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Studies on the vibrational frequencies and molecular electrostatic potential surfaces of the *trans*-bis-[O-3-methyl-1-butyl-(ferrocenyl)dithiophosphonato]nickel(II) complex

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Abstract: Vibrational spectroscopy (FT-IR and Raman) of *trans*-bis-[O-3-methyl-1-butyl-(ferrocenyl)dithiophosphonato]nickel(II) complex, [Ni(FcL)$_2$], which was known previously has been reported. On the other hand, the density functional theory (DFT) calculations on the compound [Ni(FcL)$_2$] have been performed to compare the experimental vibrational frequencies obtained from calculated vibrational frequencies of [Ni(FcL)$_2$] complex for the first time. A relatively good correlation between experimental and theoretical frequencies were found for [Ni(FcL)$_2$]. The molecular electrostatic potential (MEP) surface of the complex was also composed by DFT calculation using the optimized geometry at a B3LYP/LANL2DZ level.

Keywords: Ferrocenyl dithiophosphonato complexes, density functional theory, FT-IR, vibrational frequencies, molecular electrostatic potential

Trans-bis-[O-3-metil-1-bütil-(ferrosenil)ditiyofosfonato]nikel(II) kompleksinin titreşim frekansları ve moleküler elektrostatik potansiyel yüzeyleri üzerine çalışmalar

Özet: *Trans*- bis -[O-3- metil- 1- bütil- (ferrosenil) ditiyofosfonato]nikel(II) kompleksinin [Ni(FcL)$_2$] titreşim spektroskopisi (FT-IR ve Raman) bildirildi. Öte yandan, [Ni(FcL)$_2$] kompleksinin hesaplanan titreşim frekanslarından elde edilen deneysel titreşim frekanslarını ilk kez karşılaştırmak için [Ni(FcL)$_2$] bileşiği üzerinde yoğunluk fonksiyonel teorisi (DFT) hesaplamaları yapılmıştır. [Ni(FcL)$_2$] için deneysel ve teorik frekanslar arasında iyi bir korelasyon bulundu. Kompleksin moleküler elektrostatik potansiyeli (MEP) yüzeyi de B3LYP/LANL2DZ seviyesinde optimize edilmiş geometri kullanılarak DFT hesaplaması ile oluşturulmuştur.

Anahtar Kelimeler: Ferrosenil ditiyofosfonato kompleksleri, yoğunluk fonksiyonel teorisi, FT-IR, titreşim frekansları

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1. INTRODUCTION

After the discovery of elemental phosphorus in 1669 by Hennig Brand [1], organophosphorus compounds were progressively synthesized. Among them is the phenyl monothiophoshonic acid, which was prepared for the first time in 1877 by Köhler [2]. However, organo-dithiophoshorus compounds have not drawn that much attention until 1945, presumably due to their disagreeable odor. But the realization of the potential industrial uses of dithiophosphates, dithiophosphonates and dithiophosphinates which are a member of organo-dithiophoshorus compounds accelerated the investigations on these compounds. The ability of the organothiophosphorus compounds to chelate transition metal ions opened a wide range of mining applications for them in the second half of the last century [3-7]. At later times, pesticides [8] and medical imaging agents [9] containing dithiophosphorus compounds have also emerged. Studies of anticancer activities of dithiophosphinic acid [10] and dithiophosphonic acid derivatives [11, 12] have been shown to be discouraging.

Historically, at least three different methods have been used to synthesize dithiophosphonic acids (DTPOA) [17, 18]. Two of them are today regarded as laborious and lead to undesirable side products. The procedure currently used is based on the use of perthiophosphonic acid anhydrides and was invented in 1952 by Lecher at. all [10]. These scientists treated the above-mentioned compounds with alcohols and came up with DTPOAs. Lawesson realized that the perthiophosphonic acid anhydride, [2,4-*bis*(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide], was also a good general thionation agent [11] and so the name Lawesson's reagent for the compounds. Later, analogs of Lawesson's reagent, LR, were developed [21]. One of these analogs, [2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane-2,4-disulfide], (FcLR), has found wide use for the synthesis of ferrocenyl ditihophosphonates, (Fc-DTPOA) [12].

