



HAL
open science

Six New Transition Metal Mononuclear Complexes Of N'-(5- bromo-2-hydroxybenzylidene)nicotinohydrazide Schiff Base. Synthesis, Spectroscopic Characterization And X-ray structure Determination of the Zinc(II) Complex

Amadou Gueye, Farba Bouyagui Tamboura, Adama Sy, Mohamed Gaye,
Nathalie Gruber, Abdelaziz Jouaiti

► To cite this version:

Amadou Gueye, Farba Bouyagui Tamboura, Adama Sy, Mohamed Gaye, Nathalie Gruber, et al.. Six New Transition Metal Mononuclear Complexes Of N'-(5- bromo-2-hydroxybenzylidene)nicotinohydrazide Schiff Base. Synthesis, Spectroscopic Characterization And X-ray structure Determination of the Zinc(II) Complex. IOSR Journal of Applied Chemistry, 2019, 12, pp.24 - 30. 10.9790/5736-1204012430 . hal-03005007

HAL Id: hal-03005007

<https://hal.science/hal-03005007>

Submitted on 13 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Six New Transition Metal Mononuclear Complexes Of N'-(5-bromo-2-hydroxybenzylidene)nicotinohydrazide Schiff Base. Synthesis, Spectroscopic Characterization And X-ray structure Determination of the Zinc(II) Complex.

Amadou Gueye^a, Farba Bouyagui Tamboura^b, Adama Sy^a, Mohamed Gaye^a,
Nathalie Gruber^c, Abdelaziz Jouati^c

^aDepartment of Chemistry, University Cheikh Anta Diop, Dakar, Sénégal

^bDepartment of Chemistry, University Cheikh Alioune Diop, Bambey, Sénégal

^cLaboratoire de Chimie de Coordination Organique, URA 422, Université Louis Pasteur, 4 rue Blaise
Pascal 67008 Strasbourg France

Corresponding Author: Amadou Gueye

Abstract: The reactions of the Schiff base N'-(5-bromo-2-hydroxybenzylidene)nicotinohydrazide (H₂bhbn), with metal transition ions (Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II)) afforded two different types of complexes formulated as [M(H₂bhbn)₂(Cl)₂(H₂O)_x](H₂O)_y (M: Mn, Co, Ni or Zn) and [M(Hbhn)(Cl)(H₂O)_x] (M: Fe or Cu). These compounds have been characterized by elemental analysis, UV-Vis, IR, ¹H and ¹³C NMR spectroscopies, molar conductivity and room temperature magnetic measurements. The structure of Zinc (II) complex has been determined by X-ray crystallography. The complex crystallizes in the monoclinic system with Cc space group, a = 25.8196(11) Å, b = 7.2881(3) Å, c = 17.4662(8) Å, β = 120.566(2)°, V = 2830.0(2) Å³, Z = 4, R₁ = 0.0355 (0.0384) and wR₂ = 0.0922. The environment geometry around the Zn (II) center is best described as a slightly distorted tetrahedral.

Keywords: Schiff base, 5-bromo-2-hydroxybenzaldehyde, Metal complexes, X-ray crystallography

Date of Submission: 07-04-2019

Date of acceptance: 23-04-2019

I. Introduction

Schiff bases obtained by condensation of nicotinic hydrazide and a ketoprecursor are widely used in the synthesis of transition metal complexes [1-5]. Those complexes are particularly interesting in various fields such as magnetism [6], catalysis [7] and medicine [8]. Antibacterial activities are also reported [9-13]. The presence of phenolic groups suggests antioxidant properties for these kind of complexes as reported in the literature [9]. Nicotinic fragment was found to be an important chemical species which causes drastic damage in cellular process. It can act in gene expression and in enzyme activities [14]. Its role in the inhibition of caspases-3 has been recently demonstrated [15]. In recent studies, nicotinic hydrazide complexes have been prepared and have shown enzyme-like activities [16-17]. In the present paper, we report the synthesis and the structural characterization of transition metal complexes with the hydrazone ligand H₂bhbn (H₂bhbn is N'-(5-bromo-2-hydroxybenzylidene)nicotinohydrazide). The powder compounds were characterized with spectroscopic techniques. The new zinc (II) complex formulated as [Zn(Cl)₂(H₂bhbn)₂] was characterized by X-ray diffraction.

