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Synthesis, Spectroscopic and Physico-chemical Studies and X-Ray Structure determination of a Metal transitions Complexes from ligand generated by benzoylpyridine

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***Abstract**: Metals transition complexes, $[M(L^i)(H_2O)_2]\cdot(X)_2\cdot(H_2O)_n$, (M= Mn, Ni, Cu or Zn; i=1 or 2; n=0, ½, 1 or 2) where L^1 is the neutral tridentate Schiff base (E)-N^1-(2-(phenyl(pyridin-2-yl)methyleneamino)ethyl)ethane-1,2-diamine and L^2 is the neutral tetradentate Schiff base N-(phenyl(pyridine-2-ylmethylene)-2-(2-(2-(phenyl(pyridine-2-yl)methyleneamino)ethoxy)ethoxy)ethanamine both derived from benzoylpyridine. All these complexes were synthesized and characterized by physicochemical methods and spectroscopic studies. Both ligands are coordinated to the central atom as tetradentate through four nitrogen atoms. Each metal ion is also coordinated with two water molecules yielding octahedral complexes. The single crystal X-ray determination was also used to establish the structure of the complex (**2**) formulated as $[Ni(L^1)(H_2O)_2]\cdot(Cl)_2$. The asymmetric unit contains one molecule of the complex and two uncoordinated chloride anions. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 8.590 (1) Å, b = 8.786 (1) Å, c = 13.134 (1) Å, α = 88.684 (1)°, β = 76.883 (1)°, γ = 86.789 (1)°, V = 963.81 (17) $Å^3$, Z = 2, R_1 = 0.0312 and wR_2 = 0.0762. The coordination polyhedron around the Ni atom is best described as a distorted octahedron.*

***Keywords:** Schiff base, Complex, NMR, IR, Octahedral, Crystal structure.*

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I. Introduction

Schiff bases are widely used in the field of coordination chemistry to prepare materials with particular properties [1-3]. Compounds that can be used in catalysis [4], magnetism [5], luminescence [6] or biological activity studies [7] have been synthesized and their properties extensively studied over the past decade. The Schiff bases prepared from 2-benzoylpyridine are numerous [8-11] and offer original coordination possibilities depending on the amine used for the condensation. These Schiff bases have the ability to form complexes with transition metals leading to very varied molecular architectures [12-14]. 2-Benzoylpyridine is one of the most widely studied Schiff base precursors because of its ability to form acyclic ligands with wider cavities and free arms which can serve as spacers.

In recent years [15] we have developed an important work on the synthesis, characterization and study of the properties of transition metal complexes from acyclic ligands derived from 2-benzoylpyridine. In this paper, we report our results with the acyclic ligand derived from 2-benzoylpyridine and amines which can act as tetradentate ligand with four N atoms donor sites.

II. Experimental Section

2.1. Starting materials and Instrumentations

Commercially available benzoylpyridine, bis-(aminoethyl)amine, 2-(2-(2-aminoethoxy)ethoxy)ethanamine and metals transition salts were purchased from Aldrich and used without further purification. The analyses for carbon, hydrogen and nitrogen were carried out using a LECO CHNS-932 instrument. The IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum Two spectrophotometer (4000–400 cm^{-1}). UV–VIS spectra were recorded in methanol solution concentration of 10^{-3} M at 25°C and wavelength was reported in nm using a Perkin Elmer Lamba 365 UV/VIS spectrophotometer. The molar conductance of 10^{-3} M solution of the metal complex in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibility of the powdered sample was measured using a Johnson Matthey scientific magnetic susceptibility balance (calibrant $Hg[Co(SCN)_4]$).

