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FT-IR, NMR SPECTROSCOPIC and QUANTUM MECHANICAL INVESTIGATIONS OF TWO FERROCENE DERIVATIVES

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ABSTRACT. New ferrocene derivatives as N-(3-piperidin-1-ylpropyl)ferrocenamide (Fc-3ppa) and N-(pyridine-3-ylmethyl)ferrocenamide (Fc-3pica) and structural investigations were carried out with ^{1}H, ^{13}C, DEPT 45 or 135, HETCOR, COSY NMR and FT-IR spectroscopic techniques. Characterization of Fc-3ppa ($FeC_{19}H_{26}N_2O$) and Fc-3pica ($FeC_{17}H_{16}N_2O$) was also supported by density functional theory (DFT) used by B3LYP functional and 6-31G(d) or 6-311++G(d,p) basis sets. From the combination of all the results, it can be clearly seen that syntheses of Fc-3ppa and Fc-3pica have been successfully achieved. Theoretical values are successfully compared against experimental data and B3LYP method is able to provide satisfactory results for predicting NMR properties and vibrational frequencies of the synthesized ferrocene based systems.

KEY WORDS: Ferrocene derivatives, FT-IR, NMR, DFT, B3LYP

INTRODUCTION

Ferrocene derivatives have widespread applications in chemistry. Because of the redox potential of the ferrocene, different types of organic materials which contain ferrocene moiety were prepared and used in several applications [1-7]. On the other hand, some ligands and complexes including ferrocene moiety were prepared for the inorganic applications [8-11]. Ferrocenoyl amino acids and peptides were prepared using acyl ferrocenes and investigated in detail [12-15].

Fc-3ppa and Fc-3pica compounds are examples of 1,1'-bisferrocene amides. Ferrocene amides have been prepared by amide formation between amines and ferrocenecarboxylic acid derivatives. In these methods, ferrocene carboxylic acid was activated by transforming into; the acid chloride [16] succinimide [17], 1-hydroxybenzotriazole ester in the presence of dicylcohexylcarbodiimide (DCC) [17] or in situ activation of carboxylic acid by O-(1H-benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) or O-(1H-benzotriazol-1-yl)-N,N,N',N'-tetramethyluroniumtetrafluoroborate, (TBTU) [18]. Acid fluoride of ferrocene carboxylic acid was prepared for the derivatisation of ferrocenoyl group using cyanuric fluoride [19].

NMR is used extensively as a practical tool for identifying chemical structures. It has been used in chemistry, material science and geochemistry and it provides to get faster and easier structural information. The standard 1D and 2D hetero and homonuclear NMR experiments are enough to afford complete assignment of compounds and very useful to clarify molecular structures [20-22]. For the theoretical NMR investigations, the gauge including atomic orbitals/density functional theory (GIAO/DFT) approach is widely used for various types of compounds [23-31]. The DFT/B3LYP method exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of inorganic or ionic compounds [32, 33] as well as organic and neutral compounds [34-40].

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In this research two new ferrocene derivatives Fc-3ppa and Fc-3pica were synthesized and characterized by using 1D or 2D NMR experiments such as ^1H, ^{13}C, DEPT 45-135, HETCOR and COSY techniques. FT-IR spectra were also reported to identify some important vibrational bands of the compounds. Further, the optimized structural parameters, normal mode frequencies, potential energy distribution (PED) data, ^1H and ^{13}C NMR chemical shifts of Fc-3ppa and Fc-3pica were examined by B3LYP method with 6-31G(d) and 6-311++G(d,p) basis sets. The results of the theoretical and spectroscopic studies are reported here.

