Synthesis and Theoretical Study of Zinc(II) and Nickel(II)-Complexes of 5-Methoxyisatin 3-[N-(4-chlorophenyl)thiosemicarbazone]

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Abstract. Zinc(II) and nickel(II)-complexes of 5-methoxyisatin 3-[N-(4-chlorophenyl) thiosemicarbazone] (H_2MICP) were synthesized and characterized by infrared, ultraviolet and ^{1}H-NMR spectroscopies as well as elemental analysis. Model of H_2MICP and its zinc(II) and nickel(II)-complexes were optimized with B3LYP method using 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) basis sets. The calculated ^{1}H-NMR, UV and IR spectra data were compared with experimental results. In addition to the Natural Bond Orbital (NBO) analysis of H_2MICP and its Zinc(II) and Nickel(II) complexes, Fukui functions of H_2MICP were also reported.

Keywords: *DFT; isatin thiosemicarbazones; Zn (II) and Ni (II)-complexes.*

1 Introduction

Isatin 3-thiosemicarbazone derivatives and their metal complexes have a broad range of biological activities namely antimicrobial [1], antiviral [2,3], antitumor, anti-inflammatory and antibacterial activities [4]. The investigation of the structure-activity relationships of isatin β-thiosemicarbazones for antiviral chemotherapeutic activity revealed that the substitution at the C=O position of the side-chain by another atom or group should result in loss of activity [2]. Recently, structure-activity relationship of 5-fluoro-*1H*-indole-2,3-dione-3-thiosemicarbazones and 5-fluoro-1-morpholino/piperidinomethyl-*1H*-indole-2,3-dione-3-thiosemicarbazones were evaluated for *in vitro* antituberculosis activity against *Mycobacterium tuberculosis* H37Rv and studied using ETM–ANN method [5,6]. Antimicrobial activity of Schiff and Mannich bases derived from isatin derivatives has been reported. *N*-[4-(4′-chlorophenyl) thiazol-2-yl] thiosemicarbazide and 1-[*N*,*N*-dimethylaminomethyl]-5-bromo isatin-3′-{1′-[4″-(*p*-chlorophenyl)thiazol-2″-

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yl] thio semicarbazone showed the most favorable antimicrobial activity [1]. 1-(1-((Substituted)methyl)-5-methyl-2-oxoindolin-3-ylidene)-4-(substituted pyridine-2-yl)thiosemicarbazide has been reported to show significant anti-inflammatory and analgesic activity [1].

There are a number of studies on the synthesis of isatin β-thiosemicarbazone derivatives. We have reported synthesis, characterization and mechanistic of 5-methoxyisatin 3-[N-(4-chlorophenyl)thiosemicarbazone] [7]. In the present study, zinc(II) and nickel(II)-complexes of 5-methoxyisatin 3-[N-(4-chlorophenylthiosemicarbazone) have been synthesized. The structures of complexes have been determined by ^{1}H-NMR, IR and UV spectra and elemental analysis (C, H, N, S). Moreover, electronics parameters of H_2MICP and its zinc(II) and nickel(II)-complexes have also been calculated using B3LYP with the basis set of 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p). Natural Bond Orbital (NBO) analysis is also reported.

2 Experimental

2.1 Material and Methods

5-methoxyisatin was purchased from Sigma Aldrich. Metal salts were purchased from E. Merck and used without further purification. Infrared spectrum of 5-methoxy isatin and its complexes were measured using KBr pellet on Shimadzu FT-IR 8201 spectrometer. The elemental analysis was carried out on CHNS-932 (LECO) and ^{1}H-NMR spectra were measured at 400 MHz on a BRUKER DPX-400 spectrometer at the TUBITAK ATAL instrumental analyses laboratory. The electronic spectra of UV–visible zone (200–600 nm) of all the compounds were measured (1 cm quartz cell, 0–2.5 absorbance values range) using Shimadzu UV-1601PC spectrophotometer.

2.2 Synthesis

H_2MICP ligand molecule was synthesized according to literature procedure [7].

Bis{5-methoxyisatin-3-[N-(4-chlorophenyl)thiosemicarbazonato]}zinc(II) [Zn(HMICP)$_2$.H$_2$O]

[Zn(HMICP)$_2$] were synthesized by dissolving 1 mmol (0.361 g) H_2MICP and 0.5 mmol (0.106 g) zinc(II) acetate in warm ethanol. Subsequently, the solution was refluxed for 3 hours. Brown solid was isolated by filtration and washed with 95% ethanol, diethylether and dried in vacuum at room temperature. [(calc. (%): C = 48.95, H = 3.08, N = 14.27, S = 8.16, found. (%):

C = 49.09, H = 3.18, N = 14.24, S = 8.84). ^{1}H-NMR (DMSO-d$_6$, ppm): 3.55 (s, CH_3-methoxy), 6.85-7.66 (aromatic C-H), 10.65 (δ, NH), 10.81 (s, indole-NH)].

Bis{5-methoxyisatin-3-[N-(4-chlorophenyl))thiosemicarbazonato]}nickel(II) [Ni(HMICP)$_2$.H$_2$O]

[Ni(HMICP)$_2$] were synthesized by dissolving 1 mmol (0.361 g) H$_2$MICP and 0.5 mmol (0.088 g) nickel(II) acetate in warm ethanol. Subsequently, the solution was refluxed for 2 h, and stirred for two days at room temperature. A brown solid was isolated and washed with 95% ethanol and diethylether [(calc. (%): C = 48.26, H = 3.29, N = 14.07, S = 8.05, found. (%): C = 48.13, H = 3.22, N = 13.86, S = 7.31)].

3 Theoretical Calculations

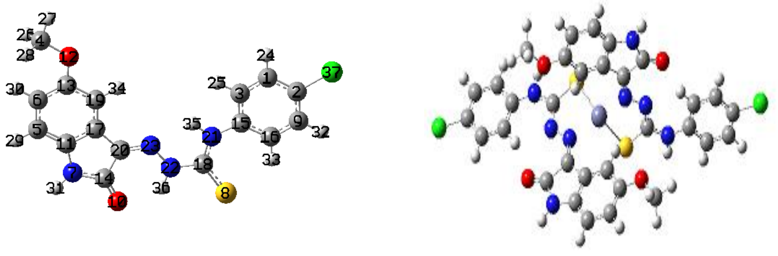
All calculations were carried out by employing density functional theory (DFT) with the basis set levels [8-10] of B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p) for the ligand and B3LYP/6-31G(d,p), B3LYP/6-311G(d,p) for the zinc(II) and nickel(II)-complexes. UV calculation for H$_2$MICP ligand was also performed by DFT at the level of BP86/CEP* using 3/76=1000003000, 3/77=0720007000, 3/78=0810010000, 3/74=406 iop values.

4 Results and Discussion

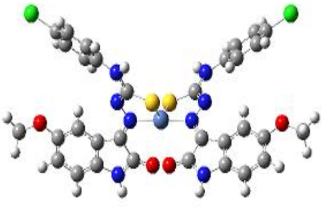
The B3LYP/6-311G(d,p) optimized structures of H$_2$MICP and its zinc(II) and nickel(II)-complexes were shown in Figure 1.

