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Synthesis and Spectroscopic Studies of Cu(II), Co(II), Ni(II) and Zn(II) Schiff Base Complexes from 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-on with 2-Hydroxynaphthaldehyde

by M. Sönmez

Department of Chemistry, Faculty of Science and Arts, Yüzüncü Yıl, University, 65080, Van, Turkey
E- mail: vansonmez@hotmail.com

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Cu(II), Co(II), Ni(II) and Zn(II) metal complexes of a new heterocyclic Schiff base derived from 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-on with 2-hydroxynaphthaldehyde have been synthesized and characterized by elemental analyses, electronic, IR and ^{1}H NMR spectra, and also by molar conductivity and magnetic moment measurements. It has been found that the Schiff bases behave as a neutral tridentate (ONO) ligand, forming chelates with 1:2 (metal:ligand) stoichiometry. It is suggested that all the complexes have octahedral structure and are non-electrolytes.

Key words: heterocyclic Schiff bases complexes, 2-hydroxynaphthaldehyde

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications [1–3]. In recent years, metal complexes of Schiff bases have attracted considerable attention, due to their remarkable antifungal, antibacterial and antitumor activity [4,5]. Metal chelates of 2-hydroxynaphthaldehyde are well known for their biological activities [6,7]. We recently reported the synthesis and characterization of heterocyclic complexes obtained from N-aminopyrimidine-2-one with salicylaldehyde [8].

This paper describes the synthesis of a new Schiff base ligand (Figure 1) containing a ring of the pyrimidine and their metal complexes. Spectral and magnetic studies have been used to characterize the structure of the complexes. IR, ^{1}H NMR and ^{13}C NMR spectra were obtained to determine the structure of the ligand LH.

EXPERIMENTAL

MeOH, EtOH, $CHCl_3$, DMF, toluene, diethylether, n-heptane and 2-hydroxynaphthaldehyde were obtained from Fluka and Aldrich. The metal salts $Cu(AcO)_2\cdot H_2O$, $Co(AcO)_2\cdot 4H_2O$, $Zn(AcO)_2\cdot 2H_2O$ and $NiCl_2\cdot 6H_2O$ were obtained from E. Merck. All solvents were dried and purified before use. 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-on was prepared as described previously [9].

Physical measurements: Elemental analyses (C, H, N) were performed by using a Carlo Erba 1106 elemental analyser. IR spectra were obtained using KBr discs (4000–400) cm^{-1} on a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained in DMF on a Unicam UV2-100 UV/Visible spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of the Schiff base ligand and their transition metal complexes were determined in DMF at room temperature by using a Jenway model 4070 conductivitymeter. The ^1H NMR and ^{13}C NMR spectra of the Schiff base were recorded with a Varian XL-200 NMR instrument.

Synthesis of the Schiff base (LH): The Schiff base ligand was prepared by the condensation of the 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-on (0.291 g, 1 mmole) with the 2-hydroxynaphthaldehyde (0.172 g, 1 mmole) in butanol (40 ml) achieved by boiling the mixture under reflux for 2 h. The precipitated ligand was filtered off, recrystallized from BuOH and dried in a vacuum dessicator. Yield was 0.302 g (68%), m.p. 217°C.

Synthesis of the complexes: 0.89 g (2.00 mmole) of the ligand was dissolved in 30 ml of chloroform, and a solution of 1.00 mmole of the metal salt [$Cu(AcO)_2{\cdot}H_2O$ (0.20 g), $Co(AcO)_2{\cdot}4H_2O$ (0.25 g), $Zn(AcO)_2{\cdot}2H_2O$ (0.22 g) and $NiCl_2{\cdot}6H_2O$ (0.24 g)] in 15 ml methanol was added dropwise with continuous stirring. The mixture was stirred further for 1.5–2.5 h at 80°C. The precipitated solid was then filtered off, washed with diethyl ether, followed by cold methanol and dried in a vacuum dessicator.