II. Experimental

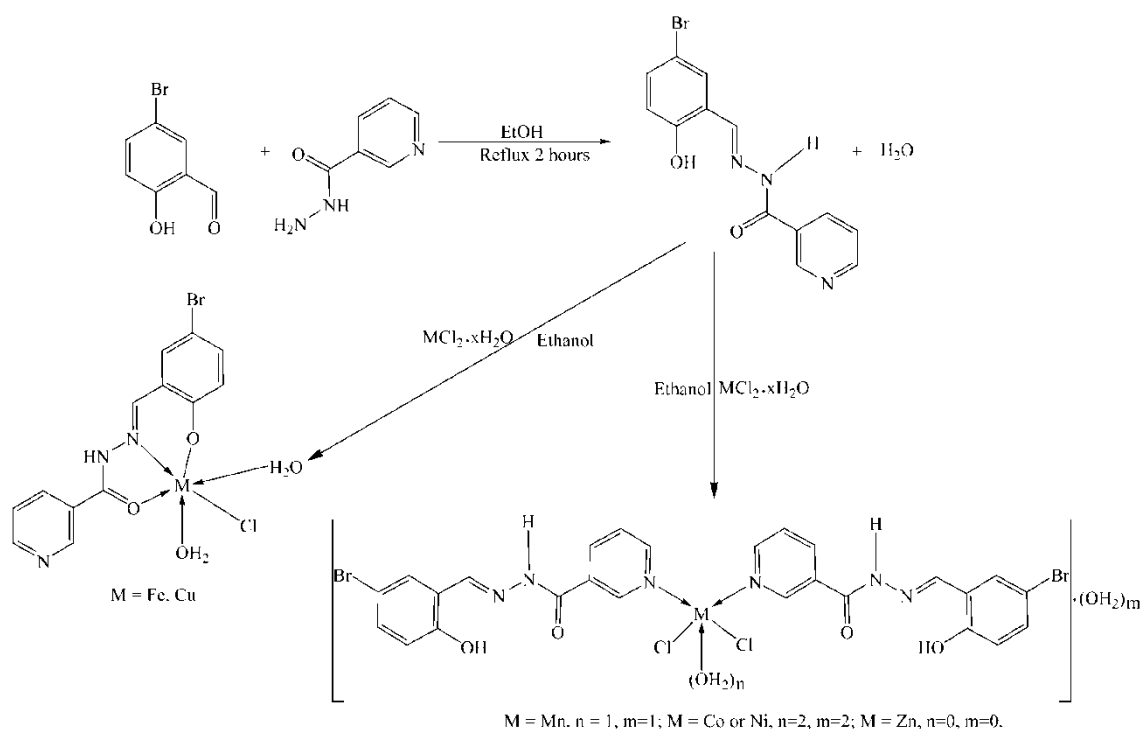
2.1. Materials and Procedures

Nicotinic acid hydrazide, 5-bromo-2-hydroxybenzaldehyde as well as MCl₂·nH₂O (M = Mn (II), Fe (II), (Co (II), Ni (II), Cu (II) or Zn (II)) were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyses were performed in a Carlo-Erba EA microanalyser. Infrared spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. LSI-MS were recorded using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix. The ¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆ on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were run on a Shimadzu UV-2501 PC Recording spectrophotometer (1000-200 nm). The molar conductance of 10⁻³ M in DMSO solutions of the metal complexes was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured

using a Johnson Matthey scientific magnetic susceptibility balance {calibrantHg[Co(SCN)₄]}. Melting points were recorded on a Büchi apparatus and are uncorrected.

2.2. Synthesis of *N'*-(5-bromo-2-hydroxybenzylidene)nicotinohydrazide (**H₂bhn**)

The nicotinic acid hydrazide (5.46 g, 39.79 mmol) was dissolved in 20 mL of absolute ethanol by heating gently on water bath. The 5-bromo-2-hydroxybenzaldehyde (8 g, 39.79 mmol) was added to the mixture and stirring was continued under reflux for 7 h (Scheme 1). The yellow precipitate obtained was allowed to stay at room temperature for 10 h before filtered, washed with 20 mL of cold ethanol and dry under vacuum. The mass obtained is 10.83 g. Yield 85%. M.P. = 205°C. Anal. Calc for [C₁₃H₁₀BrN₃O₂]: C, 48.77; H, 3.15; N, 13.13 %. Found: C, 48.74; H, 3.17; N, 13.10 %. IR (ν, cm⁻¹): 3246 (NH); 3201 (OH); 3080-3000; 1648 (C=O); 1594 (C=N); 1560; 1477; 1417 (C=C); 1353; 1284 (C-O phenolic); 1159 (N-N); 820; 780; 797; 615 (C-H). RMN ¹H (δ, ppm): 12.31 (s, OH); 11.21 (s, NH); 9.06 (s, HC=N); 8.70-6.83 (m, Harom.). ¹³C (δ, ppm): 161.65 (C=O); 156.53 (C-Br); 153.48 (C=N); 148.56 (C-O phenolic); [146.25; 135.56; 133.77; 130.46; 128.57; 123.63; 121.21; 118.68; 110.58] (C_{Ar}) [18-20].



Scheme 1. Synthetic scheme for the ligand and the mononuclear complexes preparation

2.3. Synthesis of the complexes of **H₂bhn** with Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II)

H₂bhn (0.47 mmol) was dissolved in methanol (10 mL) to give a colorless solution. The appropriate chloride metal salt (0.47 mmol) in 5 mL of MeOH was added. The resulting solution was stirred at room temperature for two hours, thus filtered and left to slow evaporation. After three days, the zinc (II) complex solution gives yellow crystals suitable for X-ray analysis. The other solutions give precipitates which are recovered by filtration. The precipitates were washed successively with cold methanol and diethyl ether before drying in air. Unlike Singh[21], the preparation of these complexes was carried out at room temperature.

[Mn(H₂bhn)₂(Cl)₂(H₂O)]·H₂O. Color: Yellow. Yield: 45 %. M.P.: > 260°C. Anal. Calc. for [MnC₂₆H₂₄Br₂Cl₂N₆O₆]: C, 38.93; H, 3.02; N, 10.48 %. Found: C, 38.95; H, 3.06; N, 10.46%. IR (KBr, cm⁻¹): 3546; 3193, 3069; 1669; 1600; 1564; 1289. UV-vis (liquid, λ(nm)): 347; 417. μ_{eff} = 5.54 MB. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 21; after 15 days: 20.