The possible tautomeric structures for H$_2$MICP were calculated using B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p) basis sets. There is no negative imaginary frequency observed for possible tautomeric forms, indicating that all structures are true minima. The B3LYP/6-311G(d,p) optimized structures of possible tautomeric forms were shown in Figure 2. As summarized in Table 1, the A form was found to be most stable than the other forms with all calculation methods like the study in [11].

The energy differences between most stable and unstable tautomeric forms were found as 34.78 kcal/mol; 21.21 kcal/mol; 32.50 kcal/mol; 31.16 kcal/mol at B3LYP method with 6-31G(d,p), 6-311G (d,p), 6-311++G(d,p) and 6-311++G(2d,2p) basis sets respectively. The dipole moment of A form is the highest of all calculated basis sets while E_{HOMO} of A form is the lowest one.



H_2MICP [Zn(HMICP)$_2$]



[Ni(HMICP)$_2$]

Figure 1 The structures of H_2MICP and its zinc(II) and nickel(II)-complexes optimized with B3LYP/6-311G(d,p).

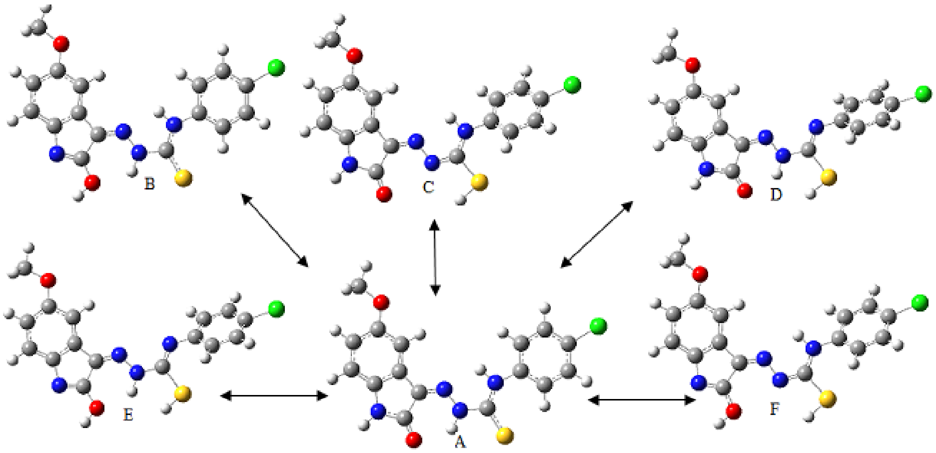


Figure 2 The possible tautomer structures of H_2MICP optimized with B3LYP/6-311G(d,p).

Table 1 The sum of the zero point and electronic energies (au), polarizibility (α), dipole moment (μ), E_{HOMO}, E_{LUMO}, hardness (η) and softness (σ) for the possible tautomer structures of H_2MICP.

Tautomer structures	6-31G(d,p)		6-311G(d,p)		6-311++G(d,p)		6-311++G(2d,2p)	
	Sum of the zero point and electronic energies (au)							
A	-1845.119402		-1845.396917		-1845.414918		-1845.451098	
B	-1845.092834		-1845.370541		-1845.389447		-1845.425976	
C	-1845.087848		-1845.342684		-1845.387149		-1845.423678	
D	-1845.087842		-1845.371603		-1845.391259		-1845.429274	
E	-1845.063968		-1845.342684		-1845.363113		-1845.401429	
F	-1845.067024		-1845.345660		-1845.366705		-1845.404319	
	E_{HOMO} (au)							
A	-0.21650		-0.22428		-0.22803		-0.22688	
B	-0.21305		-0.22142		-0.22558		-0.22430	
C	-0.19856		-0.21499		-0.21096		-0.20994	
D	-0.19856		-0.21901		-0.22329		-0.22234	
E	-0.20648		-0.21499		-0.21967		-0.21868	
F	-0.19656		-0.20484		-0.20951		-0.20844	
	E_{LUMO} (au)							
A	-0.09655		-0.10433		-0.10921		-0.10823	
B	-0.09932		-0.10701		-0.11173		-0.11031	
C	-0.08034		-0.09519		-0.09371		-0.09308	
D	-0.08039		-0.09331		-0.09911		-0.09872	
E	-0.08754		-0.09519		-0.10075		-0.09992	
F	-0.08412		-0.09166		-0.09695		-0.09575	
	η (au)	σ (au^{-1})	η (au)	σ (au^{-1})	η (au)	σ (au^{-1})	η (au)	σ (au^{-1})
A	0.060	8.337	0.060	8.337	0.059	8.416	0.059	8.428
B	0.057	8.793	0.057	8.740	0.057	8.783	0.057	8.773
C	0.059	8.459	0.060	8.347	0.059	8.529	0.058	8.557
D	0.059	8.462	0.063	7.955	0.062	8.053	0.062	8.089
E	0.059	8.408	0.060	8.347	0.059	8.409	0.059	8.420
F	0.056	8.894	0.056	8.835	0.056	8.884	0.056	8.874
	α	μ (D)	α	μ (D)	α	μ (D)	α	μ (D)
A	282.02	9.22	294.54	9.22	316.48	8.98	324.25	8.85
B	285.15	5.64	297.80	5.68	320.43	5.36	327.28	5.19
C	284.49	4.22	289.70	4.75	317.05	4.14	324.34	4.03
D	284.58	4.22	286.02	7.52	307.21	7.27	314.30	7.22
E	279.10	4.64	289.70	4.75	311.12	4.49	317.38	4.39
F	287.68	0.98	298.93	1.01	320.54	1.22	326.97	1.20

Fukui functions of H_2MICP were calculated using AOMix program [11,12]. Fukui functions give information about the reactive regions for nucleophilic and electrophilic attack. $f_k^+ = \rho_k(N+1) - \rho_k(N)$ measures the changes as the molecule gains electrons which indicating the reactivity for nucleophilic attack, while $f_k^- = \rho_k(N) - \rho_k(N-1)$ measures the changes as the molecule losses electrons which indicating the reactivity for electrophilic attack. Table 2 summarizes the Fukui functions for the HOMO and the LUMO of the molecules.

Table 2 Neutral and protonated Fukui functions for the HOMO and the LUMO of the H_2MICP using the different basis sets.