Fc-DTPOA-type compounds are usually synthesized through the reaction of FcLR with nucleophilic reagents such as alcohols. These compounds are difficult to purify as such, while their ammonium salts are stable. So, Fc-DTPOAs are converted to ammonium salts for purification. Ammonium salts are then treated with metal salts for the corresponding heterodinuclear complexes [23]. A number of these heterodinuclear complexes have already been reported with nickel(II) compounds being the most widely studied species [13]. Dinuclear Ni(II)-Fc-DTPOA complexes are of a square-planar coordination geometry as is the case with other soft base-type ligands [14-16]. Unlike Ni(II), the cations Zn(II) and Cd(II) are known to form four-coordinated, dimeric heterodinuclear complexes with Fc-DTPOAs [17].

The density functional theory (DFT) is widely used in methods in computational quantum chemistry by using the ab initio calculation of electronic structures of many-particle systems [18]. In the literature, the DFT has a great accuracy in reproducing the experimental values in geometry, dipole moment, vibrational frequency and the molecular electrostatic potential (MEP) surface of organic and inorganic compounds [19-22]. In this study, to compare the experimental vibrational frequencies obtained from calculated vibrational frequencies and to investigate reactive sites for electrophilic and nucleophilic attack of *trans*-bis-[O-3-methyl-1-butyl-(ferrocenyl)dithiophosphonato]nickel(II) complex, $[Ni(FcL)_2]$ was investigated by using DFT with B3LYP/LANL2DZ level. The MEP area of $[Ni(FcL)_2]$ was determined by DFT computation at the same level to study reactive sites for electrophile and nucleophilic attack of the studied complex.

2. MATERIAL AND METHOD

The IR spectral data of the complex $[Ni(FcL)_2]$ were used according to the literature [23] for theoretical calculations.

2.1. Computational methods

2.2.1. DFT Calculation

The Gaussian 09 software package and the Gauss View visualization program [24, 25] were used to perform the density functional theory calculations on the compound $[Ni(FcL)_2]$. The geometry optimization and vibrational band analyses were performed by DFT using the Becke-3–Lee–Yang–Parr (B3LYP) Density Functional [26, 27] with the Los Alamos effective core potentials plus double-zeta (LANL2DZ) [28] basis set in the ground state. The molecular electrostatic potential surface was also evaluated by using a B3LYP/LANL2DZ level to investigate the reactive sites and to identify the sites of *intra*- and *inter*-molecular interactions of the molecule. In order to compensate for systematic errors and thereby obtain accurate vibrational wavenumbers for the investigated compound in the solid phase, we calibrated the vibrational wavenumbers by using a scale factor value of 0.960 for individual primitive internal coordinates at the B3LYP/LANL2DZ level of theory [29]. The assignments of each vibratory mode were provided using the VEDA 4 program based on B3LYP [30]. The visual check for the vibrational band assignments were also performed by using Gauss-View molecular visualization program.

3. RESULTS AND DISCUSSION

In this study, we introduced theory studies for $[Ni(FcL)_2]$ which were previously synthesized and characterized (Figure 1). The compound $[Ni(FcL)_2]$ was first identified by experimental and theoretical studies for FTIR and Raman spectroscopy using by density functional theory, (DFT). The DFT calculations were also first studied on the basis of the MEP.

