Experimental and theoretical investigation of spectroscopic properties of Zn(II) complex with 4-Pyridinethioamide

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ABSTRACT

A novel compound of zinc (II) ion, $[ZnCl_2(peta)_2]$ [peta: 4-Pyridinethioamide] was synthesized and characterized by XRD and FT-IR spectroscopy. The geometry around the Zn (II) center can be described as distorted tetrahedron. The crystal packing was stabilized by N–H⋯Cl, N–H⋯S and C–H⋯S intermolecular hydrogen bonds. Molecular modeling of the Zn(II) complex was done by using the Hartree-Fock (HF) and Density Functional Theory (DFT) with 6-311++G (d, p) basis set. The calculated vibrational frequencies were compared with the corresponding experimental data. The time dependent DFT (TD-DFT) method by applying the integral equation formalism-polarized continuum model (IEF-PCM) was performed to investigate the electronic transitions in water and DMSO solvent.

Keywords: X-ray Diffraction, FTIR, HF, DFT

4-Piridinetiyonamid ile Zn(II) kompleksinin spektroskopik özelliklerinin deneysel ve teorik olarak incelenmesi

ÖZ

Zn(II) iyonunun yeni bir kompleksi olan $[ZnCl_2(peta)_2]$ [peta: 4-Pyridinethioamide] sentezledi. Yapısı tek kristal X-ışınları kırınım yöntemi ve FT-IR spektroskopisi kullanılarak aydınlatıldı. Zn(II) merkezi etrafındaki geometrinin bozulmuş tetrahedron olduğu belirlendi. Moleküller arası N–H⋯Cl, N–H⋯S ve C–H⋯S hidrojen bağlarının kristal paketlenmeyi dengelediği görüldü. Yapının moleküler modellemesi Hartree-Fock (HF) ve yoğunluk fonksiyonel teorisi (YFT) ile 6-311++G (d, p) baz seti kullanarak yapıldı. Deneysel olarak elde edilmiş titreşim frekansları teorik olarak hesaplanan değerlerle karşılaştırıldı. Çözücü ortamındaki elektronik geçiler zamana bağlı yoğunluk fonksiyonel teorisine sürekli polarizasyon modeli (IEF-PCM) uygulanarak hesaplandı.

Anahtar kelimeler: X-ışınları Kırınımı, FTIR, HF, DFT

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1. INTRODUCTION

Pyridine, also called azobenzene and azine, is a basic heterocyclic compound with one C–H group replaced by a nitrogen atom. Pyridine and its derivatives have immense importance in the synthesis of various pharmacologically and biologically active compounds. Its complexes are reported to possess many pharmacological properties like antimicrobial [1], antifungal [2],[3] and antitubercular [4]. Its derivatives can also be used as nonlinear materials and photo chemicals [5]. Thioamides have gathered great attention due to their many potential applications in the medicinal chemistry (antibacterial, antifungal and antisecretorial) and polymer chemistry [6],[7].

In this study, we have reported the synthesis and the spectroscopic characterization of [ZnCl₂(peta)₂] complex. The optimized geometry and vibrational frequencies have been calculated by means of HF/6-311++G (d,p) and DFT/B3LYP/6-311++G (d,p) methods. The energetic behavior of the Zn(II) compound in two solvent media (DMSO and water) have been studied at TD-DFT/B3LYP the 6-311G ++(d, p) basis set by applying the IEF-PCM.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Preparation of Zn(II) Complex

An aqueous solution of 4-Pyridinethioamide (1 mmol) in ethanol was added to an aqueous solution of ZnCl₂ (1 mmol) in ethanol. The resulting mixture was refluxed for 2 h. The solid compound was precipitated and the yellow crystals were filtrated off.

2.2. Instrument

The FT-IR spectrum (KBr pellet) of the title complex was recorded using Vertex 80v Bruker FTIR spectrometer.