EXPERIMENTAL

Compounds were prepared according to following method [41]: 3-piperidino-propylamine (1 eq.) or 3-picolylamine (1 eq.) and 1-(ferrocenylcarbonyl)-1*H*-benzotriazole (1 eq.) were dissolved in freshly distilled chloroform in a round bottom flask. The flask was placed into the single cavity microwave equipment and reflux condenser was connected on flask. The reaction mixture was exposed to 90W MW for 30 min. After reaction was completed, the mixture was extracted with 2 M NaOH (3 x 50 mL). The collected organic layers were dried with magnesium sulfate and solvent was removed with vacuum. Reaction mixture was purified by column chromatography using EtOAc:hexane mixture as eluent to get Fc-3ppa and Fc-3pica in 97% and in 96% yields, respectively.

NMR experiments were performed on a Bruker AVANCE 500 spectrometer using 5 mm BBO probe. The operating frequencies were 500.13 MHz and 125.76 MHz for ^1H and ^{13}C, respectively. Fc-3ppa (6 mg mL^{-1}) and Fc-3pica (6 mg mL^{-1}) were dissolved in $CDCl_3$. Fc-3ppa was also dissolved in MeOD. Chemical shifts are reported in ppm relative to TMS for ^1H and ^{13}C. For ^{13}C NMR spectroscopy, the pulse sequence used a delay (D1) and acquisition time (AQ) of 2.0 s and 1.3 s (1.1 s), respectively, a spectral width of 25252.5 Hz (29761.9 Hz), 64K data points, 90^0 pulse 8.3 μs and 15000 scans. For ^1H NMR spectroscopy, the pulse sequence used a delay and acquisition time of 1.0 s and 5.5 s (5.9 s), respectively, a spectral width of 6009.6 Hz (5498.5 Hz), 64K data points, 90^0 pulse 14.15 μs and 256 (32) scans. The numbers given in parentheses belong to Fc-3pica compound.

DEPT spectra were obtained at $\theta_z = 45^0$ where CH, CH_2 and CH_3 appear in the positive phase and $\theta_z = 135^0$ where CH, CH_3 appear in the positive phase and CH_2 appears in the negative phase. Two-dimensional HETCOR and COSY techniques were measured using standard micro-programs provided by Bruker. FT-IR spectra were recorded in the region of 400-4000 cm^{-1} with Perkin-Elmer FT-IR 2000 using KBr pellet technique at a resolution of 4 cm^{-1}.

The compounds were analyzed for Fe with Perkin Elmer 4300 ICP-OES and for C, H and N with Fisons EA-1108 elemental analyser. Fe metal atom was investigated at 238.204 nm. The results are as following: (found % / calculated %) $FeC_{19}H_{26}N_2O$ (MW: 354.27): C(64.38/64.41), H(7.34/7.40), N(7.82/7.91), Fe(15.64/15.76). $FeC_{17}H_{16}N_2O$ (MW: 320.17): C(63.71/63.77), H(4.99/5.04), N(8.67/8.75), Fe(17.33/17.44).

CALCULATIONS

All the calculations were performed by Gaussian 03 program [42]. Structures in Figure 1 were first optimized in the gas phase by B3LYP functional using 6-31G(d) basis set. The optimized geometric structures related to minimum on the potential energy surface were provided by solving self-consistent field equation iteratively and optimizations were performed without any molecular restrictions.

