Synthesis, Characterization and DFT calculations of Novel Mononuclear Nickel (II), Cobalt (II) and Iron (II) Complexes derived from 2-(1H-benzimidazol-2-yl)- phenol Ligand

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Abstract

In this study, the novel mononuclear complexes, K_2 [Ni $(L)_2$ Cl_2]· $2H_2O$ (**C1**), K_2 [Co $(L)_2$ Cl_2]· H_2O (**C2**) and K_2 [Fe $(L)_2$ Cl_2]· $4H_2O$ (**C3**), was L is the 2-(2-hydroxyaryl)-1*H*-benzimidazole, have been synthesized and characterized. The structures of these compounds were approved by FT-IR, UV-Vis, ^{1}H-, ^{13}C-NMR, ICP and elemental analyses (C, H and N). The purity of the compounds was ascertained by melting point (m.p.) and TLC. Based on the combined experimental and theoretical studies, the structure of all compounds are six-coordinated octahedral. The geometry optimization, , stability of the compounds and vibrational frequency calculations of the compounds were carried out in Gaussian 09 program using B3LYP/TZVP level of theory.

Key words: 2-(1H-benzimidazol-2-yl)-phenol, Metal complexes, DFT calculations

1. Introduction

Schiff bases and their transition metal complexes have been studied extensively over the past few decades [1-3]. The transition metal complexes of Schiff bases derived from heterocyclic compounds containing nitrogen and oxygen atoms are of current interest as simple structural models of biological systems. These ligands when coordinated with metal ions yield stable complexes which present interesting physical, chemical, biological and catalytic Properties. They play an important role in inorganic chemistry as they can easily form stable complexes with most of the transition metal ions. One of these ligands is benzimidazolylphenol rings, which is formed *via* the fusion of benzimidazole and phenol rings, which have been attracted due to their usage in many applications such as anticonvulsant, antiulcer [4], antibacterial, antivirals, antifungals, anticancers [5], antihistaminics and antihypertensive [6]. Benzimidazolylphenols by a large number of carbonyl compounds and amines have been prepared [7].

In this work, we report the synthesis and characterization of nickel (II), cobalt (II) and iron (II) chloride complexes with 2-(1H-benzimidazol-2-yl)-phenol. Density functional theory (DFT) calculations of the electronic properties of the compounds were performed which were in good agreement with the experimental results.

2. Experimental

2.1. Materials and Measurements

All chemicals and solvents were reagent grade and have been used as purchased without further purification. The compounds were characterized by elemental analyses (Perkin Elmer model 2400 series 2, made in USA), ICP (3410ARL model made in Swiss), FT-IR spectra (Shimadzu FT-IR 8400 spectrometer), UV-Vis spectra (Shimadzu, UV-1700 spectrophotometer) and NMR spectra (Bruker AVANCE-300 instrument).

2.2. Synthesis of the Ligand

2.2.1. 2-(1H-Benzimidazol-2-yl)-phenol (L)

2-hydroxybenzaldehyde and sodium metabisulfide, dissolved in ethanol and water, respectively. The reaction mixture was stirred and more ethanol was added. The mixture was kept in a refrigerator for several hours. Obtained salt and 1, 2-phenylenediamine in dimethyl formamide (DMF) were refluxed for 4 h at 130^{o}C in an oil bath. The completion of reaction was monitored by TLC. Then the mixture was poured in an ice bath. The resulted compound was filtered and recrystallized from ethanol. Obtained ligand was used for the synthesis of the complexes.

2.3. General Procedure for Synthesis of the Complexes (C1-C3)

Solution of metal salt in methanol was added to a solution of ligand and KOH in methanol. The solution color was immediately changed. The reaction was stirred for several hours at room temperature. The completion of reaction was monitored by TLC. Resulting precipitate was separated by filtration, washed with diethyl ether and dried in vacuum.