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2.2. Synthesis of complexes (1-4)

In a round bottomed flask benzoylpyridine (0.49 g, 2.6 mmol) is dissolved in 10 mL of methanol. To this mixture 10 mL of $MCl_2{\cdot}nH_2O$ (2.6 mmol) solution in methanol was added (M^{2+} = Mn^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}) (Scheme 1). The resulting solution was stirred for 60 min at room temperature before addition of 10 mL of a methanolic solution of bis-(aminoethyl)amine (0.402 g, 3.9 mmol). The colored solution was stirred for 3 hours at room temperature before filtered. The filtrate was left until apparition of precipitate (M^{2+} = Mn^{2+}, Cu^{2+} or Zn^{2+}). Green crystals suitable for X-ray diffraction for Ni^{2+} was obtained after three weeks.

Complex (**1**): $[Mn(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)_2$: $C_{16}H_{28}MnCl_2N_4O_4$. Yield 63 %. Anal. Calc. C, 41.22; H, 6.05; N, 12.02; Cl, 15.21. Found C, 41.39; H, 6.15; N, 12.11; Cl, 15.36. μ_{eff} = 5.68 μ_B. Λ_M (S cm^2 mol^{-1}): 138. IR (cm^{-1}): 3440, 3220, 3179, 1636, 1558, 1489, 1286, 775, 746. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 555 (0.09), 500 (0.07), 265 (0.89), 225 (0.99).

Complex (**2**): $[Ni(L^1)(H_2O)_2]{\cdot}(Cl)_2$: $C_{16}H_{24}NiCl_2N_4O_2$. Yield 59 %. Anal. Calc. C, 44.28; H, 5.57; N, 12.91; Cl, 16.34. Found: C, 44.35; H, 5.61; N, 12.95; Cl, 16.42. μ_{eff} = 2.88 μ_B. Λ_M (S cm^2 mol^{-1}): 165. IR (cm^{-1}): 3442, 3217, 1628, 1554, 1482, 1283, 770, 742. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 903 (0.89), 750 (2.82), 610 (0.92), 264 (0.89), 226.

Complex (**3**): $[Cu(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)$: $C_{16}H_{26}CuCl_2N_4O_3$. Yield 57 %. Anal. Calc. C, 42.06; H, 5.74; N, 12.26; Cl, 15.52. Found: C, 42.28; H, 5.77; N, 12.45; Cl, 15.34. μ_{eff} = 1.77 μ_B. Λ_M (S cm^2 mol^{-1}): 152. IR (cm^{-1}): 3379, 3208, 1618, 1544, 1481, 1276, 763, 736. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 610 (0.05), 266 (0.82), 223 (0.98).

Complex (**4**): $[Zn(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)_2$: $C_{16}H_{28}ZnCl_2N_4O_4$. Yield 71 %. Anal. Calc. C, 40.31; H, 5.92; N, 11.75; Cl, 14.87. Found: C, 40.40; H, 5.87; N, 12.88; Cl, 14.34. Λ_M (S cm^2 mol^{-1}): 147. IR (cm^{-1}): 3410, 3221, 1612, 1544, 1483, 1280, 772, 743.