H_2MICP	6-31G(d,p)		6-311G(d,p)		6-311++G(d,p)	
Atoms	f_k^-	f_k^+	f_k^-	f_k^+	f_k^-	f_k^+
C2	-	-	-	-	1.05	-
C5	3.40	-	3.71	-	2.90	-
C6	11.86	5.68	12.13	5.86	11.06	5.81
N7	8.07	1.64	8.35	1.57	6.61	1.63
S8	15.07	8.37	13.40	8.55	19.78	9.01
O10	6.82	8.12	6.75	7.65	5.95	7.45
C11	14.66	3.10	14.98	3.01	13.25	2.79
O12	9.03	-	9.31	-	7.32	-
C13	9.97	-	10.29	-	8.93	-
C14	1.73	8.22	1.88	9.07	1.80	10.03
C17	6.26	3.43	6.32	3.77	5.66	3.58
C18	-	5.86	-	5.76	1.04	5.13
C19	-	6.31	-	6.61	-	6.86
C20	2.18	13.97	2.15	14.25	2.31	14.09
N21	-	1.83	-	1.75	1.62	1.95
N22	4.38	4.14	4.32	3.96	1.95	4.11
N23	1.76	25.01	1.73	24.47	1.55	24.30

Although the compositions of the HOMO and the LUMO for H_2MICP depend on the basis set, the changes are not significant. For the HOMO, the contributions are mainly from thiosemicarbazone group (S8: 19.78%, N22: 4.32%, N23: 1.73%) and isatin group (C5: 3.71%, C6: 12.13%, C11: 14.98%, C13: 10.29%, C14: 1.73%, C17: 6.32%, C20: 2.15%, N7: 8.35%, O10: 6.75%, O12: 9.31%).

The NBO program performs the analysis of a many-electron molecular wavefunction in terms of localized electron-pair bonding units. The program carries out the determination of natural atomic orbitals (NAOs), natural hybrid orbitals (NHOs), natural bond orbitals (NBOs), and natural localized molecular orbitals (NLMOs). These parameters are applicable to perform natural population analysis (NPA) [13]. Bond orbital coefficients as well as the hybrids (percents of *s* and *p* character) for H_2MICP, Zn(II) and Ni(II)-complexes are summarized in Tables 3 and 4.

As shown in Table 3, C6-C13, C5-C11, C17-C19 bonds belonging to the benzene ring of isatin group of H_2MICP have double bond character and the NBO bonds calculated with B3LYP/6-311++G(2d,2p) are 0.7054 C_6 ($sp^{1.86}$) +

0.7088 C_{13} ($sp^{1.60}$) + 0.7249 C_6 (p) + 0.6889 C_{13} (p) for C6-C13 bond; 0.6966 C_5 ($sp^{1.85}$) + 0.7175 C_{11} ($sp^{1.53}$) + 0.7087 C_5 (p) + 0.7055 C_{11} (p) for C5-C11 bond; 0.7196 C_{17} ($sp^{1.62}$) + 0.6943 C_{19} ($sp^{1.80}$) + 0.7187 C_{17} (p) + 0.6953 C_{19} (p) for C17-C19 bond. While the calculations which carried out using B3LYP/6-311G(d,p) basis set is 0.7074 C_6 ($sp^{1.81}$) + 0.7068 C_{13} ($sp^{1.60}$) + 0.7252 C_6 (p) + 0.6885 C_{13} (p), 0.6986 C_5 ($sp^{1.79}$) + 0.7156 C_{11} ($sp^{1.55}$) + 0.7090 C_5 (p) + 0.7052 C_{11} (p) and 0.7163 C_{17} ($sp^{1.64}$) + 0.6978 C_{19} ($sp^{1.75}$) + 0.7195 C_{17} (p) + 0.6945 C_{19} (p). It was shown that there are no significant changes in the calculation results using both the 6-311++G(2d,2p) and 6-311G(d,p) basis sets. Therefore, further calculations were then performed by only the 6-311G(d,p) basis set for the Zn(II) and Ni(II)-complexes. From the NBO analysis, C6-C13, C5-C11, C17-C19 bonds of the benzene ring of isatin group of H_2MICP have same character for pair bond (Table 4).

NBO bonds of C6-C13, C5-C11, C17-C19 which calculated by B3LYP/6-311G(d,p) basis set are 0.7072 C_6 ($sp^{1.81}$) + 0.7070 C_{13} ($sp^{1.61}$) + 0.7220 C_6 (p) + 0.6919 C_{13} (p), 0.6893 C_5 ($sp^{1.79}$) + 0.7158 C_{11} ($sp^{1.55}$) + 0.7147 C_5 (p) + 0.6994 C_{11} (p), 0.7162 C_{17} ($sp^{1.65}$) + 0.6979 C_{19} ($sp^{1.78}$) + 0.7242 C_{17} (p) + 0.6896 C_{19} (p), respectively for [Zn(HMICP)$_2$] complex and 0.7078 C_6 ($sp^{1.80}$) + 0.7065 C_{13} ($sp^{1.61}$) + 0.7210 C_6 (p) + 0.6930 C_{13} (p), 0.6988 C_5 ($sp^{1.78}$) + 0.7153 C_{11} ($sp^{1.56}$) + 0.7165 C_5 (p) + 0.6976 C_{11} (p) and 0.7175 C_{17} ($sp^{1.63}$) + 0.6965 C_{19} ($sp^{1.80}$) + 0.7310 C_{17} (p) + 0.6824 C_{19} (p), respectively for [Ni(HMICP)$_2$]. There are no significant changes in these bonds for either Zn(II) nor Ni(II)-complexes. C20-N23 NBO of the thiosemicarbazone group of H_2MICP ligand, and its Zn(II) and Ni(II)-complexes are 0.6326 C_{20} ($sp^{2.00}$) + 0.7745 N_{23} ($sp^{1.30}$) + 0.6778 C_{20} (p) + 0.7353 N_{23} (p), 0.6254 C_{20} ($sp^{1.99}$) + 0.7803 N_{23} ($sp^{1.34}$) + 0.6363 C_{20} (p) + 0.7714 N_{23} (p) and 0.6370 C_{20} ($sp^{2.02}$) + 0.7794 N_{23} ($sp^{1.35}$) + 0.6370 C_{20} (p) + 0.7708 N_{23} (p), respectively. The percentage of C20 atom for H_2MICP ligand and its Zn(II) and Ni(II)-complexes is 40.02, 39.11 and 39.26. In the formation of σ, s% character of C20 for them is 33.32, 33.40 and 33.13 respectively. s% character of C20 atom for H_2MICP ligand does not change significantly in the formation of Zn(II) and Ni(II)-complexes. C20% of π NBO bond for H_2MICP ligand, and its Zn(II) and Ni(II)-complexes is 45.94, 40.49 and 40.58, while those of N23 are 54.06, 59.51 and 59.42, respectively. In the complex formation, bond is polarized (about 59.51% for Zn(II)-complex and about 59.42% for Ni(II)-complex) toward N23. S8-C18 bond having double bond character in the H_2MICP ligand calculated with B3LYP/6-311++G(2d,2p) method, however it shows single bond character in the Zn(II) and Ni(II)-complexes (NBO bond of S8-C18 is 0.6353 S_8 ($sp^{4.38}$) + 0.7723 C_{18} ($sp^{1.57}$) + 0.8278 S_5 (p) + 0.5611 C_{18} (p) for H_2MICP, 0.6994 S_8 ($sp^{4.80}$) + 0.7429 C_{18} ($sp^{2.04}$) for Zn(II)-complex, and 0.6638 S_8 ($sp^{4.96}$) + 0.7479 C_{18} ($sp^{2.02}$) for Ni(II)-complex)

Table 3 Calculated NBO analysis data for H_2MICP calculated with 6-311++G(2d,2p) and 6-311G(d,p) basis set.