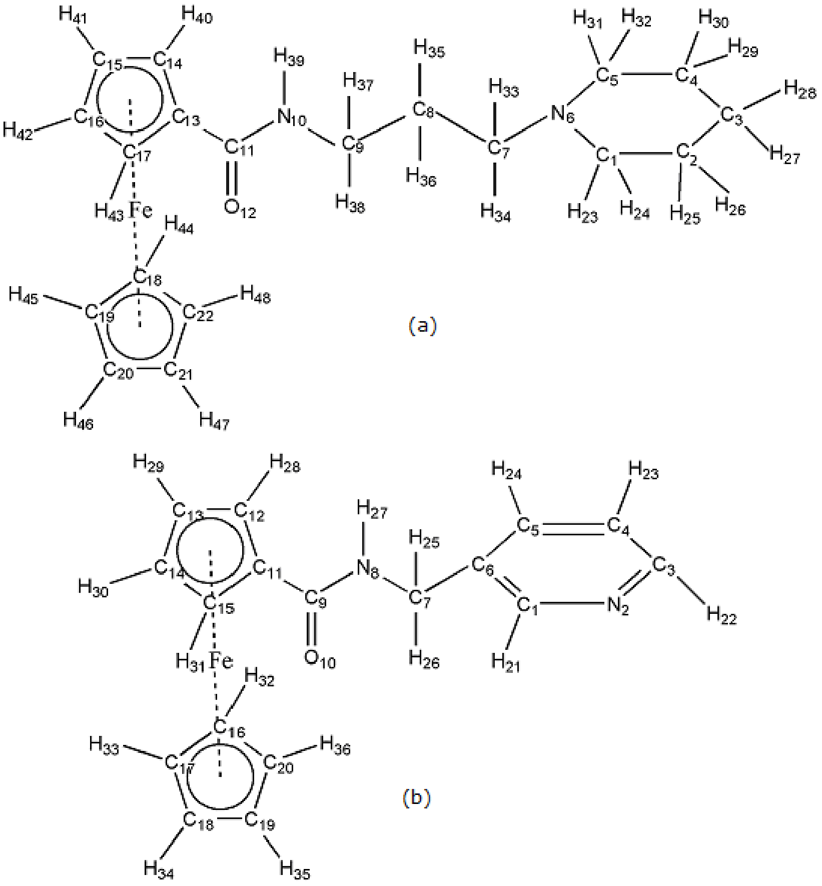

Figure 1. Suggested molecular structures for Fc-3ppa (a) and Fc-3pica (b).

After the optimization, in order to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies, harmonic vibrational frequencies of the present compounds were determined using analytic second derivatives with the B3LYP/6-31G(d) method and then scaled by 0.955 (above 1800 cm^{-1}) and 0.967 (under 1800 cm^{-1}) [40, 43]. Additionally, the absence of imaginary frequencies confirmed that the optimized structures are located on a certain minima. PED calculations were carried out by vibrational energy distribution analysis (VEDA 4) program [44].

For the NMR calculations, molecular structures of Fc-3ppa and Fc-3pica were first fully optimized at B3LYP/6-31G(d) level in chloroform ($\varepsilon = 4.9$) using the IEFPCM method [27-30]. After optimization, ^{1}H and ^{13}C NMR chemical shifts (δ_H and δ_C) were calculated using the GIAO method [23-30] in chloroform at the B3LYP/6-311++G(d,p)//6-31G(d) level of theory. Relative chemical shifts were then estimated by using the corresponding TMS shieldings calculated in advance at the same theoretical levels as the reference. Calculated ^{1}H and ^{13}C isotropic chemical shieldings for TMS at the B3LYP/6-311++G(d,p)//6-31G(d) in chloroform using the IEFPCM were 31.87 ppm and 183.76 ppm, respectively. Experimental ^{1}H and ^{13}C chemical shieldings for TMS are given as 30.84 ppm and 188.10 ppm, respectively [45].

RESULTS AND DISCUSSION

The optimized structures for the synthesized ferrocene based compounds are shown in Figure 1. The optimized geometric parameters of Fc-3ppa such as bond lengths and angles calculated by B3LYP/6-31G(d) are also listed in Table 1. The calculated bond lengths and angles for piperidine, propylamine and ferrocene molecules in Fc-3ppa compound are compared with their previously reported experimental data. The optimized geometric parameters of Fc-3ppa obtained by B3LYP/6-31G(d) method are in good agreement with previously reported data [46-50] as given in Table 1. A brief discussion of the experimental and theoretical NMR and vibrational properties of the title compounds is presented.

Table 1. Optimized geometric parameters of Fc-3ppa calculated by B3LYP/6-31G(d).