2.3. Synthesis of complexes (5-8)

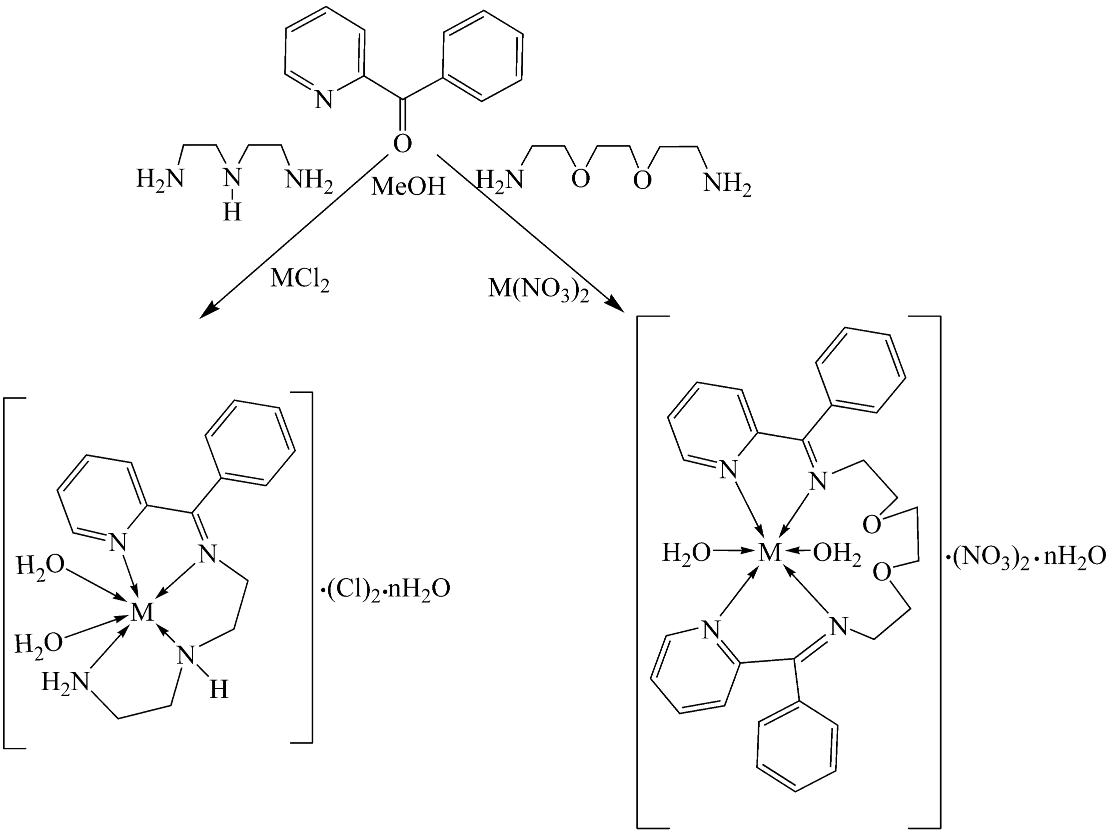
To 2-benzoylpyridine (0.3750 g, 2 mmol) in 10 mL of methanol was added dropwise a solution 2-(2-(2-aminoethoxy)ethoxy)ethanamine (0.1516 g, 1 mmol) in 10 mL of methanol (Scheme 1). The mixture was refluxed for 5 hours yielding a yellow solution. On cooling a solution of $M(NO_3)_2{\cdot}xH_2O$ (2 mmol) in 5 mL of methanol (M^{2+} = Mn^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}) was added. The solution was refluxed for two hours before cooling. After filtration, the solution was left at room temperature for several days. Appropriate precipitate were obtained by slow evaporation of the methanol.

Complex (**5**): $[Mn(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)_{1/2}$: $C_{30}H_{35}MnN_6O_{10.5}$. Yield 50 %. Anal. Calc. C, 51.29; H, 4.98; N, 11.96. Found: C, 51.39; H, 4.98; N, 11.89. μ_{eff} = 5.63 μ_B. Λ_M (S cm^2 mol^{-1}): 213. IR (cm^{-1}): 3430, 3211, 1635, 1556, 1485, 1385, 1280, 771, 742. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 560 (0.09), 505 (0.08), 266 (0.93), 222 (0.98).

Complex (**6**): $[Ni(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)$: $C_{30}H_{36}NiN_6O_{11}$. Yield 39 %. Anal. Calc. C, 50.37; H, 5.07; N, 11.75. Found: C, 50.42; H, 4.99; N, 11.70. μ_{eff} = 2.79 μ_B. Λ_M (S cm^2 mol^{-1}): 144. IR (cm^{-1}): 3402, 3211, 1629, 1550, 1486, 1382, 1275, 772. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 909 (0.93), 755 (2.18), 602 (0.82), 260 (0.93), 225 (1.05).