2.4. Computational details

DFT calculations were performed with the Gaussian 09 package using the B3LYP (hybrid GGA functional of Becke-Lee, Parr, and Yang [8,9]) level of theory, since as reported before, in the molecular simulation of transition metal containing systems better agreement with the experimental results can be obtained with this method [10-14]. In all cases the electronic configuration of the molecular systems was described with the triple-ζ basis set augmented with one polarization functions of Ahlrichs and coworkers (TZVP keyword in Gaussian) [15]. The electronic ground state for the computed complexes, Ni (II), Co (II) and Fe (II) chloride, was the triplet, the quartet and the Quintet, respectively. Overall, open shell calculations were performed. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the global minima and that there are only positive Eigen values [16, 17]. The optimized geometry of compounds furnished the total energy E. The zero-point energy values in a.u. obtained by using the DFT calculations are: L (−686 a.u.), whereas C1 (−3801 a.u.), C2 (−3675 a.u.) and C3 (−3556 a.u.) reflecting that more stability is in the complexes with less electronic energies [18].

3. Results and Discussions

All compounds were characterized by FT- IR spectra, UV-Vis, NMR, ICP and elemental analysis (C, H and N). The analytical data are given in Table1.

3.1. FT-IR spectra

Vibrational properties of the ligand and complexes have been performed by using the DFT calculations with B3LYP/TZVP level. Figure 1 (a,b) and Figure 2 (a,b) show the measured and calculated FT-IR spectra of the ligand and the **C1** complex . The characteristic ν(O–H) and ν(N–H) vibration frequencies of the ligand appear separately at 3325 and 3245 cm^{-1} in the IR spectra, because of weak intramolecular hydrogen bonding. The corresponding peak in theoretical spectrum was calculated at ~3253 cm^{-1}.The lack of free hydroxyl band in the FT-IR spectra of the complexes indicates coordination through the oxygen of the phenolic group to metal. The characteristic ν(C–H) modes of ring for the compounds are observed in the wave region about 3058-3184 cm^{-1} [19]. Also, the medium bands at the 675–862 cm^{-1} range are due to the out-of-plane deformation bands for the aromatic C–H. The benzene C= C and the imidazole C=N stretching frequencies are expected to appear at 1591 and 1629 cm^{-1} for the ligand and for the complexes about 1529 and 1623 cm^{-1} in the IR spectra, respectively. Slight and specific differences between spectra of the free ligand and the complexes in this region lead to the conclusion of the formation of new complexes. These results are in agreement with the theoretical calculations.

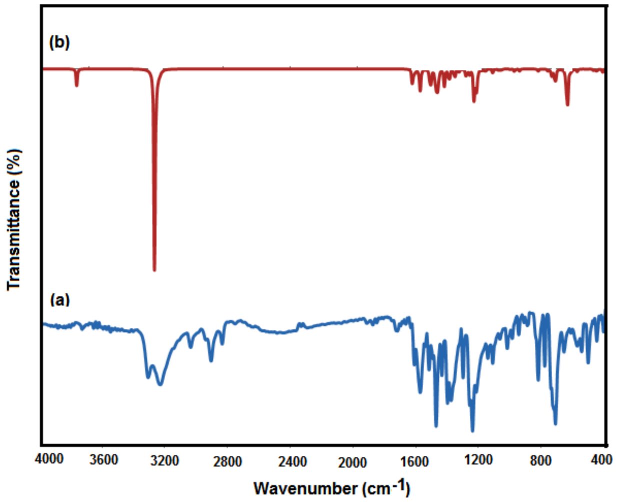


Figure 1. The comparison of (a) experimental (b) theoretical FT-IR, calculated at B3LYP/TZVP level, spectra for ligand

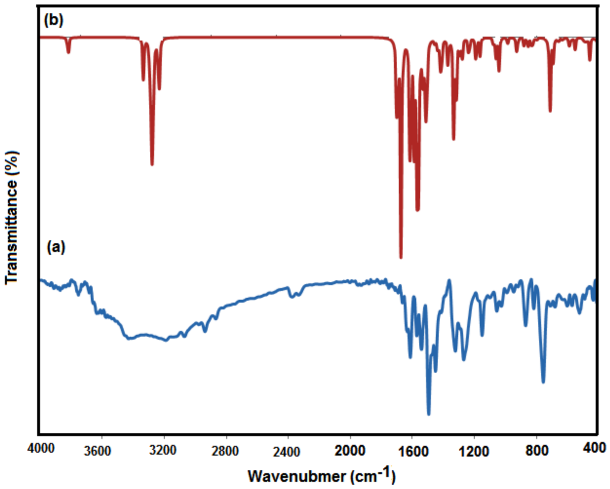


Figure 2. The comparison of (a) experimental, (b) theoretical FT-IR, calculated at B3LYP/TZVP level, spectra for complex **C1**.