Parameters	[a]Experimental Piperidine	[b]Theoretical Piperidine	[c]Theoretical Propylamine	[d,e]Experimental Ferrocene	B3LYP 6-31G(d)
Bond Lengths (Å)					
Fe-Cp (subst.)					2.049[f]
Fe-Cp (uns.)				2.054	2.053[f]
C13-C14					1.433
C15-C16					1.428
C16-C17					1.425
C13-C11					1.490
C-C (Uns. Cp)				1.435	1.428[f]
C11-O12					1.230
C11-N10					1.370
C14-H40					1.081
C15-H41					1.082
C16-H42					1.082
C17-H43					1.083
C-H (uns. Cp)				1.073	1.082[f]
N6-C5	1.469	1.464			1.466
N6-C1					1.466
C5-C4	1.530	1.532			1.532
C1-C2					1.533
C4-C3	1.530	1.536			1.534
N6-C7					1.463
C7-C8			1.528		1.534
C8-C9			1.525		1.534
C9-N10			1.456		1.455
C7-H33					1.109
C7-H34			1.085		1.096
C8-H35			1.089		1.098
C8-H36					1.098
C9-H37			1.086		1.093
C9-H38			1.093		1.099
N10-H39			1.002		1.010
∠C-H (piperidine)	1.098	1.100			
C1-H23					1.111
C1-H24					1.094
C2-H25					1.098
C2-H26					1.097
C3-H27					1.100
C3-H28					1.097
C4-H29					1.098

C4-H30					1.097
C5-H31					1.111
C5-H32					1.097
Bond Angles (°)					
∠H-C-H (piperidine)	110.0	107.1			
H23-C1-H24					106.8
H25-C2-H26					107.3
H27-C3-H28					106.7
H29-C4-H30					107.3
H31-C5-H32					106.8
H33-C7-H34					106.2
H35-C8-H36					107.0
H37-C9-H38					107.4
C1-N6-C5	110.7	112.0			110.8
C1-C2-C3	109.6	110.6			110.9
C5-C4-C3					111.0
C4-C3-C2	111.1	110.7			110.0
N6-C1-C2	110.5	109.5			111.2
N6-C5-C4					111.2
C7-C8-C9			112.9		111.7
C8-C9-N10			110.7		112.5

[a-e]Taken from Ref. 34-38, respectively. [f]Average value of C-H and C-C bond lengths. [g]Subs.: substituted, Uns.: unsubstituted, Cp: Cyclopentadienyl.

NMR studies

As can be seen in Figure 1a, Fc-3ppa shows eleven different carbon atoms consistent with structure on the basis of molecular symmetry. Due to electronegative oxygen atom, C11 appears at the highest frequency field region. The most intense singlet appearing at 69.73 ppm arises from unsubstituted ferrocene ring interacting with Fe atom (Figure 2a). C13 atom has been overlapped by solvent peak in $CDCl_3$. Therefore, Figure 2b is obtained in MeOD and C13 has been identified. The peak appearing at 170.00 ppm in ^{13}C NMR spectrum cannot be observed in DEPT 45 and 135 spectra (Figure 2d). Henceforth, it can be concluded that it is C11. In DEPT 135 spectrum, CH_2 appears in the negative phase. In DEPT 45 spectrum, CH and CH_2 appear in positive phase. For that reason, ferrocene protons can easly be differentiated from other protons in Fc-3ppa. ^1H NMR spectrum is given in Figure 2f. Ferromagnetic Fe atoms effect the relaxation mechanism of the compounds. Therefore, we observe broadened proton peaks. The broad signals are observed in the spectrum may also indicate paramagnetic impurities. The peak which appears at 7.48 ppm belongs to the (–NH–) amide group, so it doesn't have any interaction in HETCOR spectrum (Figure 3a). The correlations between C1-H23,24, C5-H31,32, C2-H25,26, C4-H29,30, C3-H27,28, C7-H33,34, C8-H35,36, C9-H37,38, C14-H40, C15-H41, C16-H42, C17-H43 and CH (unsubstituted Cp ring) are also clearly observed in HETCOR spectrum. From COSY spectrum (Figure 3c), it is clear that there is a correlation between H35,36-H33,34, H35,36-H37,38 and H37,38-H39.