Complex (**7**): $[Cu(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)$: $C_{30}H_{36}CuN_6O_{11}$. Yield 42 %. Anal. Calc. C, 50.03); H, 5.04); N, 11.67. Found: C, 49.98; H, 5.10; N, 11.61. μ_{eff} = 1.70 μ_B. Λ_M (S cm^2 mol^{-1}): 155. IR (cm^{-1}): 3409, 3213, 1622, 1550, 1484, 1379, 1273, 762. UV–Vis (λ, nm) (ε, M^{-1} cm^{-1}) 602 (0.06), 261 (0.94), 223 (1.08).

Complex (**8**): $[Zn(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)_2$: $C_{30}H_{38}ZnN_6O_{12}$. Yield 32 %. Anal. Calc. C, 48.69; H, 5.18; N, 11.36. Found: Calc. C, 48.61; H, 5.25; N, 11.29. Λ_M (S cm^2 mol^{-1}): 165. IR (cm^{-1}): 3415, 3219, 1620, 1548, 1481, 1388, 1281, 775.



$[M(L^1)(H_2O)_2](Cl)_2(H_2O)_n$ $[M(L^2)(H_2O)_2](NO_3)_2(H_2O)_n$

$M^{2+} = Mn^{2+}, Ni^{2+}, Cu^{2+}$ or Zn^{2+} ; n=0, 1/2, 1 or 2.

Scheme 1. Synthetic scheme for complexes preparation

2.4. X-ray data collection, structure determination and refinement

Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an *ENRAF NONIUS Kappa CCD* diffractometer with graphite monochromatized MoK_α radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [16]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [17]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using *ORTEP-3* [18].

Table-1. Crystallographic data and refinement parameters for the Ni^{II} complex.

Formula of refinement	$(C_{16}H_{20}N_4)\cdot(H_2O)_2\cdot(Ni^{2+})\cdot(Cl^-)_2$
Molecular weight (g/mol)	434.00
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.590(1)
b (Å)	8.786(1)
c (Å)	13.134(1)
α (°)	88.684(1)
β (°)	76.883(1)
γ (°)	86.789(1)
V (Å^3)	963.81(17)
Z	2
D_c (g cm^{-3})	1.495
Crystal size (mm)	0.80 × 0.50 × 0.40
Crystal colour	clear light brown
Crystal habit	prismatic

Mo K_{α}(Å)	0.71073
μ (mm^{-1})	1.30
T(K)	150
θ_{min}, θ_{max}	4.7620, 28.5840
*hkl*range	-11, 11 ; -11, 11 ; -17, 6
Measured reflections	10845
Independent reflections	4498
Reflections with [$I > 2\sigma(I)$]	3814
No. of parameters	322
R_{int}	0.025
R_1 (F) [$I > 2\sigma(I)$]	0.031
wR_2 (F^2)	0.076
Goodness-of-fit	1.05
$\Delta\rho_{min, max}$ (e $Å^{-3}$)	−0.45, 0.50