	H_2MICP	
	Hybrids	
Atom numbers	**B3LYP/6-311++G(2d,2p)**	**B3LYP/6-311G(d,p)**
C3-C15	0.6991 $C_3 (sp^{1.85})$ + 0.7151 $C_{15} (sp^{1.83})$	0.7005 $C_3 (sp^{1.80})$ + 0.7137 $C_{15} (sp^{1.84})$
C15-C16	0.7183 $C_{15} (sp^{1.66})$ + 0.6957 $C_{16} (sp^{1.95})$	0.7163 $C_{15} (sp^{1.64})$ + 0.6978 $C_{16} (sp^{1.75})$
	0.7125 C_{15} (p) + 0.7017 C_{16} (p)	0.7195 C_{15} (p) + 0.6945 C_{16} (p)
C1-C3	0.7068 $C_1 (sp^{1.80})$ + 0.7074 $C_3 (sp^{1.73})$	0.7071 $C_1 (sp^{1.78})$ + 0.7071 $C_3 (sp^{1.72})$
	0.6978 C_1 (p) + 0.7163 C_3 (p)	0.6975 C_1 (p) + 0.7166 C_3 (p)
C9-C16	0.7080 $C_9 (sp^{1.79})$ + 0.7062 $C_{16} (sp^{1.80})$	0.7084 $C_9 (sp^{1.77})$ + 0.7058 $C_{16} (sp^{1.78})$
C1-C2	0.7048 $C_1 (sp^{1.84})$ + 0.7094 $C_2 (sp^{1.60})$	0.7068 $C_1 (sp^{1.78})$ + 0.7075 $C_2 (sp^{1.58})$
C2-C9	0.7109 $C_2 (sp^{1.58})$ + 0.7033 $C_9 (sp^{1.83})$	0.7109 $C_2 (sp^{1.56})$ + 0.7033 $C_9 (sp^{1.78})$
	0.6978 C_2 (p) + 0.6806 C_9 (p)	0.7338 C_2 (p) + 0.67.94 C_9 (p)
C2-Cl37	0.6766 $C_2 (sp^{3.42})$ + 0.7363 $Cl_{37} (sp^{4.68})$	0.6997 $C_2 (sp^{3.52})$ + 0.7426 $Cl_{37} (sp^{4.40})$
C6-C13	0.7054 $C_6 (sp^{1.86})$ + 0.7088 $C_{13} (sp^{1.60})$	0.7074 $C_6 (sp^{1.81})$ + 0.7068 $(C_{13}sp^{1.60})$
	0.7249 C_6 (p) + 0.6889 C_{13} (p)	0.7252 C_6 (p) + 0.6885 C_{13} (p)
C13-C19	0.7100 $C_9 (sp^{1.73})$ + 0.7042 $C_{19} (sp^{1.88})$	0.7066 $C_9 (sp^{1.75})$ + 0.7076 $C_{19} (sp^{1.84})$
C5-C6	0.7087 $C_5 (sp^{1.78})$ + 0.7055 $C_6 (sp^{1.77})$	0.7056 $C_5 (sp^{1.78})$ + 0.7056 $C_6 (sp^{1.76})$
C5-C11	0.6966 $C_5 (sp^{1.85})$ + 0.7175 $C_{11} (sp^{1.53})$	0.6986 $C_5 (sp^{1.79})$ + 0.7156 $C_{11} (sp^{1.55})$
	0.7087 C_5 (p) + 0.7055 C_{11} (p)	0.7090 C_5 (p) + 0.7052 C_{11} (p)
C17-C19	0.7196 $C_{17} (sp^{1.62})$ + 0.6943 $C_{19} (sp^{1.80})$	0.7163 $C_{17} (sp^{1.64})$ + 0.6978 $C_{19} (sp^{1.75})$
	0.7187 C_{17} (p) + 0.6953 C_{19} (p)	0.7195 C_{17} (p) + 0.6945 C_{19} (p)
C11-C17	0.7060 $C_{11} (sp^{1.97})$ + 0.7082 $C_{17} (sp^{2.27})$	0.7054 $C_{11} (sp^{1.95})$ + 0.7088 $C_{17} (sp^{2.24})$
N7-C11	0.7849 $N_7 (sp^{1.80})$ + 0.6196 $C_{11} (sp^{2.77})$	0.7850 $N_7 (sp^{1.77})$ + 0.6195 $C_{11} (sp^{2.75})$
N7-C14	0.7910 $N_7 (sp^{1.88})$ + 0.6118 $C_{14} (sp^{2.33})$	0.7919 $N_7 (sp^{1.86})$ + 0.6107 $C_{14} (sp^{2.322})$
C14-C20	0.6984 $C_{14} (sp^{1.86})$ + 0.7157 $C_{20} (sp^{2.16})$	0.6975 $C_{14} (sp^{1.85})$ + 0.7166 $C_{20} (sp^{2.17})$
C17-C20	0.7106 $C_{17} (sp^{2.21})$ + 0.7036 $C_{20} (sp^{1.84})$	0.7088 $C_{17} (sp^{2.20})$ + 0.7054 $C_{20} (sp^{1.86})$
O10-C14	0.8010 $O_{10} (sp^{1.51})$ + 0.5987 $C_{14} (sp^{1.94})$	0.8045 $O_{10} (sp^{1.44})$ + 0.5939 $C_{14} (sp^{1.96})$
	0.8415 O_{10} (p) + 0.5402 C_{14} (p)	0.8376 O_{10} (p) + 0.5463 C_{14} (p)
O12-C13	0.8010 $O_{10} (sp^{1.99})$ + 0.5987 $C_{14} (sp^{3.03})$	0.8213 $O_{12} (sp^{1.97})$ + 0.5705 $C_{14} (sp^{3.00})$
C4-O12	0.5605 $C_4 (sp^{3.54})$ + 0.8281 $O_{12} (sp^{2.47})$	0.5846 $C_4 (sp^{3.42})$ + 0.8254 $O_{12} (sp^{2.56})$
C20-N23	0.6328 $C_{20} (sp^{2.07})$ + 0.7743 $N_{23} (sp^{1.32})$	0.6326 $C_{20} (sp^{2.00})$ + 0.7745 $N_{23} (sp^{1.30})$
	0.6791 C_{20} (p) + 0.7341 N_{23} (p)	0.6778 C_{20} (p) + 0.7353 N_{23} (p)
N22-N23	0.7233 $N_{22} (sp^{2.27})$ + 0.6906 $N_{23} (sp^{2.93})$	0.7202 $N_{22} (sp^{2.25})$ + 0.6938 $N_{23} (sp^{2.80})$
C18-N22	0.6138 $C_{18} (sp^{2.45})$ + 0.7723 $N_{22} (sp^{1.65})$	0.6153 $C_{18} (sp^{2.41})$ + 0.7883 $N_{22} (sp^{1.62})$
S8-C18	0.6353 $S_8 (sp^{4.38})$ + 0.7723 $C_{18} (sp^{1.57})$	0.6349 $S_8 (sp^{4.02})$ + 0.7651 $C_{18} (sp^{1.63})$
	0.8278 S_5 (p) + 0.5611 C_{18} (p)	0.8291 S_5 (p) + 0.5591 C_{18} (p)
C18-N21	0.6144 $C_{18} (sp^{2.10})$ + 0.7723 $N_{21} (sp^{1.69})$	0.6146 $C_{18} (sp^{2.05})$ + 0.7888 $N_{21} (sp^{1.67})$
C15-N21	0.6126 $C_{15} (sp^{2.70})$ + 0.7904 $N_{21} (sp^{1.66})$	0.6133 $C_{15} (sp^{2.68})$ + 0.7899 $N_{21} (sp^{1.64})$
O12	1.96357 $O_{12} (sp^{1.63})$	Unpaired electrons
	1.84823 O_{12} (p)	1.96232 $O_{12} (sp^{1.61})$
S8	1.98378 $S_8 (sp^{0.22})$	1.84485 O_{12} (p)
	1.86980 $S_8 (sp^{99.99})$	1.98517 $S_8 (sp^{0.24})$
O10	1.97581 $O_{10} (sp^{0.66})$	1.87217 $S_8 (sp^{99.99})$
	1.85808 $O_{10} (sp^{99.99})$	1.97502 $O_{10} (sp^{0.70})$
N7	1.66393 N_7 (p)	1.85401 $O_{10} (sp^{99.99})$
N23	1.92026 $N_{23} (sp^{2.15})$	1.66484 N_7 (p)
N22	1.58580 N_{22} (p)	1.92038 $N_{23} (sp^{2.29})$
N21	1.63011 N_{21} (p)	1.58989 N_{22} (p)
Cl37	1.99201 $Cl_{37} (sp^{0.21})$	1.62631 N_{21} (p)
	1.97125 Cl_{37} (p)	1.99224 $Cl_{37} (sp^{0.22})$
	1.93017 Cl_{37} (p)	1.97100 Cl_{37} (p)
		1.93049 Cl_{37} (p)