2.3. Geometrical Structure

Intensity data (Table 1) were measured on a Bruker APEX-II diffractometer equipped with graphite-monochromatic MoK$_\alpha$ radiation at 296 K. The structure was solved and refined using SHELXS-97 and SHELXL-97 [8], respectively. DIAMOND 3.0 (demo) [9] program was used to prepare drawing.

2.4. Theoretical Methodology

The entire computations were performed at HF and DFT methods using GAUSSIAN 09W software [10]. The output files were visualized by means of GaussView tool

[11]. The optimized structure and vibrational bands of the zinc (II) complex were carried out using the HF and DFT/B3LYP with 6-311++G (d, p) basis set [12], [13]. All the vibrations peaks of the zinc (II) complex were real. The fundamental vibrational modes were clarified by means of the Potential Energy Distribution (PED) calculated by using VEDA4 program [14]. Electronic transitions of the title complex were computed using TD-DFT/6-311++G (d, p) level in the gas phase. These transitions were also stimulated for the title molecule in solvent media with two kinds of solvent (DMSO and water) by using IEF-PCM.

3. RESULT AND DISCUSSION

3.1. Crystal Description of the Zn(II) Complex

The crystal structure of the Zn(II) compound is shown in Fig.1. Some important structural parameters are given in Tables 1 and 2. The XRD results show that the Zn(II) ion are coordinated by two chlorine ions and two nitrogen atoms, one from each *peta* ligand. This arrangement causes the formation of a distorted tetrahedral configuration (Fig. 1). The Zn–N (2.050(2) Å -2.040(2) Å) bond distances are similar to those reported for other tetrahedral Zn(II) complexes [15], [16], [17].
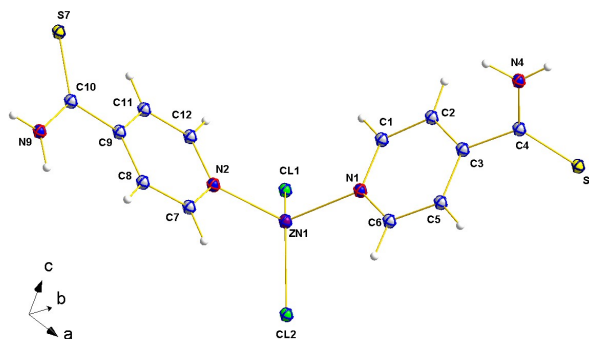

Figure 1. Diamond drawing of Zn(II) complex with thermal ellipsoids at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii.

The Zn-Cl bond lengths [Zn1-Cl1=2.2346(7) Å and Zn1-Cl2=2.2252(7) Å] are in good agreement with the related lengths reported for [L¹ZnCl₂] [Zn1-Cl1 = 2.237(2) Å; Zn1-Cl2 = 2.226(2) Å][18], [Zn(Aqin)₂Cl₂O] [Zn1-Cl1 = 2.2303(9) Å; Zn1-Cl2 = 2.2240(9) Å][19], [Zn(1-ExMe-2-Melm)₂Cl₂] [Zn1-Cl2 = 2.2507(7) Å; Zn1-Cl3 = 2.2233(8) Å][20], [ZnCl₂(HL1)₂] [Zn-Cl = 2.2298(6) Å][16], [(EDT-TTF-4py)₂ ZnCl₂] [Zn1-Cl1 = 2.23 Å; Zn1-Cl2 = 2.24 Å][17], [Zn(L¹)₂Cl₂]·CH₃OH [Zn1-Cl1 = 2.2220(7) Å; Zn1-Cl2 = 2.2737(7) Å][21]. The N-Zn-N and Cl-Zn-Cl angles are 113.46(8) and 121.56(3), respectively. The dihedral angle between the pyridine

rings is 70.07 Å. The torsion angles [C2-C3-C4-S2] and [C5-C3-C4-N4] are -115.5(3)° and -120.3(3)°.