As can be seen in Figure 1b, Fc-3pica molecule contains eleven different carbon atoms consistent with the structure on the basis of molecular symmetry. Due to electronegative oxygen atom, C9 appears at the highest frequency field region. The most intense singlet appearing at 69.75 ppm arises from unsubstituted ferrocene ring interacting with Fe atom (Figure 2c). When integration values of ^1H NMR spectrum are investigated from Figure 2g, it can be seen that total integration values are in compliance with the total number of protons in Fc-3pica. Ferromagnetic atoms effect the relaxation mechanism of the compounds. Therefore, we observe broadened proton peaks. The peaks those appear at 170.63 ppm, 134.59 ppm and 75.57 ppm in

^{13}C NMR spectrum can not be observed in DEPT 135 spectrum (Figure 2e). Henceforth, it can be concluded that they belong to carbon atoms C9, C6 and C11, respectively. In DEPT 135 spectrum, CH_2 appears in the negative phase. Therefore, the peak which is located at 41.12 ppm can be assigned to C7 atom. It is clear from HETCOR spectrum (Figure 3b) that there is no H atom bonded to C9, C6 and C11 as expected. Thus, HETCOR spectrum is in agreement with the DEPT 135 spectrum. The peak which appears at 6.12 ppm belongs to the (–NH–) amide group, therefore, it doesn't have any interaction in the HETCOR spectrum. The correlations between C1-H21, C3-H22, C4-H23, C5-H24, C7-H25,26, C12-H28, C15-H31, C13-H29, C14-H30 and C-H (ferrocene ring) are also clearly observed in HETCOR spectrum. From the COSY NMR spectrum (Figure 3d), it is clear that there is a correlation between H23-H22,24, H27-H25,26 and between the substituted ferrocene ring's hydrogen atoms.

Experimental and calculated ^{13}C and ^{1}H NMR chemical shifts of Fc-3ppa and Fc-3pica are given in Table 2. The largest difference between experimental and computed chemical shifts for proton / carbon of Fc-3ppa and Fc-3pica is 0.58 ppm / 3.39 ppm and 0.72 ppm / 2.98 ppm, respectively. In order to compare experimental and calculated chemical shifts, the correlation graphics have been performed and the correlation values for proton and carbon chemical shifts of Fc-3ppa and Fc-3pica are found to be 0.99491 / 0.99959 and 0.98985 / 0.99975 for B3LYP/6-311++G(d,p)//6-31G(d) model, respectively.