III. Results And Discussions

3.1. General Studies

The transition metal complexes was synthesized by mixing benzoylpyridine solution, $MCl_2 \cdot nH_2O$ and bis-(aminoethyl)amine in a molar ratio 1:1:1.5 for complexes (**1-4**) or benzoylpyridine solution, $M(NO_3)_2 \cdot nH_2O$ and 2-(2-(2-aminoethoxy)ethoxy)ethanamine in a molar ratio 2:2:1 for complexes (**5-4**). Suitable X-ray crystals diffraction were obtained after slow evaporation of a solution of the nickel complex (**2**). The afforded compounds are soluble in polar organic solvent such as methanol, DMSO and DMF. Elemental analyses give results in agreement with the chemical formulae obtained from spectroscopic analyses and X-ray diffraction structure determination. The IR spectra of the complexes (**1-8**) (Table 2) show a strong band near 1630 cm^{-1} which can be attributed to C=N upon coordination to metal ion through the azomethine atom of the ligands. The bands pointed in the regions 1600-1580 and 745-765 cm^{-1} are due to the aromatic rings. The NH stretching are observed in the range 3330-3280 cm^{-1} in the spectra of the complexes (**1-4**). These observations are indicative of the involvement of the azomethine in the coordination. The broad band pointed at ~3200 cm^{-1} and the band at 820 cm^{-1} can be assigned to a coordinated water molecule stretching vibrations [19]. The broadness of this band is probably due to hydrogen bond between the OH of the water molecules and nitrogen atoms of the ligands. IR spectra of the nitrate complexes gives information regarding the possible binding modes of the nitrate moiety. Spectra of complexes (**5-8**) exhibit strong and sharp band near 1380 cm^{-1}, typical of non-coordinated nitrate group. No other bands assignable to another coordination mode is observed. Additional band near 3490 cm^{-1} attributable to hydroxyl group is observed in both spectra indicating the presence of lattice water molecules [20].

Table-2. Main IR bands of the complexes (**1-8**).

Compound	**Pyridine/Phenyl**	**ν(C-N)**	**ν(C=N)**	**ν(NO_3)**
$[Mn(L^1)(H_2O)_2]\cdot(Cl)_2\cdot(H_2O)_2$	1558, 1489	1286	1636	-
$[Ni(L^1)(H_2O)_2]\cdot(Cl)_2$	1554, 1482	1283	1628	-
$[Cu(L^1)(H_2O)_2]\cdot(Cl)_2\cdot(H_2O)$	1544, 1481	1276	1618	-
$[Zn(L^1)(H_2O)_2]\cdot(Cl)_2\cdot(H_2O)_2$	1544, 1483	1280	1612	-
$[Mn(L^2)(H_2O)_2]\cdot(NO_3)_2\cdot(H_2O)_{1/2}$	1556, 1485	1280	1635	1385
$[Ni(L^2)(H_2O)_2]\cdot(NO_3)_2\cdot(H_2O)$	1550, 1486	1275	1629	1382
$[Cu(L^2)(H_2O)_2]\cdot(NO_3)_2\cdot(H_2O)$	1550, 1484	1273	1622	1379
$[Zn(L^2)(H_2O)_2]\cdot(NO_3)_2\cdot(H_2O)_2$	1548, 1481	1281	1620	1388

The electronic data for the complexes are summarized in Table 3. In the case of the manganese (II) complex d^5: $t_{2g}^3e_g^2$, electronic transitions necessarily lead to a spin change of S = 5/2 to S = 3/2; *ie.* $t_{2g}^3e_g^2 \rightarrow t_{2g}^2e_g^3$. These d-d transitions are doubly forbidden by rules selection [21]. As a result, the intensities of the absorption bands observed are very low molar extinction coefficient value in both complexes (**1**) and (**5**). The values of the magnetic moment of 5.68 μ_B (**1**) and 5.63 μ_B (**5**) at room temperature for these complexes are indicative of mononuclear octahedral configuration around the Mn(II) metal ions [22]. These complexes are 2:1 electrolyte in DMF solution [23] as shown by the values of the molar conductivities which are respectively 138 S cm^2 mol^{-1} and 147 S cm^2 mol^{-1} for (**1**) and (**5**). For Ni(II) complexes the electronic spectra recorded in methanol reveal the environment around metal ion. The raised bands from the electronic spectra of the Ni(II) complexes (**2**) and (**6**) are in accordance with an octahedral geometry around the Ni^{2+}. These transitions bands assignable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ are respectively showed in the ranges 11070-11090 cm^{-1}, 13200-13340 cm^{-1} and 16350-16505 cm^{-1} for the two nickel(II) complexes (**2**) and (**6**) [23]. The values of the magnetic moment of 2.88 μ_B (**2**) and 2.79 μ_B (**6**) at room temperature for the Ni(II) complexes are indicative of high-spin mononuclear with octahedral configuration around the Ni(II) metal atoms [25]. The molar conductivities which are respectively 165 S cm^2 mol^{-1} and 144 S cm^2 mol^{-1} for (**2**) and (**6**) show that the complexes are 2:1 electrolyte in DMF solution [23]. The electronic spectrum of the Cu(II) complexes (**3**) and (**7**) reveal low intensities absorption bands at 16393 cm^{-1} and 16611 cm^{-1} respectively which are assignable to $^2E_g \rightarrow {}^2T_{2g}$ indicating octahedral environment around the copper(II) ions [26]. The molar conductivities which are respectively 152 S cm^2 mol^{-1} and 155 S cm^2 mol^{-1} for (**3**) and (**7**) show that the complexes are 2:1 electrolyte in DMF solution [23]. The values of the magnetic moment of 1.77 μ_B (**3**) and 1.70 μ_B (**4**) at room temperature for the Cu(II) complexes indicate strong covalent bonds on comparison with copper complexes having ionic or weak bonds (1.9-2.2 μ_B) [27]. These facts are indicative of mononuclear octahedral configuration around the Cu(II) metal atoms [27]. The diamagnetic Zn(II) complexes (**4**) and (**8**) are 2:1 electrolyte [23] in nature according to the values of the measured molar conductance in DMF solutions : 147 S cm^2 mol^{-1} and 165 S cm^2 mol^{-1} for (**4**) and (**8**) respectively. Additional bands are shown in both electronic spectra in the range 300-220 nm assignable to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions.