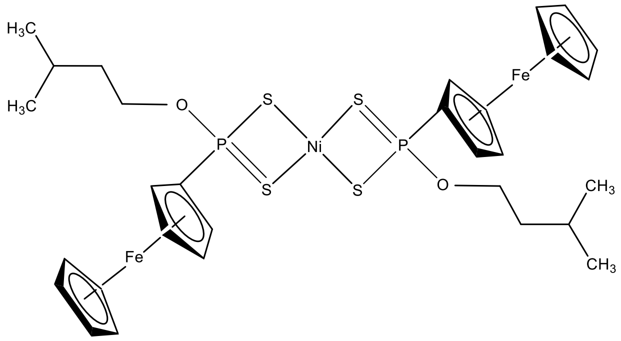

Figure 1. Structure of [Ni(FcL)$_2$].

3.1. The vibrational band assignments of [Ni(FcL)$_2$]

The [Ni(FcL)$_2$] vibrational bands were assigned at the B3LYP/LANL2DZ level of the theory. The important characteristic vibrational frequencies were analyzed and, the results relating to the complex [Ni(FcL)$_2$] were compared with the experimental counterparts to verify the assignments made. The comparison of the selected experimental (Exp.) and calculated vibrational frequencies (cm^{-1}) for [Ni(FcL)$_2$] are given in Table 1.

Table 1. Comparison of the selected experimental and calculated vibrational frequencies (cm^{-1}) for [Ni(FcL)$_2$].

Exp. FT-IR	Exp. Raman	B3LYP/LANL2DZ Unscaled freq.	B3LYP/LANL2DZ Scaled freq.	Band assignments
3106	3113	3306	3174	$\nu_s(CH)_{Cp}$
3071	3076	3267	3136	$\nu_{as}(CH)_{Cp}$
		3136/3125	3011/3000	$\nu_{as}(CH_2)$
2952	-	3117/3108	2992/2983	$\nu_{as}(CH_3)$
		3089	2965	$\nu_{as}(CH_2)$
		3068	2945	$\nu_s(CH_2)$
2903	2874	3024	2903	$\nu_s(CH_3)$
1426	1409	1492	1432	sci(CH_2)
1385	1388	1443/1428/1423	1385/1371/1366	$\nu(CC)_{Cp}$
1365	1369	1419	1362	$\nu(_2HC\text{- }CH_2)$
1340	-	1399	1343	w(CH_2)
1316	-	1397/1386/1376/1350	1341/1330/1320/1296	$\nu(CC)_{Cp}$
1254	-	1296	1244	$\delta(CH)_{Cp}$
1232	-	1287/1256	1236/1206	Tw(CH_2)
1177	1189,1180	1175	1128	$\gamma(CH_2)$
1106	1108	1201/1123	1153/1078	Breathing-Cp
1041	1030	1095/1091/1084	1051/1047/1041	$\delta(CH)_{Cp}$
1025	1065,1055	1077	1033	$\nu(CH_2\text{-}CH_2)$
984	1003	1013	919	$\nu(O\text{-}CH_2)$
898	904	903	867	$\nu(P\text{-}OC)_{aliph.}$
825	838	852	818	Breathing-Cp
611	608	581/577	558	$\tau(CCCH)_{Cp}$
595	600	555	532	$\nu(\ PS)_{asym}$
504	508	506	486	$\nu(\ PS)_{sym}$
446	451	459	441	$\nu_{as}(Fe\text{-}Cy)_{Fc}$
338	339	329	316	$\nu(Ni\text{-}S)_{asym}$
305	304	325	312	$\nu(Ni\text{-}S)_{sym}$

ν: bond stretching, δ: in-plane angle bending, γ: out-of-plane angle bending, sci: scissoring, Tw: twisting, w: wagging, τ: torsion, asym: asymmetric, sym: symmetric.

Figure 2 depicts the experimental (FT-IR and Raman) and theoretical spectra of [Ni(FcL)$_2$]. In the empirical FT-IR spectrum of [Ni(FcL)$_2$], symmetric (sym) [$\nu_s(CH)_{Cp}$] and asymmetric (asym) stretching C-H vibrations [$\nu_{as}(CH)_{Cp}$], are observed at 3106 (FT-IR)/3113 cm^{-1} (Raman) and 3071 (FT-IR)/3076 cm^{-1} (Raman). The corresponding bands are computed at 3174 cm^{-1} (sym) and 3136 cm^{-1} (asym) frequencies.