[Co(H₂bhn)₂(Cl)₂(H₂O)₂]·H₂O. Color: Brown. Yield: 37 %. M.P.: > 260°C. Anal. Calc for [CoC₂₆H₂₆Br₂Cl₂N₆O₇]: C, 37.89; H, 3.18; N, 10.20 %. Found: C, 37.85; H, 3.17; N, 10.23%. IR (KBr, cm⁻¹): 3448; 3194; 3068; 1652; 1604; 1522; 1286. UV-vis (liquid, λ(nm)): 349, 427. μ_{eff} = 3.25 MB. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 10 after 15 days: 13.

[Ni(H₂bhn)₂(Cl)₂(H₂O)₂·H₂O. Color: Green. Yield: 40 %. M.P.:> 260°C. Anal. Calc for [Ni(C₂₆H₂₆Br₂Cl₂N₆O₇): C, 37.90; H, 3.18; N, 10.20 %. Found: C, 37.92; H, 3.20; N, 10.24 %. IR (KBr, cm⁻¹): 3343; 3249; 3075; 2953; 1678; 1599; 1541; 1288. UV-vis (liquid, λ(nm)): 361, 431. μ_{eff} = 3.10 MB. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 23; after 15 days: 29.

[Fe(Hbhn)(Cl)(H₂O)₂]. Color: Dark brown. Yield: 48 %. M.P.:> 260°C. Anal. Calc for [FeC₁₃H₁₃BrClN₃O₄]: C, 34.97; H, 2.93; N, 9.41 %. Found: C, 35.03; H, 2.97; N, 9.52%. IR (KBr, cm⁻¹): 3250; 3074; 1601; 1523; 1299-1275. UV-vis (liquid, λ(nm)): 320, 376, 448, 509. 4.12 MB. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 13; after 15 days: 26.

[Cu(Hbhn)(Cl)(H₂O)₂]. Color: green. Yield: 66 %. M.P.:> 260°C. Anal. Calc. for [CuC₁₃H₁₃BrClN₃O₄]: C, 34.38; H, 2.89; N, 9.25 %: Found: C, 34.32; H, 2.88; N, 9.22 %. IR (KBr, cm⁻¹): 3220; 3043; 2620; 1604; 1562; 1179. UV-vis (liquid, λ(nm)): 293, 330, 413, 986. μ_{eff} = 1.68 MB. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 20; after 15 days: 55.

[Zn(H₂bhn)₂(Cl)₂]. Color: Yellow. Yield: 53 %. M.P.:> 260°C. Anal. Calc for [ZnC₂₆H₂₀Br₂Cl₂N₆O₄]: C, 40.21; H, 2.60; N, 10.82 %. Found: C, 40.19; H, 2.62; N, 10.78 %. IR (KBr, cm⁻¹): 3264; 3206; 3062; 1663; 1611; 1539; 1271. UV-vis (liquid, λ(nm)): 346, 403. Diamagnetic. Λ (Ω⁻¹.cm².mol⁻¹): fresh solution: 07; after 15 days: 08.

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

Single crystals of C₂₆H₂₀Br₂Cl₂N₆O₄Zn were grown by slow evaporation of MeOH solution of the complex. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer with graphite monochromatized MoK_α radiation (λ = 0.71073 Å). The crystal was kept at 173(2) K during data collection. Details of the X-ray crystal structure solution and refinement are given in Table 1. The structure was solved with the *SHELXT*[22] structure solution program using direct methods and refined with the *SHELXTL*[23] Software Package. Molecular graphics were generated using *ORTEP-3* [24].

Table-1. Crystallographic data and refinement parameters for [Zn(H₂bhn)₂(Cl)₂]

Chemical formula	C ₂₆ H ₂₀ Br ₂ Cl ₂ N ₆ O ₄ Zn
Formula weight	776.57 g/mol
Temperature	173(2) K
Crystal system	Monoclinic
Space group	Cc
Wavelength	0.71073 Å
Crystal size (mm)	0.100 x 0.100 x 0.120
<i>a</i> (Å)	25.8196(11)
<i>b</i> (Å)	7.2881(3)
<i>c</i> (Å)	17.4662(8)
β(°)	120.566(2)
<i>V</i> (Å ³)	2830.0(2)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	1.823
μ (mm ⁻¹)	3.926
<i>F</i> (000)	1536
2θ range for data collection (°)	2.38 to 30.18
<i>hkl</i> ranges	-21, 33; -10, 10; -24, 21
Measured reflections	13465
Independent reflections	6274
Reflections with [<i>I</i> > 2σ(<i>I</i>)]	5878
No. of parameters	372
<i>R</i> _{int}	0.0327
<i>R</i> 1 (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>)]	0.0355,
<i>wR</i> 2 (<i>F</i> ²)	0.0922
Goodness-of-fit on <i>F</i> ²	1.041
Δρ _{max} , Δρ _{min} (eÅ ⁻³)	0.755 / -0.469