Table 4 Calculated NBO analysis data for Zn(II) and Ni(II)-complexes calculated with 6-311G(d,p) basis sets.

Atom numbers	**[Zn(HMICP)$_2$]**	**[Ni(HMICP)$_2$]**
C3-C15	0.7007 C_3 ($sp^{1.80}$) + 0.7134 C_{15} ($sp^{1.84}$)	0.7004 C_{15} ($sp^{1.80}$) + 0.7137 C_{16} ($sp^{1.82}$)
C15-C16	0.7177 C_{15} ($sp^{1.65}$) + 0.6963 C_{16} ($sp^{1.94}$)	0.7153 C_3 ($sp^{1.69}$) + 0.6988 C_{15} ($sp^{1.88}$)
	0.7183 C_{15} (p) + 0.6957 C_{16} (p)	0.7070 C_{15} (p) + 0.7072 C_{16} (p)
C1-C3	0.7072 C_1 ($sp^{1.78}$) + 0.7070 C_3 ($sp^{1.72}$)	0.7074 C_1 ($sp^{1.78}$) + 0.7068 C_3 ($sp^{1.73}$)
	0.6981 C_1 (p) + 0.7160 C_3 (p)	0.6967 C_1 (p) + 0.7174 C_3 (p)
C9-C16	0.7095 C_9 ($sp^{1.77}$) + 0.7047 C_{16} ($sp^{1.82}$)	0.7083 C_9 ($sp^{1.77}$) + 0.7059 C_{16} ($sp^{1.77}$)
C1-C2	0.7069 C_1 ($sp^{1.78}$) + 0.7073 C_2 ($sp^{1.58}$)	0.7066 C_1($sp^{1.78}$) + 0.7076 C_2 ($sp^{1.58}$)
C2-C9	0.7095 C_2 ($sp^{1.55}$) + 0.7047 C_9 ($sp^{1.79}$)	0.7086 C_2 ($sp^{1.56}$) + 0.7056 C_9 ($sp^{1.78}$)
	0.7347 C_2 (p) + 0.67.84 C_9 (p)	0.7354 C_2 (p) + 0.6777 C_9 (p)
C2-Cl37	0.6881 C_2 ($sp^{3.55}$) + 0.7441 Cl_{37} ($sp^{4.38}$)	0.6990 C_2 ($sp^{3.53}$) + 0.7432 Cl_{37} ($sp^{4.40}$)
C6-C13	0.7072 C_6 ($sp^{1.81}$) + 0.7070 C_{13} ($sp^{1.61}$)	0.7078 C_6 ($sp^{1.80}$) + 0.7065 C_{13} ($sp^{1.61}$)
	0.7220 C_6 (p) + 0.6919 C_{13} (p)	0.7210 C_6 (p) + 0.6930 C_{13} (p)
C13-C19	0.7055 C_9 ($sp^{1.75}$) + 0.7087 C_{19} ($sp^{1.86}$)	0.7078 C_9 ($sp^{1.74}$) + 0.7064 C_{19} ($sp^{1.87}$)
C5-C6	0.7084 C_5 ($sp^{1.78}$) + 0.7058 C_6 ($sp^{1.76}$)	0.7083 C_5 ($sp^{1.79}$) + 0.7059 C_6 ($sp^{1.76}$)
C5-C11	0.6893 C_5 ($sp^{1.79}$) + 0.7158 C_{11} ($sp^{1.55}$)	0.6988 C_5 ($sp^{1.78}$) + 0.7153 C_{11} ($sp^{1.56}$)
	0.7147 C_5 (p) + 0.6994 C_{11} (p)	0.7165 C_5 (p) + 0.6976 C_{11} (p)
C17-C19	0.7162 C_{17} ($sp^{1.65}$) + 0.6979 C_{19} ($sp^{1.78}$)	0.7175 C_{17} ($sp^{1.63}$) + 0.6965 C_{19} ($sp^{1.80}$)
	0.7242 C_{17} (p) + 0.6896 C_{19} (p)	0.7310 C_{17} (p) + 0.6824 C_{19} (p)
C11-C17	0.7042 C_{11} ($sp^{1.97}$) + 0.71.00 C_{17} ($sp^{2.26}$)	0.7050 C_{11} ($sp^{1.96}$) + 0.7092 C_{17} ($sp^{2.27}$)
N7-C11	0.7833 N_7 ($sp^{1.74}$) + 0.6216 C_{11} ($sp^{2.71}$)	0.7837 N_7 ($sp^{1.76}$) + 0.6212 C_{11} ($sp^{2.71}$)
N7-C14	0.7940 N_7 ($sp^{1.88}$) + 0.6079 C_{14} ($sp^{2.29}$)	0.7933 N_7 ($sp^{1.88}$) + 0.6088 C_{14} ($sp^{2.27}$)
C14-C20	0.6946 C_{14} ($sp^{1.85}$) + 0.7194 C_{20} ($sp^{2.18}$)	0.6928 C_{14} ($sp^{1.85}$) + 0.7211 C_{20} ($sp^{2.41}$)
C17-C20	0.7103 C_{17} ($sp^{2.17}$) + 0.7039 C_{20} ($sp^{1.85}$)	0.7099 C_{17} ($sp^{2.18}$) + 0.7043 C_{20} ($sp^{1.68}$)
O10-C14	0.8056 O_{10} ($sp^{1.38}$) + 0.5925 C_{14} ($sp^{1.91}$)	0.8046 O_{10} ($sp^{1.41}$) + 0.5939 C_{14} ($sp^{1.93}$)
	0.8298 O_{10} (p) + 0.5581 C_{14} (p)	0.8319 O_{10} (p) + 0.5549 C_{14} (p)
O12-C13	0.8207 O_{12} ($sp^{1.98}$) + 0.5713 C_{14} ($sp^{2.98}$)	0.8214 O_{12} ($sp^{1.98}$) + 0.5703 C_{14} ($sp^{3.01}$)
C4-O12	0.5643 C_4 ($sp^{3.42}$) + 0.8255 O_{12} ($sp^{2.55}$)	0.5655 C_4 ($sp^{3.40}$) + 0.8247 O_{12} ($sp^{2.56}$)