RESULTS AND DISCUSSION

The newly synthesized Schiff base ligand and its complexes are very stable at room temperature in the solid state. The ligand is soluble in common organic solvents, and its metal complexes are soluble in DMF and DMSO. The elemental analytical data of the complexes reveal that the compounds have a metal:ligand anion stoichiometry of 1:2, corresponding to the general formulae of $[M(L)_2]{\cdot}mH_2O$, where L is the anion of LH. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The colours, yields, melting points, IR and electronic absorption spectral data of all the compounds are presented in Table 1 and Table 2. All the complexes did not show electrolytic properties (0.8–2.8 Ω^{-1} cm^2 mole^{-1}).

Table 1. Physical data and electronic absorption spectral data of all the compounds.

Compounds	Yield %	μ_{eff} [B.M]	Colour	M.p. (°C) (Dec.)	λ_{max} (ε_{max}, M^{-1} cm^{-1})
LH	68		Yellow	217	390 (3967), 300 (4805), 235 (9354)
$[Cu(L)_2]$ $C_{56}H_{36}N_6O_6Cu$ (951.54 g/mole)	72	1.92	Brown	213	742 (12), 595(38), 514(89), 380 (3540)
$[Co(L)_2]{\cdot}3H_2O$ $C_{56}H_{38}N_6O_7Co$ (964.93 g/mole)	65	5.10	Dark-Red	122	670, 554 (57), 410 (1816), 365 (3602)
$[Ni(L)_2]{\cdot}2H_2O$ $C_{56}H_{40}N_6O_8Ni$ (982.71 g/mole)	70	3.20	Orange	201	765(6), 595(42), 359(3828)
$[Zn(L)_2]{\cdot}3H_2O$ $C_{56}H_{42}N_6O_9Zn$ (1007.37 g/mole	85	Dia	Red	174	368(1681), 245(4670)

Condensation of the 2-hydroxynaphthaldehyde with 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-on readily gives rise to the corresponding imines (Figure 1), which were easily identified by IR, ^1H NMR and ^{13}C NMR spectra.

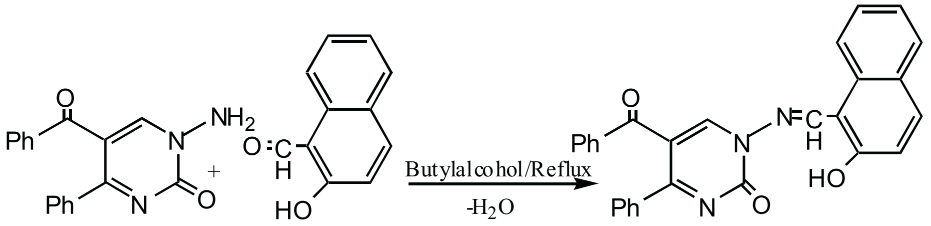


Figure 1. Scheme for the preparation of the ligand LH.

Tridentate complexes were obtained from 1:2 molar ratio reactions with metal ions and LH ligand. The ligand LH, on reaction with $Co(CH_3COO)_2{\cdot}4H_2O$, $Cu(CH_3COO)_2{\cdot}H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$, and $NiCl_2{\cdot}6H_2O$ salts yields complexes corresponding to the general formula $[Co(L)_2]{\cdot}H_2O$, $[Cu(L)_2]$, $[Zn(L)_2]{\cdot}3H_2O$, and $[Ni(L)_2]{\cdot}2H_2O$. The complexes were prepared by the general reaction:

$$2LH + M(CH_3COO)_2{\cdot}nH_2O \xrightarrow{\text{methanole/chloroform}} [M(L)_2]{\cdot}mH_2O + 2CH_3COOH + xH_2O$$

$$\begin{array}{lllllll} M & = & Co(II), & Cu(II), & Zn(II), & Ni(II) & \qquad LH = C_{28}H_{19}N_3O_3 \\ n & = & 4 & 1 & 2 & 6 & \\ m & = & 1 & – & 3 & 2 & \\ x & = & 3 & 1 & – & 4 & \end{array}$$

The metal-to-ligand ratio of all the complexes was found as 1:2. But the Co(II), Ni(II) and Zn(II) complexes have one, two and three additional molecules of crystallization water.