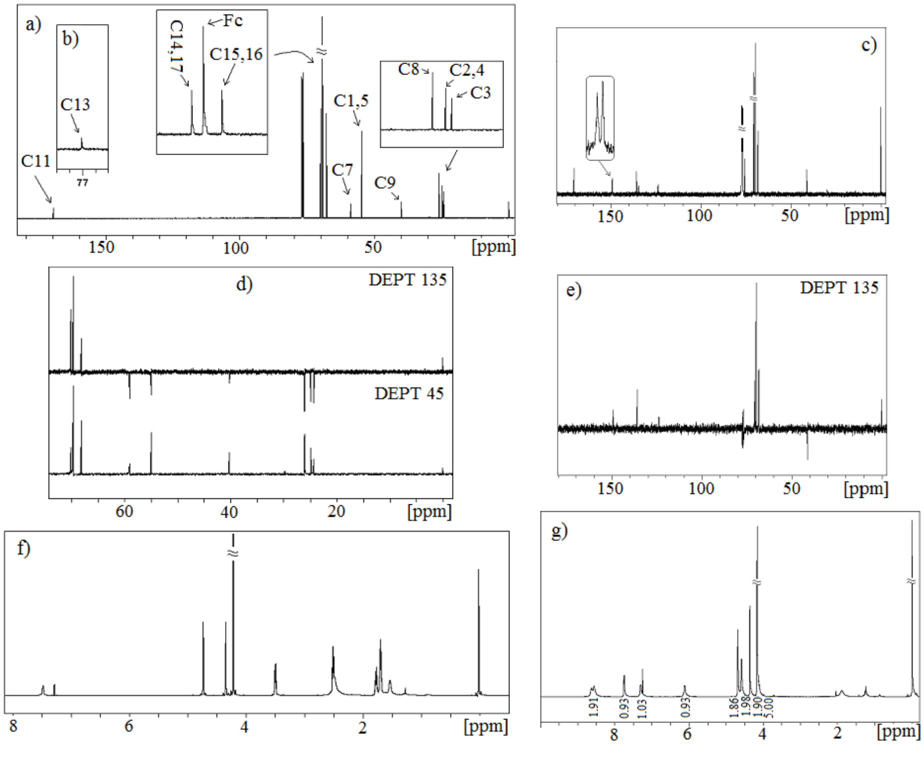

Figure 2. ^{13}C (a, b, c), DEPT (d, e), ^{1}H (f, g) NMR spectra of Fc-3ppa (a, b, d, f) and Fc-3pica (c, e, g).

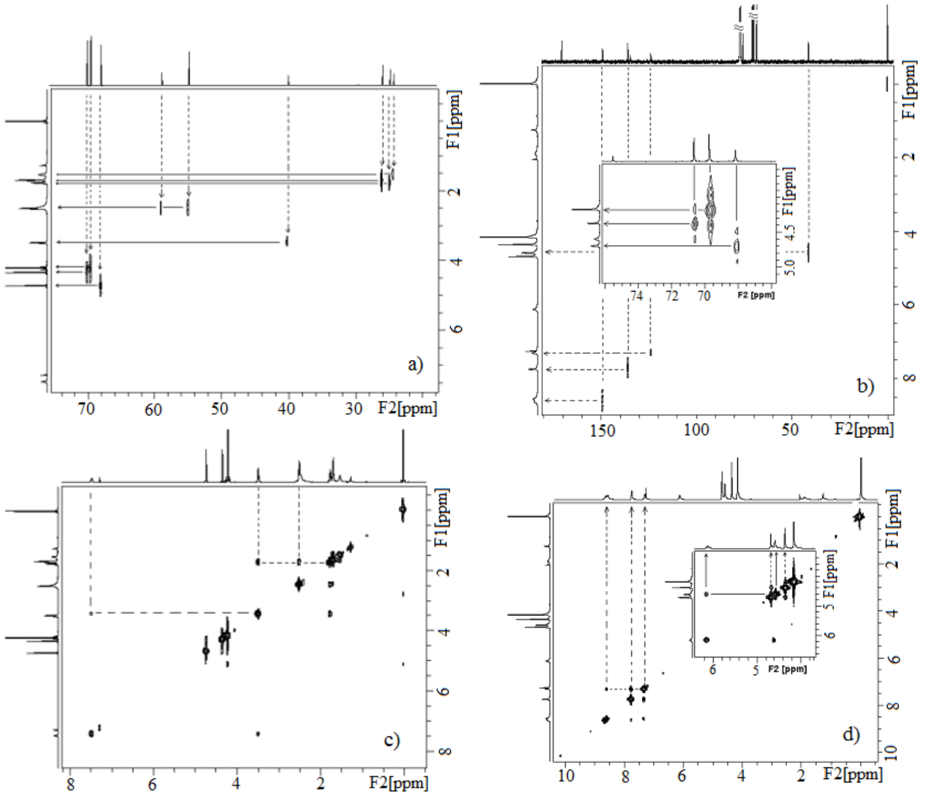

Figure 3. HETCOR (a, b) and COSY (c, d) NMR spectra of Fc-3ppa (a, c) and Fc-3pica (b, d).