The combined FT-IR signal for the ring stretching vibrations $\nu(CC)_{Cp}$ is observed at 1316 cm^{-1} while the four calculational predictions corresponding to the ring stretching modes are 1341/1330/1320/1296 cm^{-1}. The in-plane bending [$\delta(CH)_{Cp}$] is observed at 1254 cm^{-1} whereas this vibration is computed to appear at 1244 cm^{-1}. The out-of-plane bending vibrations mode $\gamma(CH_2)$ is observed at 1177/1180 cm^{-1} (FT-IR), 1189 cm^{-1} (Raman).

The twisting modes Tw(CH$_2$) is observed at 1232 cm^{-1} (FT-IR) as a combined signal. The predicted wavenumbers are at 1236 and 1206 cm^{-1}. The bond stretching modes $\nu(CH_2\text{-}CH_2)$ are observed at 1025 cm^{-1} (FT-IR, combined) and 1065, 1055 cm^{-1} (Raman). One of these modes is theoretically predicted at 1033 cm^{-1}.

One other fundamental group vibration the H-C-H scissoring, sci(CH$_2$) is observed at 1426/1409 cm^{-1} (FT-IR and Raman). The sci(CH$_2$) mode is calculated at 1432 cm^{-1}. The stretching mode $\nu(O\text{-}CH_2)$ is observed at 984 cm^{-1} (FT-IR) and 1003 cm^{-1} (Raman). This mode was calculated to appear at 919 cm^{-1}.

The P-O stretching mode gives rise to a very strong band at 898 cm^{-1} (FT-IR) and 904 cm^{-1} (Raman) while the calculated frequency for this band is at 867 cm^{-1} for the B3LYP/LANL2DZ level. The observed band at 595 cm^{-1} (FT-IR) and 600 cm^{-1} (Raman) spectra are attributed to the $\nu(PS)_{asym}$ mode and those at 504 cm^{-1} (FT-IR) and 508 cm^{-1} (Raman) to $\nu(PS)_{sym}$. The corresponding theoretical values for these modes are calculated at 532 cm^{-1} for $\nu(PS)_{asym}$ and 486 cm^{-1} for $\nu(PS)_{sym}$. The Ni-S symmetric stretching vibration, $\nu(Ni\text{-}S)_{sym}$ is observed at 305 cm^{-1} (FT-IR) and 304 cm^{-1} (Raman) whereas the Ni-S asymmetric stretching $\nu(Ni\text{-}S)_{asym}$, at 338 cm^{-1} (FT-IR) and 339 cm^{-1} (Raman). The corresponding theoretical values are 312 cm^{-1} for $\nu(Ni\text{-}S)_{sym}$ and 316 cm^{-1} for $\nu(Ni\text{-}S)_{asym}$.

The calculated values of other group vibrations show good agreement with the experimental results. As a result, the scaled fundamental vibrations are in good consistency with experimental results. Our calculations compare well with similar findings reported in the literature [31-36].