Table 2. Characteristic IR spectral data of the ligand and their metal complexes (cm^{-1}).

Compounds	OH/H_2O	C=O	C=N	C–O	M–N	M–O
LH	3435	1690 1650	1633	1288	–	–
$[Cu(L)_2]$	–	1653	1600	1266	460	530
$[Co(L)_2]{\cdot}3H_2O$	3280	1658	1610	1260	465	534
$[Ni(L)_2]{\cdot}2H_2O$	3350	1650	1610	1272	470	540
$[Zn(L)_2]{\cdot}3H_2O$	3240	1660	1598	1270	460	510

Conductivity: The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) in DMF, which are in the range [8,10,11] 0.1–5.6 Ω^{-1} $cm^2 mol^{-1}$.

Infrared spectral study: Table 2 presents the most important IR spectral bands of the ligand LH with all the metal complexes. The IR spectra of Schiff base ligand, derived from 2-hydroxynaphthaldehyde (LH), showed a broad band at 3435 cm^{-1}, which may be due to ν(OH). The free ν(OH) is generally observed between 3500–3650 cm^{-1} [12]. The intense band at 1288 cm^{-1} present in the IR spectrum of the Schiff base ligand may be assigned to phenolic (C–O) stretching mode, according to previous assignments. The pyrimidine ring shows characteristic stretching absorption bands at the 3058 cm^{-1}. The phenyl group shows C–H stretching at 3030 cm^{-1} and C=C stretching at 1550 cm^{-1}. The bands at 1583 cm^{-1} can be very safely assigned to ν(C=N) (pyrimidine) [8,9]. The absorption in the region 1615–1480 cm^{-1} of all the complexes substantiates the stretch of the naphthalene nucleus. A strong band at l690–1650 cm^{-1} and 1633 cm^{-1} in the IR spectra of the free ligand, assigned to ν(C=O) and ν(C=N) [8,11,12], is changed by ±10–30 cm^{-1} in the spectra of complexes, indicating coordination through azomethine nitrogen, phenolic oxygen and carbonyl oxygen of Schiff base (Figure 2). In the spectra of the Cu(II), Ni(II), Co(II) and Zn(II) complexes, the bands observed in the 445–470 and 420–426 cm^{-1} region may be due to ν(M–N) and ν(M–O), respectively [8,12]. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3240–3350 cm^{-1}, due to the υ(O–H) frequency of crystallization water. This water content was also identified by the elemental analyses. Broad bands of the Cu(II), Ni(II), Co(II) and Zn(II) complexes in the 3240–3350 cm^{-1} region are assigned to the ν(OH) vibration of the water molecules [8,11,12].

Proton and carbon nuclear magnetic resonance spectra: Chloroform was used as a deuterated solvent to measure the ^{1}H NMR spectra of the ligand and its Zn(II) complex, except those of Cu(II), Co(II) and Ni(II), because of their paramagnetic behaviour. The sharp singlet was observed at about δ 12.28 ppm, due to enolic proton of the ligand. The singlet at δ 9.19 ppm and 8.35 ppm is due to azomethine proton, pyrimidine ring (C–H) proton in the spectrum of the ligand, respectively. In the spectra of the Schiff base the naphthyl and phenyl multiplet was observed between δ 6.72 and 8.17 ppm. The ^{1}H NMR spectra of Zn(II) complex shows approximately the same peaks identical to those of the free ligand with exception that the peak due to the (2-OH) phenolic group resonance is absent. This is considered as an additional evidence for the deprotonation of OH enolic (α-OH in naphthaldehyde).