III. Results and discussion

3.1 General Studies

The acyclic Schiff base **H₂bhn** have been prepared following a well-known method reported in the literature [25–27]. The synthesis of the ligand was achieved in a one-step procedure using the direct condensation of nicotinic acid hydrazide and 5-bromo-2-hydroxybenzaldehyde in molar ratio (1/1) with quantitative yield (Scheme 1). The IR spectrum of the ligand shows an absorption at 3201 cm⁻¹ indicating the presence of phenolic O-H group and a broad band in the range 3246–3130 cm⁻¹ due to the ν(N-H) group. The bands of low intensity observed in the spectrum between 3080–3000 cm⁻¹ are assigned to the aromatic ν(C-H) groups. The intense absorption bands at 1648 cm⁻¹ and 1594 cm⁻¹ are assigned respectively to the stretching vibrations of ν(C=O) and ν(C=N). The vibration frequencies of the ν(C=N) and ν(C=C) bonds of the two pyridine and aromatic rings are identified between 1560 and 1417 cm⁻¹. The phenolic ν(C-O) bond is pointed at 1284 cm⁻¹. The bands at 1353 cm⁻¹ and 1559 cm⁻¹ are respectively attributed to the vibrations of the C-N and N-N bonds. The deformation vibrations of the aromatic C-H bonds are identified respectively at 820 and 615 cm⁻¹. The ¹H and ¹³C NMR spectra of the ligand were recorded in DMSO-*d*₆. ¹H NMR spectrum reveals five singlet signals at 12.31; 11.21; 9.06; 7.73 and 8.57 ppm representing one proton each [18–20]. They are respectively assigned to the hydroxyl proton (OH), the hydrazone proton (NH), the imine proton (HC=N) and the two aromatic protons. Three doublets representing one proton each are also revealed at 8.22; 7.33 and 6.83 ppm, and are respectively assigned to the aromatic protons. The triplet at 7.48 ppm is attributed to an aromatic proton. The ¹³C-NMR spectrum indicates a signal at 161.65 ppm attributed to the C=O function. The signal of the imine carbon function (C=N) is pointed at 152.38 ppm. For aromatic carbon atoms, the chemical shifts are between 148.52 and 113.75 ppm [20]. The ligand mass spectrum indicates a ion molecular peak at *m/z* = 321 and 322 corresponding respectively an [M+H]⁺ and [M+2H]²⁺. The parent peak at *m/z* = 320, which corresponds to the exact mass of the ligand. The corresponding empirical formula is C₁₃H₁₀N₃O₂Br.

Formation of the titled M(II) complexes was readily achieved by equimolecular reaction of MCl₂·xH₂O (M = Mn, Fe, Co, Ni, Cu and Zn) and the Schiff base H₂bhn in methanol at room temperature (Scheme 1). The instant color change of the H₂bhn solution upon addition of the methanolic solution of MCl₂·xH₂O indicated immediate occurrence of the coordination of the Metal (II) to the binding sites of the acyclic ligand. In all cases the complexes appear to be air stable and soluble in common organic solvents. Crystals suitable for X-ray analysis were obtained by slow evaporation of the methanolic solution of the zinc (II) complex. All compounds are characterized by elemental analysis (C, H, N), IR spectroscopy, molar conductivity, magnetic measurements, and X-ray diffraction for the zinc (II) complex. Upon complexation of H₂bhn with M (II) ions (M: Mn, Co, Ni or Zn), the infrared spectra of the complexes do not reveal a shift of the C=N band to lower frequency on comparison to the corresponding band of the free ligand. This fact is indicative of the non-participation of the imine group in the coordination [28]. The frequency of the carbonyl group increase for all complexes. Moreover, for the Fe (II) and Cu (II) complexes, the frequencies of the two previous functions (C=N and C=O) decrease drastically. This is a consequence of the involvement of these functions in coordination with those two metal ions. In the infrared spectra of Mn(II), Co(II) and Ni(II) complexes the band at high frequencies in the range 3448–3300 cm⁻¹ is attributed to the ν(OH) of the free water molecule and the band at *ca.* 3200 cm⁻¹ is representative of the ν(OH) of the phenolic function and the coordinated water molecule. The infrared spectra of Fe(II) and Cu(II) complexes reveal only band attributable the ν(OH) of coordinated water molecule in this region. The Zn(II) complex spectrum shows a band near 3206 cm⁻¹ which is probably due to the ν(OH) of the free phenolic function. The electronic spectral data of the complexes are recorded in DMF solvent and the main bands are listed in Table 2. The assignments are made by comparison with literature data [28–29]. In the case of phenolic ligand, a π → π* band which is observed around 200–250 nm is correlated to the electrons transfer in phenyl rings [28]. The band in the regions 300–350 nm and 350–400 nm are respectively due to π → π* and n → π* electron transfer in imine chromophore [29]. The intense bands observed in the spectra of the Cu, Ni and Co complexes near 250 nm is assigned to π → π* transition of the aromatic rings. In the region 300–445 nm intense bands are observed and are assigned to n → π* transition in imine chromophore [28–29]. In the electronic spectra of the complexes *d* → *d* transitions bands are observed. The electronic spectrum of the Mn (II) complex displayed two bands with very low intensities in the visible at 417 and 569 nm which are probably due, respectively, to the electronic transition ⁶A₁ → ⁴T_{2g} and ⁶A₁ → ⁴T_{1g} in accordance with an square pyramidal geometry around Mn (II) ion [31]. For the iron (II) complex typical bands for octahedral environment [31] were pointed at 448 and 509 nm and assigned, respectively, to ²E_g → ²T_{2g} and ²E_g → ²T_{1g}(P) transitions. For the cobalt (II) complex the bands pointed at 470 and 675 nm are assignable, respectively, to ²E_g → ²T_{2g} and ²E_g → ²T_{1g}(P) transitions indicating octahedral environment around Co (II) ions [32]. Two of the three bands expected for the octahedral Ni (II) complex are pointed at 431 and 503 nm in the Ni (II) complex spectrum. The absence of the third transition band is probably due to the low intensity. These two values are attributed, respectively, to ³A_{2g} → ³T_{2g}(P) and ³A_{2g} → ³T_{1g}(F) transitions for octahedral environment in Ni (II) complex [32]. In the spectrum of