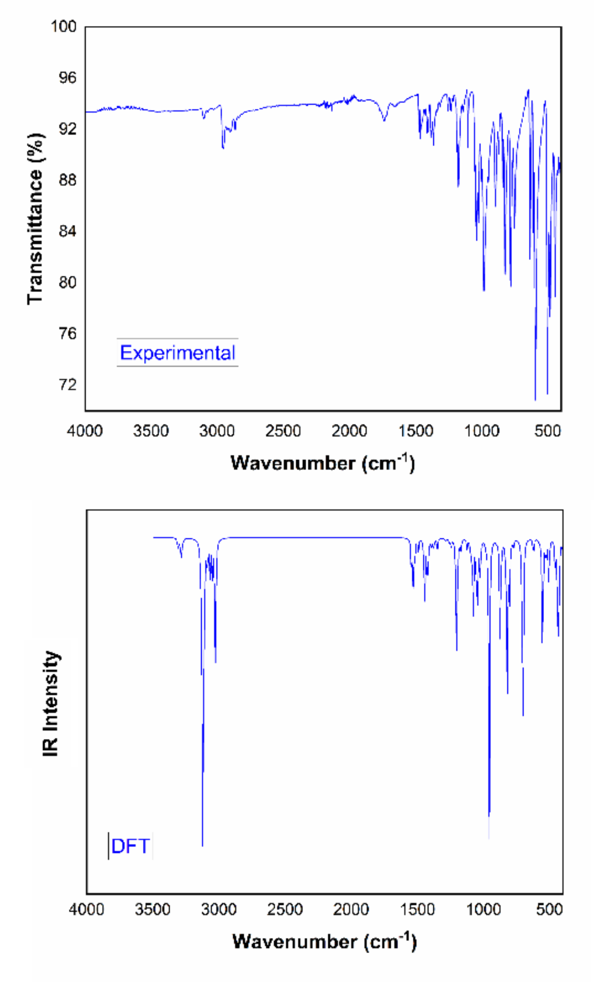

Figure 2. Experimental and theoretical infrared spectra of [Ni(FcL)$_2$].

3.2. The electrostatic surface potential of [Ni(FcL)$_2$]

The MEP surface of the title complex was composed by DFT calculation using the optimized geometry at a B3LYP/LANL2DZ level to investigate reactive sites for electrophilic and nucleophilic attack. MEP is related to the electron density and a very useful descriptor in hydrogen bonding interactions.[37] MEP also is a very good device to analyze the processes involved in drug-receptor and enzyme-substrate interactions.[38] MEP surfaces of [Ni(FcL)$_2$] are illustrated in Figure 3. The blue colors are negative regions that are related to nucleophilic reactivity whereas red and yellow colors are positive regions that are related to electrophilic reactivity. Thus, electrostatic potential decreases in the order blue-green-yellow-orange-red.