Table-3. Main UV bands of the complexes (**1**-**8**).

Compound	**μ_{eff} (μ_B)**	**$n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$**	**d→d**	**Λ (Ω^{-1}.cm^2.mol^{-1})**
$[Mn(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)_2$	5.68	265, 225	-	138
$[Ni(L^1)(H_2O)_2]{\cdot}(Cl)_2$	2.88	264, 226	903, 750, 610	165
$[Cu(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)$	1.77	266, 223	610	152
$[Zn(L^1)(H_2O)_2]{\cdot}(Cl)_2{\cdot}(H_2O)_2$	Diam	-	-	147
$[Mn(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)_{1/2}$	5.63	266, 222	-	213
$[Ni(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)$	2.79	261, 223	909, 755, 602	225
$[Cu(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)$	1.70	261, 223	602	144
$[Zn(L^2)(H_2O)_2]{\cdot}(NO_3)_2{\cdot}(H_2O)_2$	Diam	-	-	65

3.2. Crystal structure of the complex $[Ni(L^1)(H_2O)_2]{\cdot}(Cl)_2$ (2)

The titled compound crystallizes in the triclinic system with the space group P$\bar{1}$. Fig. 1(a) shows the molecular structure of the nickel complex $[Ni(L^1)(H_2O)_2]{\cdot}2Cl$. The crystallographic data of the related structure are summarized in Table 1 and selected bond lengths and bond angles are listed in Table 4. The asymmetric unit is constituted with one mononuclear unit $[Ni(L^1)(H_2O)_2]^{2+}$ and two uncoordinated chloride anions. The central nickel atom is in an O_2N_4 octahedral environment being coordinated by four nitrogen atom from the organic ligand and two oxygen atoms from water molecules (Fig. X.). The equatorial planes around the nickel ion is formed by an imino N atom, a secondary amino N atom and two O atoms from the two coordinated water molecules. The apical positions are occupied by the nitrogen atom of the pyridine ring and the secondary amino atom of the ligand which present the longest bonds lengths: Ni–N4 = 2.1020(16) Å and Ni–N2 = 