FT-IR studies

Some important measured and calculated vibrational frequencies for the present compounds along with corresponding vibrational assignments and PED data are given in Table 3 and their experimental vibrational spectra are shown in Figure 4. Fc-3ppa and Fc-3pica compounds consist of 49 and 37 atoms, so they have 141 and 105 normal vibrational modes and they belong to the point group C_1 with only identity (E) symmetry element or operation. It is difficult to determine these complexes's vibrational assignments in the observed spectrum due to its low symmetry. Therefore, the assignments of vibrational modes of these compounds have been provided by VEDA 4 in Table 3.

It is clearly observed in Figure 4 that the NH stretching band which appears as a strong broad at 3347 cm^{-1} (3268 cm^{-1}) is attributed to amide group. The CH stretching bands at between 3104-3070 cm^{-1} (3160-3042 cm^{-1}) result from ferrocene group while CH_2 antisymmetric and symmetric stretching bands having various intensities at 2850 and 2926 cm^{-1} (2937 and 2969 cm^{-1}) arise from CH_2 located on the piperidine ring (pyridine ring) and propylamine chain (methylamine chain). The very strong amide CO stretching band appears at 1630 cm^{-1} (1639 cm^{-1}). The representations given in parentheses refer to Fc-3pica compound. Other important bands observed in the spectrum of Fc-3ppa are as following: 1534 cm^{-1} (vs, CNH combination [ν_{CN}+δ_{NH}], amide), 1469 cm^{-1} and 1450 cm^{-1} (w/s, CH_2 deformation), 1432 cm^{-1} (s, δ_{NH}, amide), 1372 cm^{-1} (m, ν_{CN}, amide), 1345 cm^{-1} (w, CH_2 twisting), 1289 cm^{-1} (s, CNH combination [ν_{CN}+δ_{NH}], amide) and 772 cm^{-1} (m, NH deformation). Other important bands observed in the spectrum of Fc-3pica are as following: 1588 cm^{-1} (s, ν_{CC}, pyridine), 1530 cm^{-1} (vs, CNH combination [ν_{CN}+δ_{NH}], amide), 1474 cm^{-1} (w, CH_2 deformation), 1425 cm^{-1} (m, δ_{NH}, amide), 1375 cm^{-1} (m, ν_{CN}, amide), 1343 cm^{-1} (w, CH deformation, pyridine), 1296 cm^{-1} (vs, CNH combination [ν_{CN}+δ_{NH}], amide) and 757 cm^{-1} (m, NH deformation).

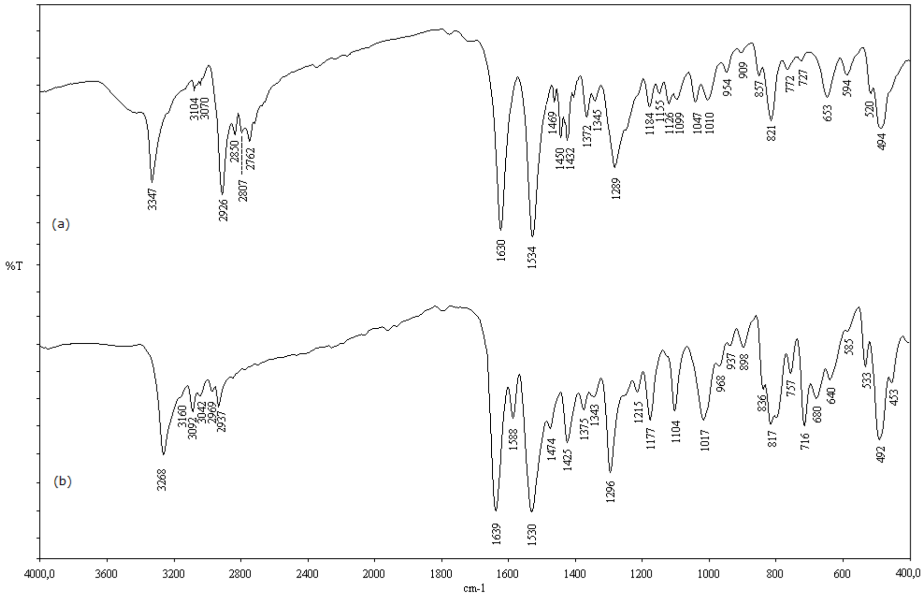

Figure 4.FT-IR spectra of Fc-3ppa (a) and Fc-3pica (b).