C20-N23	0.6254 C_{20} ($sp^{1.99}$) + 0.7803 N_{23} ($sp^{1.34}$)	0.6370 C_{20} ($sp^{2.02}$) + 0.7794 N_{23} ($sp^{1.35}$)
	0.6363 C_{20} (p) + 0.7714 N_{23} (p)	0.6370 C_{20} (p) + 0.7708 N_{23} (p)
N22-N23	0.884 N_{22} ($sp^{2.85}$) + 0.7253 N_{23} ($sp^{2.60}$)	0.6870 N_{22} ($sp^{3.02}$) + 0.7266 N_{23} ($sp^{2.77}$)
C18-N22	0.6369 C_{18} ($sp^{1.81}$) + 0.7709 N_{22} ($sp^{1.60}$)	0.6368 C_{18} ($sp^{1.85}$) + 0.7711 N_{22} ($sp^{1.60}$)
	0.5880 C_{18} (p) + 0.8089 N_{22} (p)	
S8-C18	0.6994 S_8 ($sp^{4.80}$) + 0.7429 C_{18} ($sp^{2.04}$)	0.6638 S_8 ($sp^{4.96}$) + 0.7479 C_{18} ($sp^{2.02}$)
C18-N21	0.6125 C_{18} ($sp^{2.17}$) + 0.7904 N_{21} ($sp^{1.61}$)	0.6132 C_{18} ($sp^{2.16}$) + 0.7899 N_{21} ($sp^{1.62}$)
C15-N21	0.6125 C_{15} ($sp^{2.71}$) + 0.7904 N_{21} ($sp^{1.63}$)	0.6154 C_{15} ($sp^{2.67}$) + 0.7883 N_{21} ($sp^{1.65}$)
O12	1.96168 O_{12} ($sp^{1.61}$)	1.96204 O_{12} ($sp^{1.60}$)
	1.84425 O_{12} (p)	1.84653 O_{12} (p)
S8	1.97855 S_8 ($sp^{0.35}$)	1.97355 S_8 ($sp^{0.33}$)
	1.77965 S_8 ($sp^{32.32}$)	1.75694 S_8 ($sp^{94.52}$)
	1.75906 S_8 ($sp^{15.72}$)	
O10	1.97489 O_{10} ($sp^{0.72}$)	1.97486 O_{10} ($sp^{0.71}$)
	1.84876 O_{10} (P)	1.84603 O_{10} ($sp^{99.85}$)
N7	1.67306 N_7 (p)	1.67574 N_7 ($sp^{99.99}$)
N23	1.86726 N_{23} ($sp^{2.38}$)	1.74252 N_{23} ($sp^{2.22}$)
N22	1.89774 N_{22} ($sp^{1.70}$)	1.90168 N_{22} ($sp^{1.71}$)
N21	1.62448 N_{21} (p)	1.65347 N_{21} ($sp^{99.99}$)
Cl37	1.99230 Cl_{37} ($sp^{0.23}$)	1.99228 Cl_{37} ($sp^{0.23}$)
	1.97162 Cl_{37} (p)	1.97125 Cl_{37} (p)
	1.93191 Cl_{37} (p)	1.93215 Cl_{37} (p)

4.1 UV Studies

H_2MICP ligand was optimized at the basis set levels of B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p). Excitation energies were obtained with time-dependent B3LYP (TDB3LYP TDHF) with the basis set of 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p) and 6-311++G(2d,2p). Excitation energies of it is Zn(II) and Ni(II)-complexes optimized with B3LYP/6-311G(d,p) were obtained at the level of TDB3LYP/6-311G(d,p). The experimental and theoretical UV data of H_2MICP ligand and its Zn(II) and Ni(II)-complexes are summarized in Table 5, while the excitation energies (eV) and oscillator strengths (f) are summarized in Table 6. Using calculation with the 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p) basis set, the peak which observed experimentally at 370 nm were obtained at 366, 367, 373 and 378 nm, respectively. This absorption is due to 1(HOMO) -1′(LUMO) and 4-1′ electronic transition. HOMO(1) is composed of + 9.6% (S_8) 3pz - 9.2% (C_{11}) 2pz + 6.7% (C_6) 2pz - 6.4% (O_{12}) 2pz + 6.3% (C_{13}) 2pz + 5.4% (S_8) 4pz, while LUMO(1) is composed of + 16.6% (N_{23}) 2pz + 8.4% (N_{23}) 3pz - 7.4% (C_{20}) 2pz - 6.0% (C_{20}) 3pz + 5.4% (O_{10}) 2pz - 5.1% (C_{14}) 2pz, and HOMO-3(4) of + 10.7% (N_{22}) 2pz - 9.7% (S_8) 3pz + 9.3% (C_{19}) 2pz - 6.9% (C_{20}) 2pz + 6.4% (C_{19}) 3pz + 5.4% (N_{22}) 3pz atomic orbitals.

Table 5 The experimental and theoretical UV data of H_2MICP ligand and its Zn(II)-complex.