2.1061(17) Å. The distance Ni–N2 where N2 is a secondary amino nitrogen atom is longer than the average (2.088 Å) of analogous distances in the complex $[NiL](NO_3)_2$ [29] where L is *N*^{1}-(phenyl(pyridin-2-yl)methylene)-*N*^{3}-(2-(2-(phenyl(pyridin-2yl)methyleneamino)ethylamino)ethyl)propane-1,3-diamine. The distance Ni–N1 = 2.0077(16) Å where N1 is a primary amino nitrogen atom is the same value found for the complex $[Ni_2(dmpn)_2(hap)_2(\mu_{1,1}\text{-}N_3)_2]$ [30] where dmpn = N,N-dimethyl-1,3-diaminopropane and Hhap = 2-hydroxyacetophenone. The diagonal basal angles, N1–Ni–O1 = 170.31(7)° and N3–Ni–O2 = 170.48(7)° and the basal–apical angles, *ie*. N4–Ni–N3 = 78.54(6)°, N2–Ni–N3 = 81.33(6)°, N2–Ni–N1 = 83.47(7)°, N4–Ni–O1 = 90.73(7)° and N2–Ni–O2 = 101.71(7)° significantly deviate from the ideal values of 180 and 90° respectively. The angle formed by the atoms N4 and N2 which occupy the apical positions is 159.36(6)°. This can be explained by the rings formed by the ligand by binding in tetradentate fashion to the Ni^{2+} ion. The first three angles are derived from a five-atom ring. The flexibility of bonds implying atoms not engaged in ring compared to the five membered-cycle implies that the angles from those bonds are larger than in the five-membered ring. The sum of the plane angles around the nickel ion are 360.18° and is close to 360°, which would be the sum in the case of an ideal square planar. In the crystal structure no intermolecular hydrogen bonds interactions were found. As shown in figure 1(**b**) only intramolecular hydrogen bonds are observed (Table 5). The H—bond donors are the H—O of the coordinated water molecules while the acceptors are the free chloride anion which acts as counter ions.

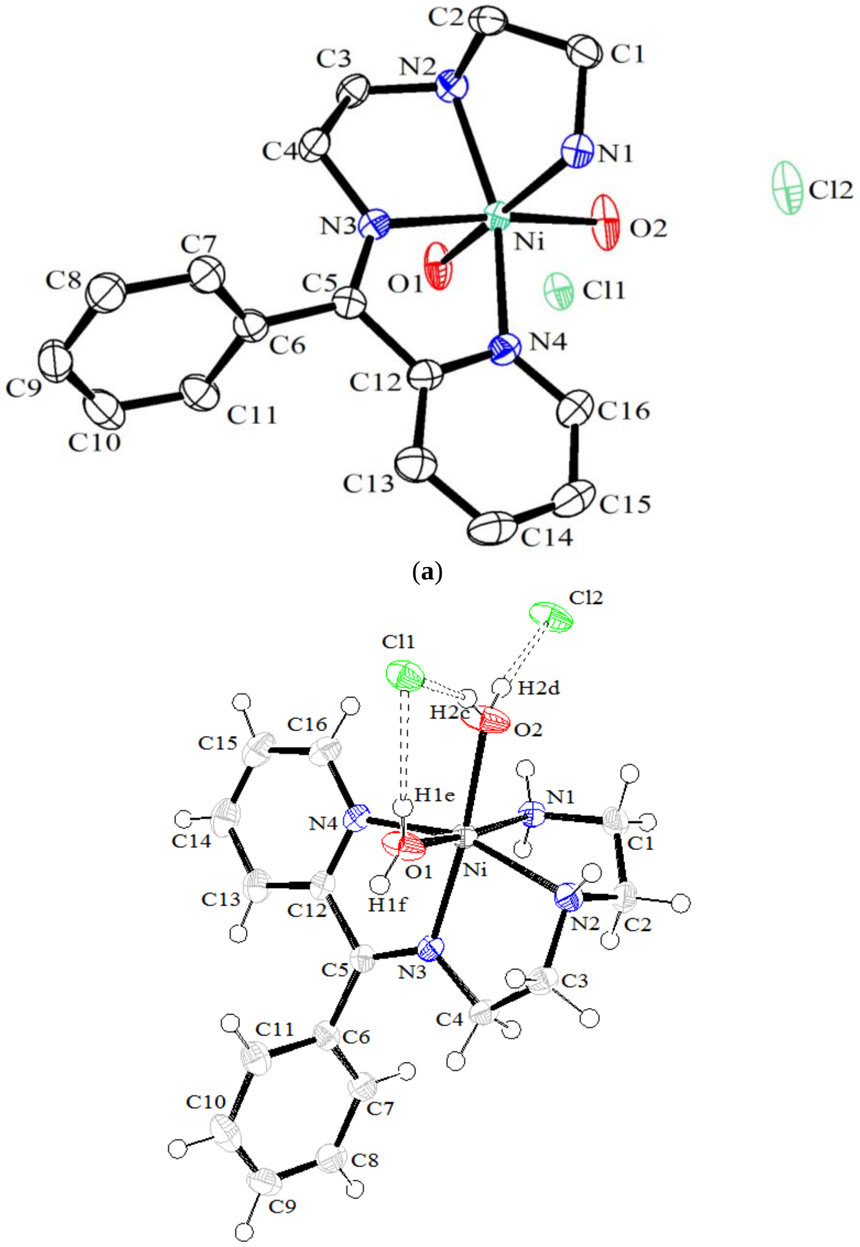
Table-4. Selected bond distances [Å] and angles [deg] for the Ni^{II} complex.