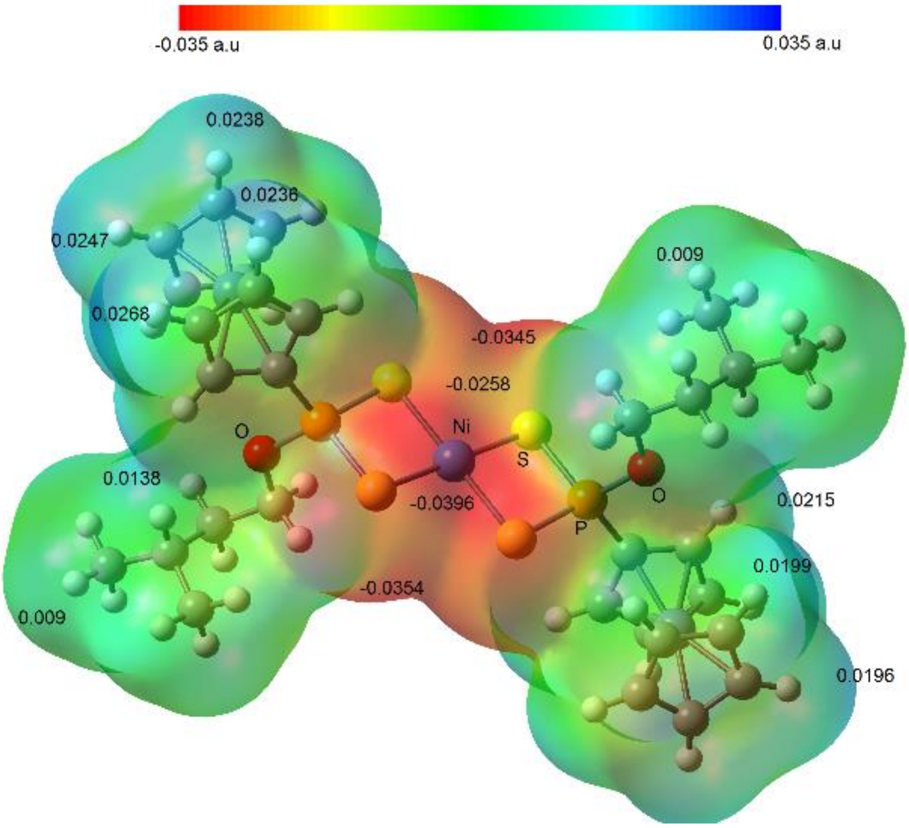

Figure 3. The molecular electrostatic potential surfaces of $[Ni(FcL)_2]$.

As shown in Figure 3, the maximum negative values lie in the range (-0.0258) – (-0.0396 a.u.) for the region of O atoms and four-membered coordination rings (S1, S2, $S1^i$ and $S2^i$) indicate possible sites of electrophilic reactivity while the positive values range of 0.0196 to 0.0268 a.u. for the region of the ferrocenyl moieties and 0.009 to 0.0138 a.u. for *iso*-amyl group indicate possible sites of nucleophilic reactivity in $[Ni(FcL)_2]$. These regions give preliminary information for the predictions of intermolecular interactions. As mentioned previously in section descriptions of the crystal structure and optimized geometry of $[Ni(FcL)_2]$, predicted reactive sites in the MEP for the investigated molecule are confirmed that the crystal structure of the $[Ni(FcL)_2]$ was also stabilized by intermolecular and intramolecular hydrogen bonds between atoms of two ferrocenyl precursors ($C3^i$-$H3^i\cdots C7^i$, $C3^i$-$H3^i\cdots C8^i$) and between O atoms and H atoms of the *iso*-amyl group (C2-H2···O1, C13-H13···O1, $C2^i$-$H2^i\cdots O1^i$, $C13^i$-$H13^i\cdots O1^i$, symmetry codes: (i) -x, -y+1, -z; (ii) x+3/2, -y+1/2, z+1/2) [23].

4. CONCLUSION

The vibrational band assignments were performed at B3LYP/LANL2DZ theory level to compare the experimental (FT-IR) and calculated vibrational frequencies of the title compound. We have analyzed the normal vibrational frequencies and compared our calculated results of the investigated compound with the experimental ones. As a result, the scaled fundamental vibrations are in good consistency with experimental results. The possible sites of electrophilic and nucleophilic reactivity in $[Ni(FcL)_2]$ were predicted by the same level of DFT. According to the MEP surface of the investigated complex, the O atoms and four-membered coordination rings (S1, S2, S1i and S2i) have maximum negative regions which indicate possible sites of electrophilic reactivity while the ferrocenyl moieties and *iso*-amyl group have the positive regions which indicate possible sites of nucleophilic reactivity in $[Ni(FcL)_2]$.

5. CONFLICT OF INTEREST

The authors declare no competing financial interest.

Ethical Approval: Ethics Approval is not required for this study.