the Cu (II) complex, the bands at 462 and 636 nm are both assigned to $d \rightarrow d$ transition [32-35]. The broadness of the band at 636 nm is indicative of a hexacoordinated environment around the copper ions. The spectrum of the Zn^{2+} complex which has a d^{10} metal center presents no absorption band over 403 nm. While the Zn (II) is diamagnetic, Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) complexes are paramagnetic and exhibit room temperature magnetic moments in solid state. The magnetic moment of the manganese (II) complex is $5.54 \mu_B$. This value is in accordance with the presence of five unpaired electrons and is indicative of a high spin d^5 configuration. These facts support octahedral geometry around the Mn^{2+} ions [36]. The magnetic moment of the mononuclear nickel (II) complex value of $3.10 \mu_B$ is indicative for one Ni^{2+} ion in octahedral environment. The value of the magnetic moment at room temperature of the mononuclear cobalt complex is $3.20 \mu_B$ in accordance with the presence of one high-spin Co (II) ions having a spin-orbit contribution is indicative of octahedral environment around the metal center [37]. The mononuclear Cu^{2+} complex presents at room temperature magnetic moment of $1.68 \mu_B$. This value is close to that of the free ion. Molar conductivities were measured for freshly prepared DMF solutions and after standing for two weeks (Table 2). The conductivities increased very slightly with time in DMF for all the complexes. For the complexes Mn (II), Fe (II), Co (II), Ni (II) and Zn (II), the conductance values are observed in the range $7-29 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$. These observations are indicative of a non-electrolytic solution in nature [38]. On the other hand, for the Cu (II) complex, the conductance goes from 20 to $55 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$. This observation is indicative of a dissociation of the copper (II) complex in DMF yielding 1:1 electrolyte [38].

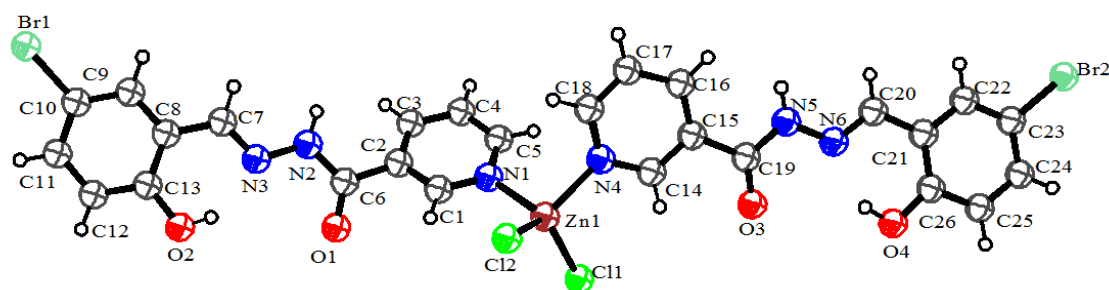


Figure 1: ORTEP plot (30% probability ellipsoids) showing the molecule structure of the Zinc (II) complex

Table-2. Electronic data, magnetic moments and conductance data of the complexes

Compound	UV Bands		Λ ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)		μ/μ_B
	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, MLCT	$d \rightarrow d$	Fresh	two weeks after	
$H_2bhn = C_{13}H_{10}BrN_3O_2$	227, 235, 290, 340				
$[Mn(H_2bhn)_2(Cl)_2(H_2O)_2] \cdot H_2O$	347, 417	569	21	20	5.54
$[Fe(Hbhn)(Cl)(H_2O)_2]$	320, 376, 448	509	13	26	6.11
$[Co(H_2bhn)_2(Cl)_2(H_2O)_2] \cdot H_2O$	349, 427	643	10	13	3.20
$[Ni(H_2bhn)_2(Cl)_2(H_2O)_2] \cdot H_2O$	361, 431	503	23	29	3.10
$[Cu(Hbhn)(Cl)(H_2O)_2]$	293, 330, 413, 636	986	20	55	1.68
$[Zn_2(H_2bhn)_2(Cl)_2] \cdot H_2O$	346, 403	----	07	08	diam

3.2. Structure determination

The complex crystallizes in the triclinic system with the centrosymmetric space group Cc . Selected bond distances and angles are listed in Table 3. The asymmetric unit consists of a mononuclear complex where two ligand molecules are coordinated to the metal center which is also coordinated to two chloride ions. Each ligand molecule acts via the nitrogen atom of the pyridine ring resulting in a tetracoordinated zinc (II) ion in N_2Cl_2 inner. The ZnN_2Cl_2 chromophore is best described as distorted tetrahedral. For the determination of the geometry around the metal center, a similar formula of Addison parameter [39] for four-coordination is used: $\tau_4 = [360 - (\alpha + \beta)]/141$ (α and β being the largest angles around the Zn (II) atom). Perfect tetrahedral geometry is indicated by the τ value of 1 while τ value of 0 is indicative of a perfect square planar geometry. For the complex $Zn(H_2bhn)_2Cl_2$, the value of $\tau_4 = 0.91$ is indicative of a slightly distorted tetrahedral geometry around the Zn ion which is formed by two nitrogen atoms of the pyridine rings and two terminal chloride atoms. The bond lengths Zn-Cl1 and Zn-Cl2 are 2.2053 (16) and 2.2091 (16) Å respectively. The bond lengths Zn-N1 is 2.057(5) Å and Zn-N4 is 2.038(5) Å (Table 3). Those distances are in the order of those found for the tetrahedral complex $[Zn(dap)_2Cl_2]$ (dap is 2,3-Diaminopyridine) [40] which are very similar to those found for our complex $[Zn-N, 2.038(3)$ and $2.05(2)$ Å]. The coordination geometry of the Zn atom is tetrahedral with N-Zn-N and Cl-Zn-Cl angles of $101.44(19)$ and $119.05(7)^\circ$ respectively. The Cl-Zn-Cl value is close proximity with the corresponding angle found by Bakir [41] in $ZnCl_2(\kappa^2-N, N'-dpknph)$ (dpknph is di-2-pyridylketone-*p*-nitrophenyl