Ni—N3	2.0184(15)	Ni—O1	2.0811(15)
Ni—O2	2.0587(16)	Ni—N4	2.1020(16)
Ni—N1	2.0770(16)	Ni—N2	2.1061(17)
C5—N3	1.273(2)	O2—Ni—N4	98.88(7)
N3—Ni—O2	170.48(7)	N1—Ni—N4	95.54(6)
N3—Ni—N1	100.03(7)	O1—Ni—N4	90.73(7)

O2—Ni—N1	89.31(7)	N3—Ni—N2	81.33(6)
N3—Ni—O1	88.43(7)	O2—Ni—N2	101.71(7)
O2—Ni—O1	82.41(7)	N1—Ni—N2	83.47(7)
N1—Ni—O1	170.31(7)	O1—Ni—N2	93.25(7)
N3—Ni—N4	78.54(6)	N4—Ni—N2	159.36(6)

Table-5. Hydrogen bonds for the Ni^{II} complex [Å and deg].

D—H···*A*	*D*—H (Å)	*H*···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O1—H1e···Cl1	0.82	2,272	3.070	165.91
O2—H2c···Cl1	0.84	2,281	3.103	165.10
O2—H2d···Cl2	0.76	2,258	3.007	169.15



(**a**)

(**b**)

Figure 1*: ORTEP* plot (30% probability ellipsoids) showing the molecule structure of the Ni^{II} complex (**a**) and the intramolecular hydrogen bonds (**b**) in the complex.

IV. Conclusion

The mononuclear isotopic complexes of the ligand L^1 (**1-4**) and the ligand L^2 (**5-8**) derived from benzoylpyridine are synthesized and characterized. The structures of these complexes are established by elemental analysis, IR and UV-Visible spectroscopies, magnetic measurements and conductivity study. The ligands show similar fashion of coordination mode for each metal ion, acting as tetradentate. Each metal center is eight coordinated with four nitrogen atom from the ligand and two oxygen atom from two water molecules. The environment around each metal for both complexes is best described as a distorted octahedral geometry. In the complex (**2**) of Ni(II) the structure is confirmed by X-ray diffraction and the metal atom is bounded to the ligand L^1 by one azomethine of the -C=N- chromophore, one primary nitrogen atom, one secondary nitrogen atom and one nitrogen atom of the pyridine ring. The Ni^{II} ion is also bounded by two oxygen atoms of two coordinated water molecules.

V. Supplementary material

CCDC- (**2**) 1810968 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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