3.2. UV-Vis spectra

The lower wavelength bands (250–300 nm) in the electronic spectrum of the ligand correspond to π→π* transitions of the aromatic rings. The medium bands above 300 nm are due to n→π* transitions. In the electronic spectra of **C1** and **C3**, there are a broad band at 350 and 510 nm region may be caused by charge transfer (L →Ni) and $^{5}T_{2}g$ (D) →^{5}Eg (D) transition, respectively. Also, the electronic spectrum of **C2** shows the three weak bands. The bands in the 350-450 nm range may be assigned to L →Co charge transfer and $^{4}T_{1}g$ (F)→ $^{4}A_{2}g$(F), $^{4}T_{1}g$ (F) →$^{4}T_{1}g$ (P) transitions, respectively. $^{4}T_{1}g$(F) →$^{4}T_{2}g$(F) transition is not observed in the spectrum of the present complex. In most instances it is seldom observed as it is inherently weak due to an orbital selection rule. These assignments are typically characteristic for an octahedral geometry of **C1-C3** complexes.

Table 1. The analytical data and physical properties of the ligand and the complexes

Compound	Elemental analysis: found (calcd) %				Yield %	m.p.	Color
	C	H	N	Metal center			
$C_{13}H_{10}N_2O$	70.52 (74.27)	4.32 (4.79)	12.22 (13.33)	-	71	239-240	Brown creamy
$K_2[Ni(L)_2Cl_2].2H_2O$ $C_{26}H_{22}N_4O_4K_2Cl_2Ni$	43.00 (47.15)	2.97 (3.32)	7.60 (8.46)	8.81 (8.86)	50	-	Olive
$K_2[Co(L)_2Cl_2].H_2O$ $C_{26}H_{20}N_4O_3K_2Cl_2Co$	57.23 (48.45)	3.77 (3.10)	9.93 (8.69)	9.40 (9.15)	62	-	Brick red
$K_2[Fe(L)_2Cl_2].4H_2O$ $C_{26}H_{26}N_4O_6K_2Cl_2Fe$	50.01 (45.00)	4.02 (3.74)	8.77 (8.05)	7.46 (8.03)	87.28	-	Brown-orange

3.3. NMR Spectra

^{1}H-, ^{13}C-NMR data of the ligand and the assignments of the peaks are present in Table 2. In the ligand ^{1}H- NMR spectrum two broad singlets are observed for the NH and OH protons at 9.44 and 13.07 ppm, respectively [19]. The phenolic and benzimidazole protons of **C1** and **C3** change their characteristics according to the ligand. In the complexes, all of the multiplet, doublet or triplet peaks change to broad singlets or broad doublets because of the metal ion’s strong perturbing effect. It can be said that, on complexation, acidic character of the benzimidazole and the phenol moiety protons is increased. In **C1** and **C3**, the singlets at 11.87 and 13.42 ppm, respectively, show that the phenolic OH hydrogen is not eliminated; however changes in the chemical shift and the coupling constant values show that a complexes is formed. ^{1}H- NMR spectrum for **C2** could not be recorded because of its low solubility in DMSO-d$_6$ and in the other solvents such as methanol and chloroform, etc. In the ^{13}C–NMR spectrum of the ligand the signals at the highest ppm values over 150 ppm belong to carbon atom bonded to the OH oxygen, and imidazole C=N carbon atom, respectively. The other signals were related to the benzimidazole and phenolic rings carbon atoms.