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Supplamentery Materials

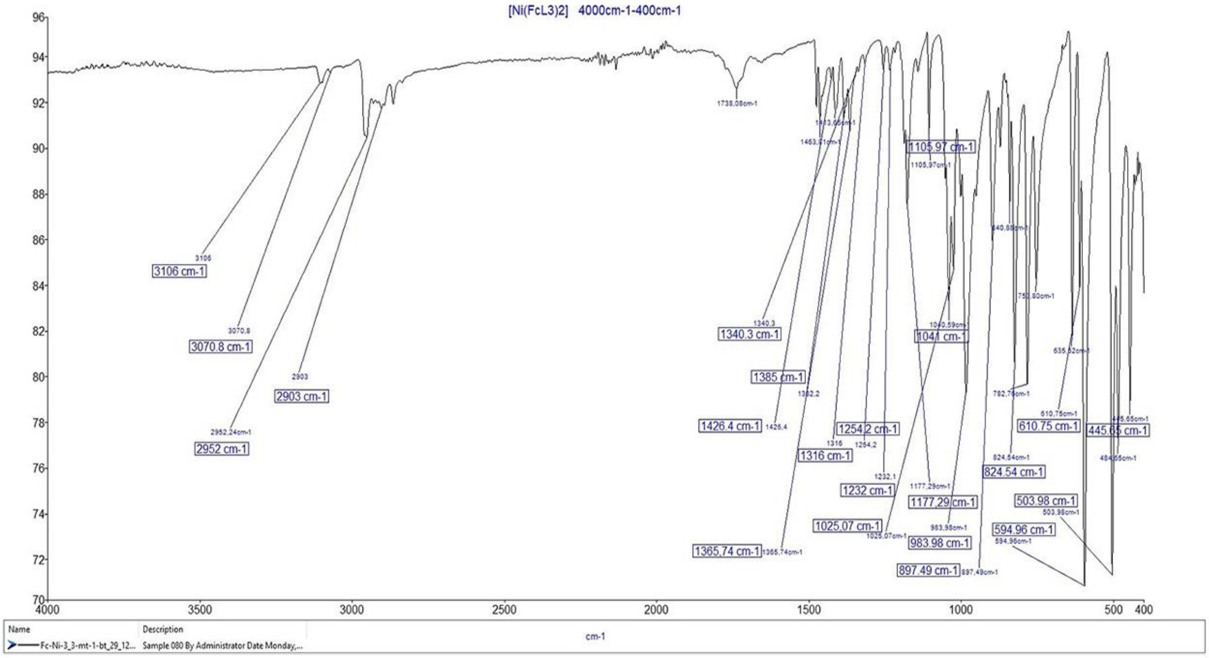

Figure SM 1a. [Ni(FcL)$_2$] (4000cm^{-1}-400cm^{-1}).