	UV-visible spectrum data (nm)						
	H_2MICP						
Experimental	-	-	258	-	270	370	-
B3LYP/6-31G(d,p)	247	-	262 260	-	264	366	-
B3LYP/6-311G(d,p)	247 241	-	263	264	267	367	-
B3LYP/6-311++G(d,p)	245	-	265	267 267	270	373	-
B3LYP/6-311++G(2d,2p)	248	-	238	269 267	272	378	-
B3LYP/6-31G(d,p) (DMSO)	256	-	-	-	263 261	370	397
B3LYP/6-311G(d,p) (DMSO)	248	-	-	-	269	376 327	-
CEP	250	-	-	-	256	350	-
	$[Zn(HMICP)_2]$						
Experimental	261	-	-	-	-	-	425
B3LYP/6-31G(d,p)	248 245 243	274 265 251	-	-	-	428 409 405	475 470 455
B3LYP/6-311G(d,p)	248 246	275 256 252 251	-	-	-	434 409 408	476 473 450

Table 6 The excitation energies (eV) and oscillator strengths (f).

	H_2MICP					
B3LYP/6-31G(d,p)	3.39(0.74)E4	4.70(0.12)E9	4.72(0.28)E10	4.77(0.15)E11	5.02(0.11)E16	-
B3LYP/6-311G(d,p)	3.38(0.75)E4	4.64(0.16)E9	4.70(0.25)E10	4.71(0.12)E11	5.01(0.09)E17	5.14(0.12)E18
B3LYP/6-311++ G(d,p)	3.32(0.73)E4	4.59(0.21)E9	4.63(0.11)E10	4.64(0.13)E11 4.68(0.11)E13	5.05(0.11)E19	-
B3LYP/6-311++G(2d,2p)	3.27(0.75)E4	4.54(0.22)E9	4.60(0.17)E11	4.64(0.10)E13	5.00(0.10)E19	
B3LYP/6-31G(d,p) (DMSO)	3.12(0.29)E3 3.34(0.69)E4	4.70(0.13)E10 4.75(0.38)E11	4.85(0.24)E12	-	-	-
B3LYP/6-31G(d,p) (DMSO)	3.29(0.64)E3 3.79(0.19)E5	4.60(0.30)E8	4.99(0.12)E15	-	-	-
CEP	3.54(0.74)E4	4.84(0.25)E9	4.94(0.17)E31	-	-	-
	[Zn(HMICP)$_2$]					
B3LYP/6-31G(d,p)	2.61(0.14)E6 2.66(0.18)E7	2.90(0.18)E11 3.06(0.16)E14	4.52(0.12)E32	4.67(0.17)E36	4.93(0.23)E50 4.99(0.14)E53 5.06(0.43)E55	5.10(0.11)E57
B3LYP/6-311G(d,p)	2.60(0.23)E5 2.61(0.12)E7 2.75(0.14)E10	2.86(0.12)E11 3.06(0.25)E13 3.04(0.18)E14	4.50(0.15)E32	4.84(010)E45 4.90(0.17)E50 4.93(0.21)E53	5.00(0.33)E55 5.04(0.17)E56	-

4.2 NMR Studies

B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p) proton chemical shift calculations at both gas phase and DMSO solution were performed for H_2MICP, while B3LYP/6-31G(d,p), and B3LYP/6-311G(d,p) proton chemical shift calculations at gas phase were conducted for [Zn(HMICP)$_2$] (Table 7). The peak due to N22-H36 in the ^{1}H-NMR spectrum of H_2MICP disappears in the spectrum of [Zn(HMICP)$_2$], both in experimental measurement and theoretical calculation. The correlation between theoretical and experimental data was calculated as minimum 97% without chemical shifts of H31 and H35 which are N-H protons. The calculated chemical shifts have increased with basis set, and minimum values were observed with 6-31G(d,p), while maximum values were observed with 6-311++G(2d,2p) methods. The chemical shift values have increased in DMSO phase.

Table 7 Experimental and theoretical proton chemical shifts for H_2MICP, and [Zn(HMICP)$_2$].

Atoms		**Gas phase**				**DMSO**		
	Exp.[a]	**6-31G (d,p)**	**6-311G (d,p)**	**6-311++ G(d,p)**	**6-311++ G(2d,2p)**	**6-31G (d,p)**	**6-311G (d,p)**	**6-311++ G(2d,2p)**
				H_2MICP*				
H34	7.35	7.20	7.39	7.51	7.59	7.38	7.58	7.59
H30	6.80	6.56	6.56	6.77	6.87	7.00	6.98	7.19
H29	6.90	6.58	6.70	6.66	6.81	7.18	7.32	7.14
H25	7.51	6.64	6.82	6.98	7.15	7.22	7.70	7.50
H33	7.51	9.79	9.90	9.95	10.31	9.62	7.74	8.76
H24	7.45	7.19	7.34	7.50	7.60	7.67	7.88	7.75
H32	7.45	7.28	7.44	7.52	7.61	7.64	7.86	7.79
H35	12.82	9.38	9.41	9.70	10.00	9.53	9.02	9.96
H36	11.05	12.66	12.44	12.63	13.18	12.98	12.90	13.24
H31	10.76	6.06	6.07	6.36	6.66	8.04	8.10	7.32
H26	3.75	3.58	3.59	3.66	3.74	3.70	3.66	3.84
H27	3.75	4.01	4.08	4.14	4.09	4.04	4.07	4.11
H28	3.75	3.58	3.59	3.66	3.74	3.69	3.67	3.84
Regr.	-	0.97	0.97	0.97	0.97	0.98	0.99	0.98
				[Zn(HMICP)$_2$]				
H34	6.85-7.66	7.14	6.88	-	-	-	-	-
H30	-	6.37	6.14	-	-	-	-	-
H29	-	6.38	6.27	-	-	-	-	-
H25	-	6.50	6.45	-	-	-	-	-
H33	-	10.20	10.03	-	-	-	-	-
H24	-	7.11	7.01	-	-	-	-	-
H32	-	7.50	7.42	-	-	-	-	-
H35	10,81	6.87	6.92	-	-	-	-	-
H31	10.65	6.03	5.86	-	-	-	-	-
H26	3.70	3.62	3.46	-	-	-	-	-
H27	3.62	3.28	3.04	-	-	-	-	-
H28	3.30	3.25	3.00	-	-	-	-	-

*without H31 and H35 for H_2MICP, a: in [14]

Table 8 Experimental and theoretical vibrational assignments of H_2MICP carried out with B3LYP method and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets.

