered and washed with cold ethanol and died over silica (**Scheme-I**).



Scheme-I: Synthesis route of 2-{[(6-{[(2-hydroxyphenyl)methylidene]amino}-2-pyridyl)imino]methyl}phenol (HMA) ligand

Elemental analysis found (calcd. based on $C_{19}H_{15}N_3O_2$: C 72.35 (71.92); H 5.02 (4.73); N 13.67 (13.24). IR (KBr pellet, ν_{max}, cm^{-1}): 3381(m), 1612 (w), 1483 (w), 1150 (m), 984-631 (m). UV-Vis [λ_{max} (MeCN)/nm (5×10^{-3} ε/dm^3 mol^{-1} cm^{-1})]: 277 (98), 374 (76). ^{1}H NMR (DMSO) δ: 8.1 (s, 1H, benzyldenimine), 7.8 (q, 1H, pyridine), 7.49 (d, 2H, pyridine), 7.4 and 7.2 (d, 2H, arom), 7.1 and 6.8 (q, 2H, arom), 5.02 (s, 1H, O-H).

Synthesis of the Zn(II) complex: A solution of zinc(II) acetate (0.034 g, 0.154 mmol) dissolved in acetonitrile added gradually to a stirred ethanol solution of the ligand [HMA (0.0512 g, 0.157 mmol)], in the molar ratio 1:1 (metal:ligand). The reaction mixture was further stirred for 3 h to ensure of the completing and precipitation of the formed complexes. The precipitated solid complexes were filtered, washed several times with 50 % (v/v) hexane-water to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether

and dried in vacuum desiccators over anhydrous $CaCl_2$. Elemental analysis found (calcd. based on $[Zn(C_{19}H_{15}N_3O_2)](OAc)_2$: C 46.13 (45.55); H 3.27 (2.99); N 8.66 (8.39). IR (KBr pellet, ν_{max}, cm^{-1}): 3371(w), 1611(w), 1453(w), 1278(m), 613-942(s), 415(s). UV-Vis [λ_{max} (MeCN)/nm (5×10^{-3} ε/dm^3 mol^{-1} cm^{-1})]: 278 (64), 314 (90), 395 (24). ^{1}H NMR (DMSO) δ: 9.4 (s, 1H, benzyldenimine), 7.95 (q, 1H, pyridine), 7.04 (d,2H, pyridine), 8.2 and 7.44 (d, 2H, arom), 6.19 and 6.98 (q, 2H, arom), 5.09 (s, 1H, O-H).

The reaction of Zn(II) acetate with the ligand, HMA, results in the formation of $[Zn(C_{19}H_{15}N_3O_2)](OAc)_2$. This complex is quite stable and could be stored without any appreciable change. The $[Zn(C_{19}H_{15}N_3O_2)](OAc)_2$ complex do not have sharp melting point but decompose above 150 °C. This is insoluble in common organic solvents, such as ethanol, methanol, chloroform or acetone. However, this is soluble in DMSO and DMF. Its structure was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and IR. Its elemental analyses are in accord with their proposed formula. The spectral data of the complex have good relationship with the literature data.

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