Table 1 Crystallographic data for the Zn(II) complex

Formula	$C_{12}H_{12}ZnN_4S_2Cl_2$
Formula weight (g)	412.67
Temperature (K)	293 K
Wavelength (Mo Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a, b, c (Å)	43.210(3), 9.0573(5), 8.4906(4)
β (°)	93.613(4)
Volume (Å^3)	3316.3(3)
Z	8
Calculated density (Mg m^{-3})	1.653
μ (mm^{-1})	2.05
F(0,0,0)	1664
Crystal size (mm)	0.15× 0.11 × 0.09
θ ranges (°)	3.3 – 28.4
İndex ranges	-53≤ h ≤53
	-11≤ k ≤11
	-10≤ l ≤10
Reflections collected	
İndependent reflections	3266 [R$_{(int)}$=0.045]
Reflection observed (> 2σ)	2937
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	3266/0/207
Goodness-of-fit on F^2	1.16
Final R indices [I>2σ(I)]	0.029
R indices (all data)	0.069
Largest diff. Peak and hole (e Å $^{-3}$)	-0.43 and -0.53

Packing analysis of the title complex indicates that there are intermolecular N–H···Cl, N–H···S, C–H···Cl and C–H···S hydrogen bonds in the crystal structure of zinc complex (see Table 3 and Fig. 2). Furthermore, there is also π-π stacking interaction between the ring 1 (Cg1):

C1/C2/C3/C5/C6/N1 and ring 2 (Cg2): C7/C8/C9/C11/C12/N2; the centroid to centroid distances is 4.4284(17) Å.
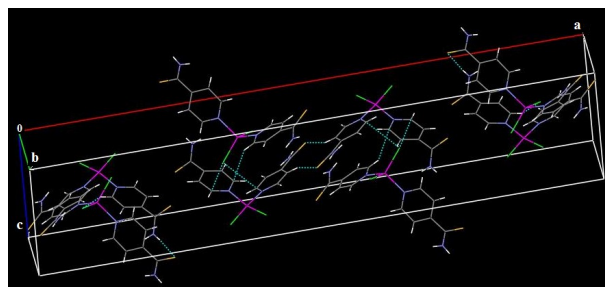

Figure 2.Packing diagram of the Zn(II) complex

Table 2 Selected geometric parameters for the title complex

	Exp.	DFT/B3LYP	HF
N1—Zn1	2.050(2)	2.1523	2.1867
N2—Zn1	2.043(2)	2.1585	2.1947
Cl1—Zn1	2.2346(7)	2.2346	2.25
Cl2—Zn1	2.2252(7)	2.2354	2.2495
S7—C10	1.664(3)	1.6583	1.6464
S2—C4	1.657(3)	1.6578	1.6452
N2-C7	1.335(3)	1.3402	1.3245
N2-C12	1.340(3)	1.344	1.3282
N9-C10	1.312(3)	1.3496	1.3294
N1-C6	1.335(3)	1.3441	1.3283
N1-C1	1.337(3)	1.3403	1.3248
N4-C4	1.306(4)	1.3505	1.3308
N1-Zn1-N2	113.46(8)	103.677	102.2691
Cl1-Zn1-Cl2	121.56(3)	137.3508	136.7873
Cl1-Zn1-N1	105.12(6)	103.0236	103.4913
Cl1-Zn1-N2	103.93(6)	102.8276	103.1506
Cl2-Zn1-N1	104.03(6)	103.5004	103.9687
Cl2-Zn1-N2	109.01(6)	102.5813	102.8156

Table 3 Hydrogen-bonding interactions for the Zn(II) complex

Hydrogen-bond geometry (Å,°)				
D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···Cl2^i	0.88(5)	2.47(5)	3.330(4)	168(4)
N4—H4B···S2^{ii}	0.80(4)	2.65(4)	3.428(3)	164(3)
N9—H9A···Cl1^{iii}	0.87(3)	2.53(4)	3.358(3)	158(3)
N9—H9B···S7^{iv}	0.84(3)	2.61(3)	3.441(3)	174(3)
C1—H1···Cl1^i	0.93	2.77	3.482(3)	135
C8—H8···Cl1^{iii}	0.93	2.75	3.656(3)	166
C11—H11···S7^v	0.93	2.86	3.588(3)	136
C11—H11···S7	0.93	2.71	3.087(3)	105

Symmetry codes: (i) x, y, 1+z; (ii) x, 1-y, ½+z; (iii) x, -1+y, z; (iv) –x, -1-y, 2-z; (v) -x, -y, 2-z.