Exp.	6-31G(d,p)		6-311G(d,p)		6-311++G (d,p)		6-311++G (2d,2p)		Assignments
	Freq.	Int.[1]	Freq.	Int.	Freq.	Int.	Freq.	Int.	
3284	3663	75	3644	75	3642	78	3648	77	$\nu(N_7H)_{indole}$
3254	3513	100	3500	108	3504	104	3517	98	$\nu(N_{21}H)_{thio}$
3230	3426	104	3422	98	3421	96	3431	100	$\nu(N_{22}H)_{thio}$
-	3252	16	3236	14	3232	16	3238	18	$\nu(C_{15}\text{-}H)_{ringC,}$ $\nu(C_9H)_{ringC}$
-	3200	12	3182	12	3181	10	3187	10	$\nu(C_6\text{-}H)_{ringA,}$ $\nu(C_5H)_{ringA}$
-	3178	10	3162	9	3161	9	3168	8	$\nu(C_1\text{-}H)_{ringC,}$ $\nu(C_3H)_{ringC}$
-	3153	22	3136	21	3137	19	3142	17	$\nu(CH_3)_{met}$
-	3078	41	3058	42	3062	37	3071	33	$\nu(CH_3)_{met}$
-	3016	69	3000	68	3004	69	3015	64	$\nu(CH_3)_{met}$
1697	1789	252	1773	284	1758	325	1747	307	ν(C-O), $\delta(N_{22}H)$
1621	1690	8	1678	10	1674	9	1671	8	$\nu(CC)_{ringA\ com.}$[2], $\delta(N_7H)$, $\delta(OCH_3)_{met,}$ $\nu(N_{20}C_{23})$
-	1654	9	1640	4	1636	4	-	-	$\nu(CC)_{ringC\ com.,}$ $\delta(N_{14}H)$, $\nu(N_{20}C_{23})$
1595	1649	98	1636	112	1633	99	1636	14	$\nu(CC)_{ringA\ com.}$, $\delta(N_8H)$, $\nu(OCH_3)_{met,}$ $\nu(N_{20}C_{23})$
1573	1644	133	1635	199	1633	174	1632	188	$\nu(CC)_{ringC\ com.}$, $\delta(N_{21}H)$
1541	1641	232	1626	196	1620	218	1630	65	$\nu(CC)_{com.,}$ $\delta(N_7H)$, $\nu(N_{20}C_{23})$, $\delta(N_{22}H)$
-	-	-	-	-	-	-	1610	213	$\nu(CC)_{ringA\ com.,}$ $\delta(N_7H)$, $\nu(N_{20}C_{23})$
1487	1590	771	1582	675	1578	680	1577	634	$\nu(CC)_{ringC\ com.,}$ $\delta(N_{21}H)$, $\nu(N_{21}C_{18})$
1481	1536	154	1527	186	1524	172	1529	178	$\nu(CC)_{ringC\ com.,}$ $\delta(N_{21}H)_{,}$ $\delta(N_{22}H)$
1430	1532	97	1521	218	1518	213	1517	38	$\nu(CC)_{ringC\ com.,}$ $\delta(N_{21}H)_{,}$ $\delta(N_{22}H)$
1397	1527	240	1518	166	1514	157	1516	221	$\nu(CC)_{ringA,}$ $\delta(N_{22}H)$, s-cis-methoxy, $\nu(C_{18}S_8)$
1383	1516	270	1504	215	1502	246	1508	304	$\nu(CC)_{ringA\ ,}\delta(N_{22}H)$, s-cis-methoxy
-	1505	6	1493	8	1493	10	1500	9	s-cis-methoxy
1308	1500	31	1489	30	1487	31	1488	30	ν-isatin, $\delta(N_{22}H)$, s-cis $(CH_3)_{met}$
1293	1485	91	1475	77	1472	63	1476	67	$\nu(CC)_{ringA\ com.}$, s-cis-methoxy
-	1446	13	1437	7	1433	6	1436	7	$\nu(CC)_{ringC\ com.,}$ $\delta(N_{21}H)_{,}$ $\delta(N_{22}H)$
1273	1436	32	1427	34	1424	32	1420	35	$\nu(CC)_{ringC\ com.,}$ $\delta(N_7H)$
1240	1405	323	1394	383	1391	385	1388	414	$\delta(N_{21}C_{18})$, $\nu(N_{22}C_{18}N_{21})$
-	-	-	1339	7	1338	8	1341	10	$\nu(CC)_{ringC\ com.}$
1195	1339	176	1327	164	1325	148	1327	151	$\nu(CC)_{ringC\ com.,}$ $\delta(N_7H)_{,}$ s-cis-OCH_3
-	1330	3	1324	5	1322	8	1320	28	$\nu(CC)_{ringC\ com.}$
1155	1324	83	1311	61	1309	57	1310	35	Δ-isatin
1112	1306	77	1293	73	1290	78	1289	65	ν-isatin$_{,}$ $\delta(N_{22}H)$, s-cis-OCH_3

[1] Intensity, [2] combination

4.3 IR Studies

Experimental and theoretical vibrational assignments of H_2MICP were carried out with the aid of B3LYP method and 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets as shown in Table 8. For studied basis sets, correlation coefficients were found as 0.971, and 0.969. Absorption bands at 3650, 3294 and 3192 cm^{-1} were identified. B3LYP results showed that the vibrational modes of $\nu(N_7H)_{indole,}$ $\nu(N_{22}H)_{thio,}$ and $\nu(N_{21}H)_{thio}$, are as follow: 3663, 3513, and 3426 cm^{-1} for 6-31G(d,p); 3644, 3500, and 3422 cm^{-1} for 6-311G(d,p); 3642, 3504, and 3421 cm^{-1} for 6-311++G(d,p); 3648, 3517, and 3431 cm^{-1} for 6-311++G(2d,2p). The band at 3294 cm^{-1} belonging to $\nu(N_{22}H)$ disappears in its zinc(II) and nickel(II)-complexes. The other two bands nearly remained unchanged in both zinc(II) and nickel(II)-complexes. According to theoretical result, the absorption between 3252 and 2936 cm^{-1} can be assigned to the vibrational modes of $\nu(C\text{-}H)_{ringC}$, $\nu(C\text{-}H)_{ringA}$, $\nu(CH_3)_{met}$. In the infrared spectrum of C=O for H_2MICP, we observe the band at 1697 cm^{-1}. By means of the DFT procedure with B3LYP/6-31G(d,p) (1789 cm^{-1}), B3LYP/6-311G(d,p) (1773 cm^{-1}), B3LYP/6-311++G(d,p) (1758 cm^{-1}), and B3LYP/6-31G(2d,2p) (1747 cm^{-1}) basis sets, we can assign the band experimentally observed at 1697 cm^{-1} (IR) is the ν(C= O) vibrational mode. The band observed at 1697 cm^{-1} for H_2MICP appeared at 1694 cm^{-1} for its zinc(II)-complex, indicating that the C=O group is not involved in coordination and at 1670 cm^{-1} for its nickel(II)-complexes indicating that C=O group is involved in coordination. The absorption at about 850 cm^{-1} for H_2MICP is assignable to the vibrational modes involving the C=S group. This absorption is assigned at about 820 cm^{-1} for its Zn(II)-complex and 818 cm^{-1} for its Ni(II)-complex due to transfer of charge from sulfur atom to the metal.

5 Conclusions

New Zn(II) and Ni(II)-complexes of H_2MICP heve been synthesized, and its theoretical study has also been conducted. For the HOMO, it was found that the main contributions due to the thiosemicarbazone group and isatin group. Vibrational study using B3LYP calculations showed that the disappearance of the ν(N22H) band of H_2MICP ligand indicates the deprotonation of the group in coordination. Anaysis of experimental and theoretical UV, IR and NMR data of H_2MICP ligand and its Zn(II) and Ni(II)-complexes showed that theoretical calculations are in line to supporting the experimental results.

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