hydrazone) complex while the N-Zn-N are largely different ($\text{Cl-Zn-Cl} = 119.67(3)^\circ$ and $\text{N-Zn-N} = 89.97(7)^\circ$). It should be noted that the angles in the studied complex have values slightly different to the ideal value of perfect tetrahedral geometry. The values of the N-Zn-Cl angles are in the range $105.10(14)^\circ$ - $111.35(14)^\circ$ and are comparable to the values of the angles found for the $[\text{ZnCl}_2(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})]$ and $[\text{ZnCl}_2(\text{H}_2\text{O})_2](\text{Me}_4\text{Pyz})_2$ complexes [42].

Table-3. Selected geometric parameters (\AA , $^\circ$)

Zn1-N4	2.038(5)	N1-Zn1-Cl1	110.98(15)
Zn1-N1	2.057(5)	N1-Zn1-Cl2	105.10(14)
Zn1-Cl1	2.2053(16)	N4-Zn1-Cl1	107.52(15)
Zn1-Cl2	2.2091(16)	N4-Zn1-Cl2	111.35(14)
N4-Zn1-N1	101.44(19)	Cl1-Zn1-Cl2	119.05(7)

IV. Conclusion

Using the Schiff base ligand N'-(5-bromo-2-hydroxybenzylidene)nicotinothiazide, six metal transition complexes have been synthesized and have been studied with spectroscopic methods and X-rays diffraction technique for the zinc (II) complex. The neutral Schiff base ligands acts in monodentate mode through the pyridine nitrogen atom with Mn(II), Co(II), Ni(II) and Zn(II) cations. When the ligand is mono deprotonated it acts in tridentate fashion through the pyridine nitrogen atom, the imino nitrogen atom and the phenolate oxygen atom with Fe(II) and Cu(II) and results in two five membered rings. The nuclearity of the complexes, the pentahedral environment around Mn(II) and the octahedral environments around Co(II), Ni(II), Fe(II) and Cu(II) are supported by the spectral data while the distorted tetrahedral environment in the Zn (II) complex is demonstrated by the X-ray diffraction structure.

V. Supplementary material

CCDC 1908462 contains the supplementary crystallographic data for the reported complex. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. or [www: http:// www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

References

- [1]. N. Novoa, F. Justaud, P. Hamon, T. Roisnel, O. Cador, B.L. Guennic, C. Manzur, D. Carrillo, J.-R. Hamon, Doubly phenoxide-bridged binuclear copper(II) complexes with one tridentate schiff base ligand: Synthesis, structural, magnetic and theoretical studies, *Polyhedron*, *86*, 2015, 81–88.
- [2]. S. Saha, S. Jana, S. Gupta, A. Ghosh, H.P. Nayek, Syntheses, structures and biological activities of square planar Ni(II), Cu(II) complexes, *Polyhedron*, *107*, 2016, 183–189.
- [3]. E. Akila, M. Usharani, S. Ramachandran, P. Jayaseelan, G. Velraj, R. Rajavel, Tetradentate-arm Schiff base derived from the condensation reaction of 3,3'-dihydroxybenzidine, glyoxal/diacetyl and 2-aminophenol: Designing, structural elucidation and properties of their binuclear metal(II) complexes, *Arabian J. Chem.*, *10*, 2017, S2950–S2960.
- [4]. M. Minelli, W. Hart-Cooper, J.G. Sinnwell, D.T. Blumberg, I.A. Guzei, L.C. Spencer, J.P.S. Vázquez, A.S. Peralta, M.S. Torres, Synthesis, structure, and characterization of molybdenum(VI) imido complexes with N-salicylidene-2-aminothiophenol, *Polyhedron*, *146*, 2018, 26–34.
- [5]. P. Baran, R. Boča, M. Breza, H. Elias, H. Fuess, V. Jorik, R. Klement, I. Svoboda, The spectroscopic and structural properties of copper(II) complexes of the novel tridentate (ONO) pyridine N-oxide ligand Hpoxap, *Polyhedron*, *21*, 2002, 1561–1571.
- [6]. A. Çapan, S. Uruş, M. Sönmez, Ru(III), Cr(III), Fe(III) complexes of Schiff base ligands bearing phenoxy Groups: Application as catalysts in the synthesis of vitamin K3, *J. Saudi Chem. Soc.*, *22*, 2018, 757–766.
- [7]. K.G. Samper, S.C. Marker, P. Bayón, S.N. MacMillan, I. Keresztes, Ó. Palacios, J.J. Wilson, Reprint of “Anticancer activity of hydroxy- and sulfonamide-azobenzene platinum(II) complexes in cisplatin-resistant ovarian cancer cells,” *J. Inorg. Biochem.*, *177*, 2017, 335–343.
- [8]. P. Kavitha, M. Saritha, K.L. Reddy, Synthesis, structural characterization, fluorescence, antimicrobial, antioxidant and DNA cleavage studies of Cu(II) complexes of formyl chromone Schiff bases, *Spectrochim. Acta, Part A*, *102*, 2013, 159–168.
- [9]. T. Chandrasekaran, M. Suresh, F.M.M. Ahamed, M.S.A. Padusha, Synthesis, characterization and antimicrobial studies of novel compound and its metal complexes derived from nicotinic acid, *Chem. Sin.*, *10*, 2014, 81–90.
- [10]. O.A.M. Ali, S.M. El-Medani, D.A. Ahmed, D.A. Nassar, Metal carbonyl complexes with Schiff bases derived from 2-pyridinecarboxaldehyde: Syntheses, spectral, catalytic activity and antimicrobial activity studies, *J. Mol. Struct.*, *1074*, 2014, 713–722.
- [11]. M. Shabbir, Z. Akhter, A.R. Ashraf, H. Ismail, A. Habib, B. Mirza, Nickel(II) and palladium(II) triphenylphosphine complexes incorporating tridentate Schiff base ligands: Synthesis, characterization and biocidal activities, *J. Mol. Struct.*, *1149*, 2017, 720–726.
- [12]. A. Panja, Mononuclear cobalt(III) and iron(II) complexes with diimine ligands: Synthesis, structure, DNA binding and cleavage activities, and oxidation of 2-aminophenol, *Polyhedron*, *43*, 2012, 22–30.
- [13]. M. Kose, P. Goring, P. Lucas, V. Mckee, Mono-, di- and tri-nuclear manganese(II) complexes derived from a quinque-dentate ligand: Superoxide dismutase and catalase mimetic studies, *Inorg. Chim. Acta*, *435*, 2015, 232–238.
- [14]. Y. Deniz, Nicotine, its metabolism and an overview of its biological effects, *Toxicol.*, *43*, 2004, 619–632.
- [15]. Y.Y. Wang, Y. Liu, X.Y. Ni, Z.H. Bai, Q.Y. Chen, Y. Zhang, F.G. Gao, Nicotine promotes cell proliferation and induces resistance to cisplatin by $\alpha 7$ nicotinic acetylcholine receptor-mediated activation in Raw2647 and E14 cells, *Oncol. Rep.*, *31*, 2014, 1480–1488