3.2. Geometry Optimization

The geometry optimization was carried out using the HF and DFT/B3LYP method. The calculated geometric parameters of the Zn(II) complex for the two different methods were compared with the experimental ones in Table 2.

The DFT/B3LYP method predicts the bond lengths and angles in good agreement with experimental values than HF. Calculated geometric parameters are slightly different than the experimental values. The N-Zn-Z angle is 113.46(8)º which is slightly larger than the typical angle for tetrahedron (109.47°). The angle was computed at 102.27º and 103.68º for the HF and B3LYP level, respectively. The orientation of the thioamide groups on the pyridine ring is defined by the torsion angles C2-C3-C4-S2 [-115.5(3)°] and C5-C3-C4-N4 [-120.3(3)°] for the XRD. These angles were calculated at -134.693º, -136.717º and -141.355º, -144.408º for the HF and DFT methods, respectively. According to XRD results, the dihedral angle between the pyridine rings is 70.07º, while this angle was computed at 75.47º for B3LYP/6-311++G (d, p) level and 78.17º for HF/6-311++G (d, p).

3.3. Electronic Properties

The electronic transitions of the Zn(II) complex in the gas phase and solvent (DMSO and water) were calculated at the B3LYP/ 6-311G ++ (d, p) level of DFT. The solvent effect was evaluated by the IEF-PCM. The UV-vis spectral data for gas phase and solvent (DMSO and water) are listed in Table 4, by using the Swizard program [22].

As can be seen from Table 4, the longest wavelengths were calculated at 478 and 468 nm for the gas phase. The electronic transitions are happened from the mixed *d→d* (LF) and *peta → d* (LMCT). These values were computed at 440-434 nm for water and 442-435 nm for DMSO. The calculated bands in the range of 329-278 nm were predicted as π→π* transitions. These transitions were computed in the range of 317-264 nm for DMSO and in the range of 316-273 nm for water. According to TD-DFT calculations, the longest absorption band corresponds to the electronic transition from the HOMO→LUMO+1 (49%).

Table 4 Calculated electronic transitions for the Zn(II) compound with the TD-DFT/ IEF-PCM method.

	λ (nm)	Osc. Str.	Major Contributions
DFT/B3LYP with 6-311++G (d, p)			
	478	0.0075	HOMO→LUMO+1(+49%) HOMO→LUMO(+47%)
	468	0.0081	HOMO-1→LUMO(+55%) HOMO-1→LUMO+1(+41%)
Gas	320	0.1014	HOMO-4→LUMO(+29%) HOMO-3→LUMO(+18%)
	316	0.054	HOMO-5→LUMO+2(+35%
	295	0.013	HOMO-4→LUMO+(+57%)
	278	0.023	HOMO-4→LUMO+4(+86%
	434	0.010	HOMO→LUMO+1(+68%) HOMO→LUMO(+20%)
	316	0.151	HOMO-2→LUMO(+85%)
Water	314	0.106	HOMO-3→LUMO+1(+54%HOMO-3→LUMO(+40%)
	276	0.013	HOMO→LUMO+2(+44%) HOMO→LUMO+3(+31%)