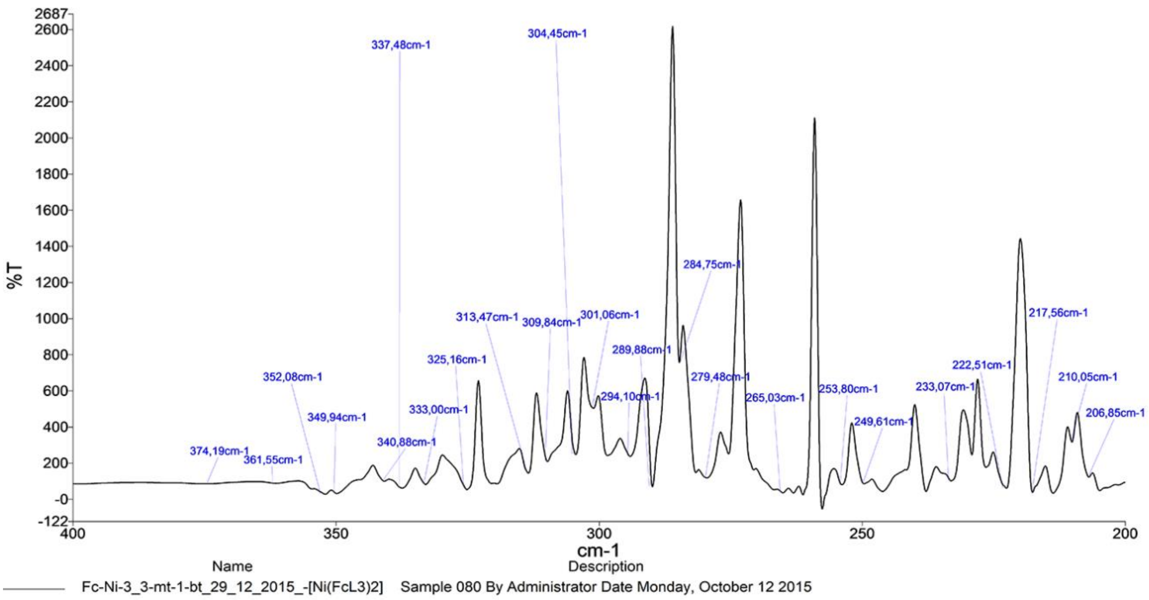

Figure SM 1b. [Ni(FcL)$_2$] (400cm^{-1}-200cm^{-1}).

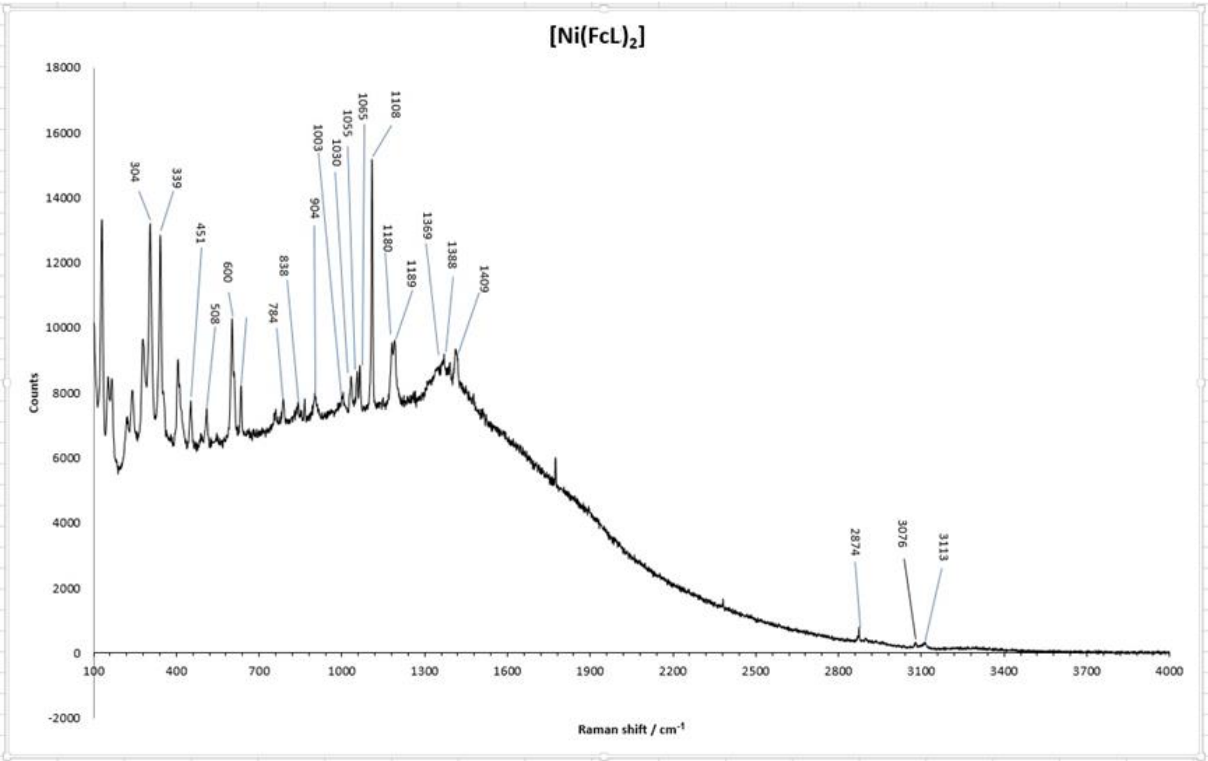

Figure SM 2. Raman spectra of **[**Ni(FcL)$_2$]