- [16]. S.Y. Ebrahimpour, M. Abaszadeh, J. Castro, M. Seifi, Synthesis, X-ray crystal structure, DFT calculation and catalytic activity of two new oxido-vanadium(V) complexes containing ONO tridentate Schiff bases, *Polyhedron*, **79**, 2014, 138–150.
- [17]. H. Briseño-Ortega, L. Juárez-Guerra, S. Rojas-Lima, L.H. Mendoza-Huizar, R.A. Vázquez-García, N. Farfán, R. Arcos-Ramos, R. Santillan, H. López-Ruiz, One pot synthesis, X-ray crystal structure of 2-(2'-hydroxyphenyl)oxazolo[4,5-b]pyridine derivatives and studies of their optical properties, *J. Mol. Struct.*, **1157**, 2018, 119–126.
- [18]. O.K. Olurotimi, A.J. Adeyemi, B.O. Agbeke, O. Olajumoke, S.T. Oluwasegun, E.G. Sunday, Structural and Biological Activity Study of (E)-N'-(5-Chloro-2-Hydroxybenzylidene)Nicotinothiazide [H2L]. and Some of its Divalent Metal Complexes, *Orient. J. Chem.*, **33**, 2017, 1623–1635.
- [19]. O.K. Ogunniran, A.M. Mesubi, A. Adekoya, O.O. Siyanbola, A. Inegbinebor, O.O. Ojo, E.A. Adedapo, A. Edobor-Osoh, T. Narender, Synthesis of (E)-N'-(5-bromo-2-hydroxybenzylidene)nicotinothiazide and its Pt(II), Zn(II), Mn(II), Ni(II) and Mo(V) complexes as potential anti-tubercular agent, *Can. J. Pure Appl. Sci.*, **9**, 2015, 3519–3534.
- [20]. S.K. Dey, A. Mukherjee, Catechol oxidase and phenoxazinone synthase: Biomimetic functional models and mechanistic studies, *Coord. Chem. Rev.*, **310**, 2016, 80–115.
- [21]. J. Singh, P. Singh, Synthesis, Spectroscopic Characterization, and In Vitro Antimicrobial Studies of Pyridine-2-Carboxylic Acid N'-(4-Chloro-Benzoyl)-Hydrazide and Its Co(II), Ni(II), and Cu(II) Complexes, *Bioinorg. Chem. Appl.*, **2012**, 2012, 104549–104549.
- [22]. G.M. Sheldrick, Integrated space-group and crystal-structure determination, *Acta Crystallogr.*, **A71**, 2015, 3–8.
- [23]. G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr.*, **C71**, 2015, 3–8.
- [24]. L.J. Farrugia, ORTEP-3 for Windows - a version of it ORTEP-III with a Graphical User Interface (GUI), *J. Appl. Crystallogr.*, **30**, 1997, 565.
- [25]. S. Sravya, S. Sruthy, N. Aiswarya, M. Sithambaresan, M.R.P. Kurup, Crystal structure of (E)-N'-(5-bromo-2-hydroxybenzylidene)nicotinothiazide monohydrate, *Acta Crystallogr.*, **E71**, 2015, 734–736.
- [26]. B. Gao, D. Zhang, Y. Li, Synthesis and photoluminescence properties of novel Schiff base type polymer-rare earth complexes containing furfural-based bidentate Schiff base ligands, *Opt. Mater. (Amsterdam, Neth.)*, **77**, 2018, 77–86.
- [27]. H. Barfeie, G. Grivani, V. Eigner, M. Dusek, A.D. Khalaji, Copper(II), nickel(II), zinc(II) and vanadium(IV) Schiff base complexes: Synthesis, characterization, crystal structure determination, and thermal studies, *Polyhedron*, **146**, 2018, 19–25.
- [28]. M. Sedighipour, A.H. Kianfar, M.R. Sabzalian, F. Abyar, Synthesis and characterization of new unsymmetrical Schiff base Zn (II) and Co (II) complexes and study of their interactions with bovin serum albumin and DNA by spectroscopic techniques, *Spectrochim. Acta, Part A*, **198**, 2018, 38–50.
- [29]. R.N. Egekenze, Y. Gulnezh, R. Butcher, Mn(III) and Mn(II) complexes of tridentate Schiff base ligands; synthesis, characterization, structure, electrochemistry and catalytic activity, *Inorg. Chim. Acta*, **478**, 2018, 232–242.