As it can be seen from Table 3, in general, there is a good agreement between the experimental and theoretical vibrational frequencies. The largest difference between the given experimental and calculated frequencies is 14 cm^{-1} for Fc-3ppa and 15 cm^{-1} for Fc-3pica. The differences between the calculated and experimental values for the some vibrational modes are often attributed to the neglected anharmonicity and incomplete inclusion of electronic correlation effects. In order to compare the given frequencies, we have found the correlation graphics based on the calculations and experimental IR data. The correlation values between the given experimental and calculated frequencies are found to be 0.99996 for Fc-3ppa and 0.99995 for Fc-3pica as seen in Figure 5.

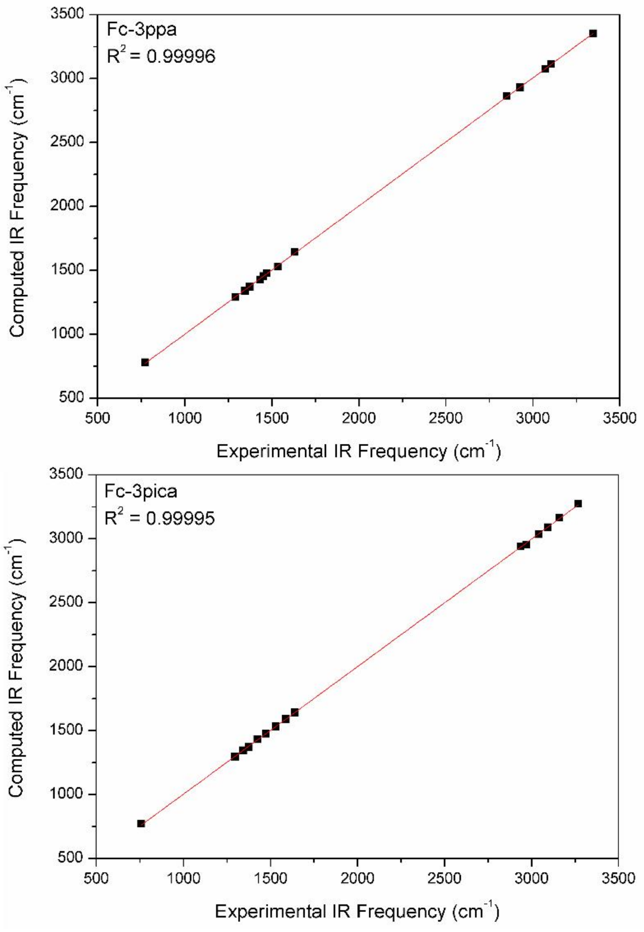

Figure 5. Plot of the calculated vs the experimental vibrational wavenumbers of Fc-3ppa and Fc-3pica.

CONCLUSIONS

We have carried out a comprehensive spectroscopic investigation for Fc-3ppa and Fc-3pica by means of NMR, FT-IR, ICP-OES and elemental analyses. According to the spectroscopic results, it can be concluded that synthesis of these compounds have been accomplished successfully. The theoretical researches of the present compounds are also performed using quantum mechanical calculations. The calculated chemical shifts and vibrational frequencies are in compliance with the experimentally reported results. All results indicate that B3LYP method is reliable and it can be used to understand the structural parameters, NMR and vibrational spectra of ferrocene based compounds. The findings of this research can be useful for better understanding possible future applications of ferrocene based systems.

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