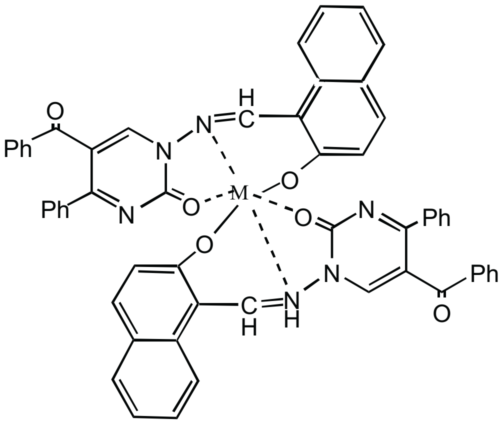
Chloroform was used as a deuterated solvent to measure the ^{13}C NMR spectra of the ligand. The ^{13}C NMR spectra of the ligand LH are characterized by the presence of a cluster of peaks at 190.5 and 197.1 ppm, due to carbonyl carbons. The spectrum of the ligand shows a peak at 175.3 ppm, which may be attributed to the CH=N group; a peak at 159.2 ppm attributed to the pyrimidine ring (C=N) group; and peaks in the region 112.6–158.0 ppm, due to aromatic carbons.

Electronic spectra and magnetic measurements: The electronic spectral data for the compounds are shown in Table 1. The spectra were recorded in DMF. In the spectrum of the Schiff base, the band of 390 nm is attributed to the azomethine chromophore $\pi\rightarrow\pi^*$ transition. The bands at 300–235 nm are associated with the naphthalene nucleus and pyrimidine rings $\pi\rightarrow\pi^*$ transition. In the spectra of the complexes, the band of the azomethine chromophore $\pi\rightarrow\pi^*$ transition is shifted to about 370 nm, indicating that the imino nitrogen is involved in coordination to the metal ion. The electronic spectra of the Zn(II) complex, which is diamagnetic, have bands in the 368–245 nm range and these bands may be due to the n$\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the naphthalene nucleus, pyrimidine rings and azomethine group.

The six coordinate [Cu(L)$_2$] complex is expected to be tetragonally distorted octahedral and this is confirmed by the characteristic absorption at 742 nm assignable to $^2E_g \rightarrow {}^2T_{2g}$, which corresponds to the d-d transition band. The geometry of this complex may be assigned as distorted square planar from the two absorptions at 595 and 514 nm of $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ respectively. The obtained values of the effective magnetic moment (1.92 B.M.) are typical for distorted octahedral Cu(II) chelates.

[Ni(L)$_2$]·2H$_2$O shows d-d transitions at 595 and 765 nm, corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ respectively with octahedral geometry. The magnetic moment values for the Ni(II) complex of the Schiff base ligand at room temperature were found to be in the normal range (2.8–3.5 B.M.) [13], *e.g.* [Ni(L)$_2$]·2H$_2$O showed magnetic moment of 3.20 B.M.

The electronic spectra of DMF solution of Co(II) complex exhibit two bands at 670 and 554 nm, which are assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively, indicating an octahedral configuration around Co(II) ion. The octahedral geometry of the Co(II) complex is further confirmed by the magnetic moment (4.89 B.M.) [13].



M = Cu(II), Co(II), Ni(II) and Zn(II)

Figure 2. Suggested structure of the octahedral complexes of the ligand LH.

Based on magnetic and conductivity measurements, their monomeric and non-electrolytic nature has been confirmed. The IR spectra of metal complexes indicate bonding through carbonyl oxygen, azomethine nitrogen and phenolic oxygen, while d-d transitions suggest an octahedral geometry [8,12,14].

Single crystals of the complexes could not be isolated from any solution, thus, no definitive structure can be described. However, the analytical, spectroscopic and magnetic data enable us to predict possible structures as shown in Figure 2.

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