- [30]. T.A. Yousef, O.K. Alduaij, S.F. Ahmed, G.M.A. El-Reash, O.A. El-Gammal, Semi- and thiosemicarbazide Mn(II) complexes: Characterization, DFT and biological studies, *J. Mol. Struct.*, **1119**, 2016, 351–364.
- [31]. E.R. Shilpa, V. Gayathri, Polymer immobilized Fe(III) complex of 2-phenylbenzimidazole: An efficient catalyst for photodegradation of dyes under UV/Visible light irradiation, *J. Saudi Chem. Soc.*, **22**, 2018, 678–691.
- [32]. S. Bibi, S. Mohamad, N.S.A. Manan, J. Ahmad, M.A. Kamboh, S.M. Khor, B.M. Yamin, S.N.A. Halim, Synthesis, characterization, photoluminescence, and electrochemical studies of novel mononuclear Cu(II) and Zn(II) complexes with the 1-benzylimidazolium ligand, *J. Mol. Struct.*, **1141**, 2017, 31–38.
- [33]. M.M.I.M. Hasnan, N. Abdullah, S.M. Said, M.F.M. Salleh, S.A.M. Hussin, N.M. Shah, Thermo-electrochemical generation capabilities of octahedral spin crossover complexes of Mn(II), Fe(II) and Co(II) with N-donor ligands and benzoate counter ion, *Electrochim. Acta*, **261**, 2018, 330–339.
- [34]. R.A. Ammar, A.-N.M.A. Alaghaz, M.E. Zayed, L.A. Al-Bedair, Synthesis, spectroscopic, molecular structure, antioxidant, antimicrobial and antitumor behavior of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of O₂N type tridentate chromone-2-carboxaldehyde Schiff's base ligand, *J. Mol. Struct.*, **1141**, 2017, 368–381.
- [35]. W. Seals, H. Arman, S. Batha, G.T. Musie, The synthesis and characterization of new nickel complexes with unusual coordination modes, *Inorg. Chim. Acta*, **448**, 2016, 16–25.
- [36]. N.C. Jana, P. Brandão, A. Saha, A. Panja, Synthesis, crystal structure and electronic property of a tetraoxolene bridged dinuclear cobalt(II) complex with bipyridyl blocking ligand, *Polyhedron*, **138**, 2017, 31–36.
- [37]. L.K. Thompson, S.K. Mandal, S.S. Tandon, J.N. Bridson, M.K. Park, Magnetostructural Correlations in Bis(μ₂-phenoxide)-Bridged Macrocyclic Dinuclear Copper(II) Complexes Influence of Electron-Withdrawing Substituents on Exchange Coupling, *Inorg. Chem.*, **35**, 1996, 3117–3125.
- [38]. W.J. Geary, The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coord. Chem. Rev.*, **7**, 1971, 81–122.
- [39]. A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2[prime or minute]-yl)-2,6-dithiaheptane]copper(II) perchlorate, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349–1356.
- [40]. C. De Cires-Mejias, Tanase, J. Reedijk, F. González-Vilchez, R. Vilaplana, A.M. Mills, H. Kooijman, A.L. Spek, Extended structures based on hydrogen bonding and π-π interactions: synthesis and characterization of two zinc complexes: [Zn(dap)Cl₂] and [Zn(dap)₂Cl₂], *Inorg. Chim. Acta*, **357**, 2004, 1494–1498.
- [41]. M. Bakir, R.R. Conry, O. Green, X-ray crystallographic and molecular sensing properties of [ZnCl₂(κ²-N,N'-dpknph)] (dpknph=di-2-pyridyl ketone-p-nitrophenyl hydrazone), *J. Mol. Struct.*, **889**, 2008, 35–44.
- [42]. Y.V. Kokunov, Y.E. Gorbunova, V.V. Kovalev, Tetrahedral complexes of zinc(II) chloride with N- and O-containing organic ligands: Synthesis and crystal structures of [ZnCl₂(C₁₂H₁₂N₂O)] and [ZnCl₂(H₂O)₂](Me₄Pyz)₂, *Russ. J. Inorg. Chem.*, **54**, 2009, 1603.

Shilpa.R. "Six new transition metal mononuclear complexes of N'-(5-bromo-2-hydroxybenzylidene)nicotinothiazide Schiff base. Synthesis, spectroscopic characterization and X-ray structure determination of the Zinc(II) complex.." *IOSR Journal of Applied Chemistry (IOSR-JAC)* **12.2** (2019): 24-30.