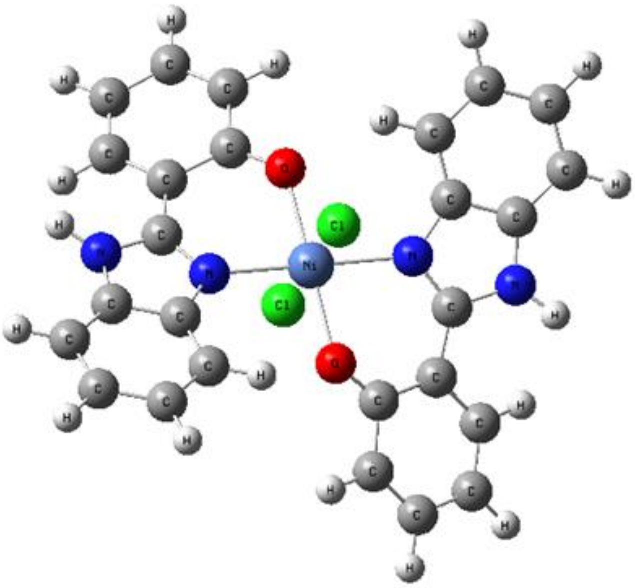
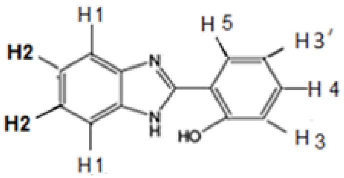


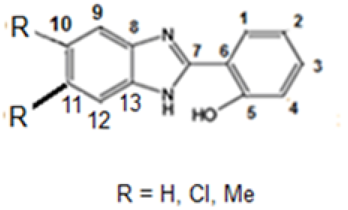
Figure 3. Optimized structure of **C1** complex at B3LYP/TZVP level of theory

Table 2. ^{1}H-, ^{13}C-NMR data (the chemical shift values (δ_H, ppm) with coupling constants (*J*, Hz)) of the ligand.

Ligand	**^{1}H-NMR spectrum data**								**^{13}C-NMR spectrum data**
	The benzimidazole protons			**The phenolic protons**					**The benzimidazole and phenolic ring carbon atoms**
	H_1	**H_2**	**NH**	**H_3**	**H_4**	**$H_3^{/}$**	**H_5**	**OH**	**C1-C13**
L	7.72 s	7.58 d J =12.72	9.44 s	7.14 d J = 8.30	6.96 t J = 7.35	7.32 m	7.32 m	13.07 s	112.08, 118.16, 119.02, 123.34, 124.37, 132.04, 151.35, 158.98

m: multiplet, s: singlet, br: broad, d: doublet, t: triplet.





3.4. Theoretical calculation and stability

According to the DFT calculations, **C1** (−3801 a.u.), **C2** (−3675 a.u.) and **C3** (−3556 a.u.) complexes, have lower energy values than ligand (−686 a.u.). According to The DFT calculations, **C1** have the lowest energy among the complexes and at result it shows the highest stability (Figure 3). According to the geometry optimization of **C1-C3** structures with DFT calculations, metal atoms are located on a octahedral center with the imine nitrogen and hydroxy oxygen atoms of benzimidazole moiety and phenol ring, respectively and associated with two chloride ions (molecular symmetry: **D_2h** for **C1-C3** complexes). The optimized geometry of ligand is shown in Figure 4.

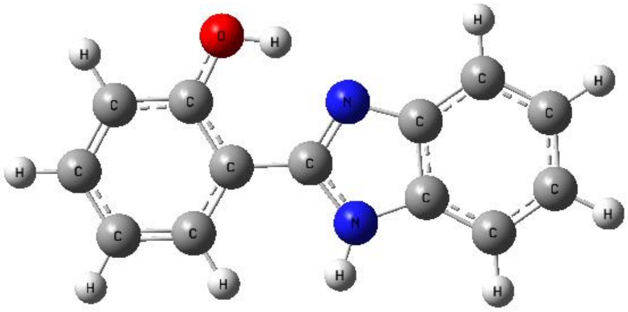


Figure 4. Optimized structure of ligand at B3LYP/TZVP level of theory

4. Conclusions

In a summary, Ni (II), Co (II) and Fe (II) chloride complexes based on 2-(1H-benzimidazol-2-yl)-phenol ligand were synthesized and characterized. In conclusion, the structures of the mononuclear complexes were confirmed by FT-IR, UV–Vis, ^{1}H-, ^{3}C-NMR, ICP, as well as by elemental analysis (C, H and N). All the analytical and spectra data are compatible with theoretical calculations. According to the geometry optimization obtained of DFT calculations, Ni (II), Co (II) and Fe (II) ions in the complexes are located on an octahedral center with the C= N nitrogen and hydroxy oxygen atoms along with two chloro atoms.

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