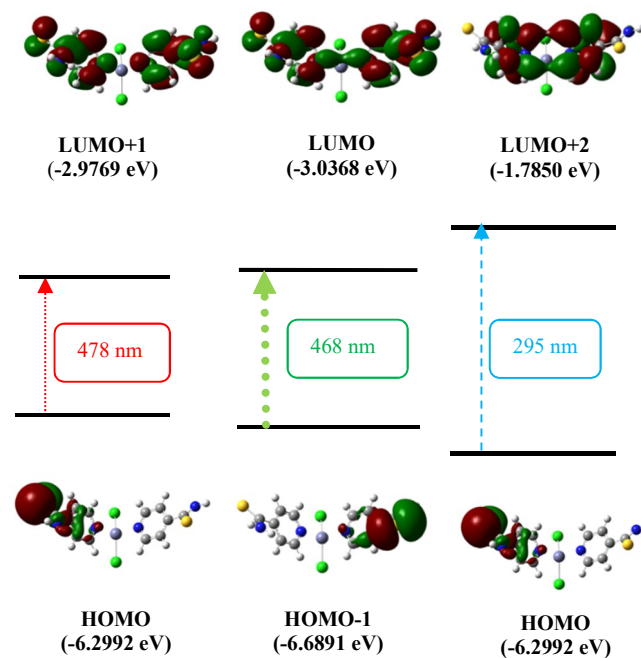|			
	266	0.019	HOMO→LUMO+4(+64%)
	263	0.014	HOMO-1→LUMO+5(+59%
	442	0.009	HOMO→LUMO(+45%) HOMO-1→LUMO(+32%)
	435	0.010	HOMO-1→LUMO+1(+40%HOMO→LUMO+1(+32%)
DMSO	317	0.156	HOMO-2→LUMO(+84%)
	276	0.014	HOMO-1→LUMO+2(+46%HOMO→LUMO+3(+20%)
	266	0.020	HOMO→LUMO+4(+40%)
	264	0.015	HOMO→LUMO+5(+36%) HOMO-1→LUMO+5(+28%)

Figure 3.The molecular orbitals of the Zn(II) complex by using DFT/B3LYP and the selected electronic transitions in the gas phase

The HOMO and LUMO energy gap was found 3.2624 eV in the gas phase, 3.8363 eV in water and, 3.8322 eV in DMSO. The small energy gap between FMOs explains that charge transfer occurs within the Zn(II) compound.

3.4. IR Assignment

FTIR spectra of the Zn(II) complex are illustrated in Figure 4. Harmonic vibrational frequencies of the Zn(II) compound were computed by using B3LYP and HF levels. The calculated vibrational frequencies were scaled as 0.983 for frequencies less than 1700 cm^{-1} and 0.958 for frequencies higher than 1700 cm^{-1} at DFT/B3LYP method. The computed frequencies for greater than 1700 cm^{-1} were scaled as 0.910 and less than 1700 cm^{-1} scaled as 0.908 for HF method [23]. The observed and calculated frequencies are gathered in Table 5.

The amines in the condensed phase give rise to bands in the region 3350-3150 cm^{-1} [24]. The FT-IR spectrum of the Zn(II) complex shows a very strong and broad band in the 3400-3100 cm^{-1} region due to stretching vibrations

of the NH_2 groups [25]. The computed $\nu(NH_2)$ vibrations of amine groups are slightly different than observed vibrations. The band observed at 3093 and 2803 cm^{-1}, which can be attributed to $\nu(CH)$ stretching vibrations of the pyridine rings, were calculated at 3068-3052 cm^{-1} for HF and 3063-3044 cm^{-1} for B3LYP level, respectively [26]. Comparison of computed and observed peaks of the $\nu(CH)$ showed good agreement.

The $\nu(NH_2)$ in-plane bending vibration was observed at 1615 cm^{-1}. This band was computed at 1629 cm^{-1} for HF and 1610 cm^{-1} for B3LYP, respectively. The FT-IR spectrum of the title complex shows a very strong peak at 1027 cm^{-1} associated with ring breathing vibration. The peak was calculated at 1019 cm^{-1} for B3LYP, 1005 cm^{-1} for HF method. As shown in Table 5, the calculated mode at B3LYP level is a good agreement with experimental data.

The frequency 917 cm^{-1} is assigned to the N-C=S group vibration. This mode was calculated at 908 cm^{-1} for HF, 910 cm^{-1} for B3LYP level. The aromatic compounds show the C–H out-of-plane bending vibrations in the range of 700–1000 cm^{-1}. The C–H out-of-plane vibration of the Zn(II) complex was observed at 906 cm^{-1} experimentally and calculated at 906 cm^{-1} for HF and 985 cm^{-1} for DFT method. The peak observed at 573 cm^{-1}, which can be attributed to $\nu(NH_2)$ out-of-plane bending vibration, was computed at 602 cm^{-1} for HF and 589 cm^{-1} for B3LYP, respectively.

Table 5 Experimental and computed vibrational frequencies of the Zn(II) complex

PED(≥10%)[a]	Exp.	B3LYP	HF	Exp.[27]	Exp.[28]
$\nu(NH_2)(92)$	3366	3413	3456	3352	3349
$\nu(NH_2)$	3294			3240	
$\nu(NH_2)$	3123				
$\nu(CH)(46)$	3093	3080	3083	3035	3083
$\nu(CH)(45)$	3067	3063	3068		3042
$\nu(CH)(55)$	2803	3044	3052		
$\nu(CH)$	2771				
$\beta(NH_2)(14)$	1615	1610	1629	1676	1631
$\nu ring(12)+\delta(CH)(16)$	1467	1556	1580	1499	1454
$\nu ring(32)+\nu(CH)(13)$	1420	1429	1428	1425	
$\nu(C-NH_2)(34)$		1354	1346		
$\nu ring(40)$	1297	1252	1220		1278
(Ring-breathing)(62)	1027	1019	1005	1059	1057
$\nu(CS)(15)+\beta(NH_2)(21)$	917	910	908	926	
$\delta(CH)(68)$	906	985	906	862	902
$\nu ring(32)+\delta ring(37)$	839	850	885	832	860
$\delta ring(11)+\delta(CH)(12)$	727	749	756	768	
$\delta ring(13)$	645	633	635		656
$\delta(NH_2)(55)$	573	589	602		
$\delta ring(41)$	416	504	540		

[a] Potential Energy Distribution (PED).
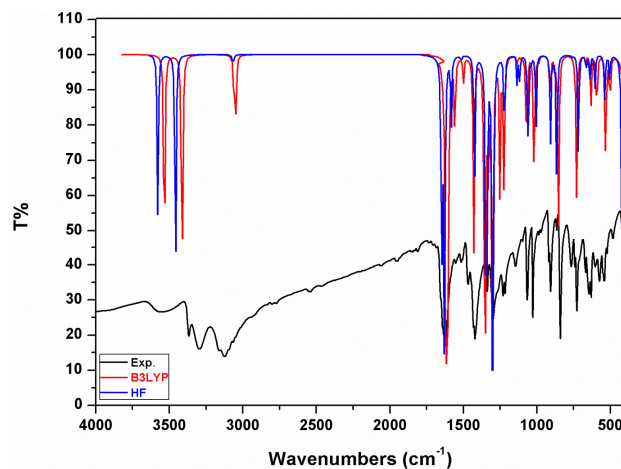ν: stretching, β: in-plane bending, δ: out-of-plane bending.

Figure 4. Experimental and calculated FT-IR spectra of the Zn(II) compound

4. CONCLUSIONS

In this paper, the molecular structure of the $[ZnCl_2(peta)_2]$ compound was reported by means of single crystal XRD study. The optimized geometries of the Zn(II) complex were predicted by HF and DFT method with B3LYP level. The X-ray crystallographic data of the title molecule compare well to those obtained by HF and DFT methods. The FT-IR spectra were recorded, and the obtained results are compared with experimental data. The theoretical results seemed to be in good agreement experimental results. The UV-Vis spectral calculations of the molecule in the gas phase exhibit the maximum absorption band at 478 nm attributed to HOMO→LUMO +1 (%49) transition.

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