Natural Sciences and Advanced Technology Education *Volume 30 Number 6, 2020* *Обучение по природни науки и върхови технологии*

https://doi.org/10.53656/nat2021-6.03

From the Research Laboratories

SEMIEMPIRICAL QUANTUM CHEMICAL AND AB INTIO STUDY OF Co(II), Ni(II),Cu(II) AND Zn(II) COMPLEXES WITH THE AZO DYE DERIVED FROM 4-AMINO ANTIPYRINE AND 2,4-DIHYDROXY ACETOPHEONE

Satya Narayan Chaulia
Rajendra (Auto) College (India)

Abstract. Semi-empirical quantum chemical calculation was made to study the nucleophilicity of the ligand and to study the mode of bonding between the ligand and the metal ions. The natural atomic charge at different atomic sites of the ligand has been calculated along with the electrostatic potential map to predict the reactive sites for electrophilic and nucleophilic attack. The theoretical spectral data such as IR, NMR and electronic have been calculated and compared with the experimentally generated data.

Keywords: Semiempirical study; Chem 3D Ultra; Natural atomic charge; Molecular polarisability

Introduction

Molecular modelling uses theoretical approaches and computational techniques to study molecular systems ranging from small molecular units to large biological molecules (Cornado & Merlin 2003). Molecular modelling provides information of geometrical parameters such as bond lengths, dihedral angles and bond angles along with the spectroscopic data with respect to vibration, electronic and NMR (Leach 2009). In addition to this, Chemical reactivity sites of the ligand and its metal complexes can also be predicted from the natural atomic charge and electrostatic potential map (Ramachandran et al. 2008). The azo dye derived from 4-aminoantipyrine and 2,4-dihydroxyacetophenone as given in fig 1 and its metal complexes as given in fig 4 have been synthesised, characterised and reported (Chaulia 2016). In this study, attempts have been made to predict the reactive sites of the ligand and metal complexes by computing the natural atomic charge and electrostatic potential map. The spectral data such as IR, electronic and NMR of the ligand are calculated and compared with the experimental spectral data.

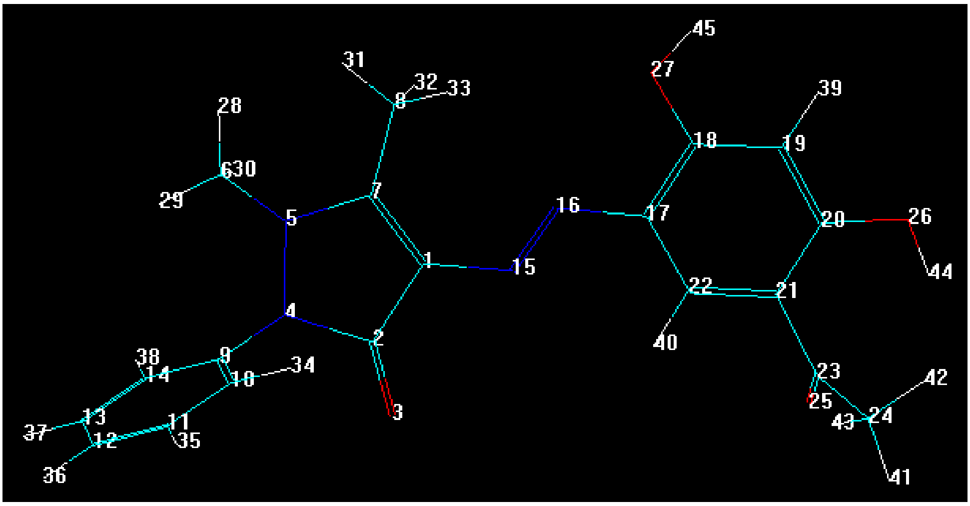


Figure 1. Optimised geometry of the ligand

Computational Details

The computational calculations were made using Ab Intio and semi empirical methods with Chem 3D Ultra programme (Chem3D Ultra Molecular modelling and Analysis, 2003). The geometry of the ligand and its metal complexes were drawn by using the programme Chem draw present in the same Chem 3D Ultra programme. The geometry of the ligand and its complexes were optimised using molecular mechanics and low lying structures were again optimised using semi empirical quantum chemical methods.

Results and Discussion

The computational study of the ligand and its metal complexes were undertaken and compared with the experimental results.

Natural atomic charge

The natural atomic charges at different atomic sites of the ligand were calculated and presented in the table 1 and fig 2. The natural atomic charge plays important role in determining the electronic properties of a compound such as dipole moment, molecular polarisability and hyperpolarizability (Bejler et al. 1990). The region of highest electron density reflects the potential sites of electrophilic attack. The highest electron densities are concentrated over nitrogen and oxygen atoms, this fact is also supported by the molecular electrostatic potential study in fig 3. Hence, these atoms have the ability to coordinate with the metal ions.

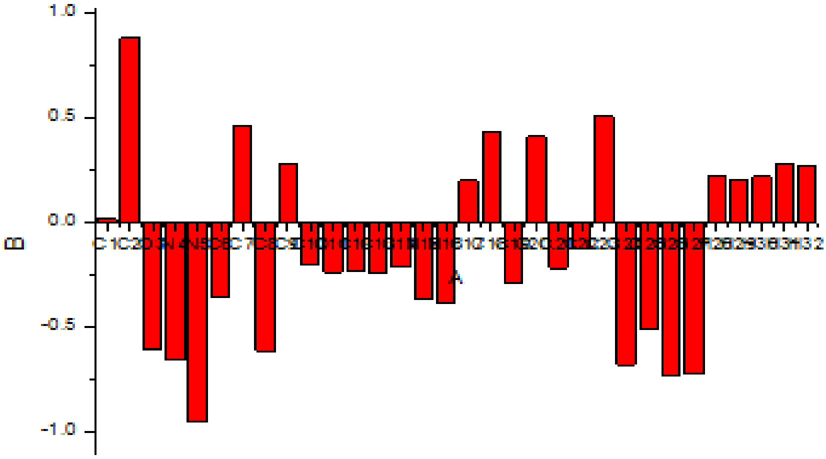


Figure 2. Natural atomic charge of the atoms present in the ligand

Table 1. Natural atomic charges

Atom	charge	Atom	charge	Atom	charge	Atom	charge
C1	0.0200	C8	-0.6356	N15	-0.3679	O24	-0.6788
C2	0.8913	C9	0.3031	N16	-0.3776	O25	-0.7209
O3	-0.6124	C10	-0.2181	C17	0.1850	O26	-0.7174
N4	-0.6725	C11	-0.2354	C18	0.4570	O27	0.7207
N5	-0.5529	C12	-0.2544	C19	-0.3103	H28	0.2265
C6	-0.3618	C13	-0.2350	C20	0.4940	H29	0.2426
C7	0.4643	C14	-0.2286	C21	-0.3421	H30	0.2059

Molecular electrostatic potential

The Electrostatic potential map gives an idea about the charge distribution and charge related properties of a molecules (Politzer & Murray 1991). The MEP of the investigated compound indicates red colour is concentrated around nitrogen and oxygen atoms and blue colour around some carbon and hydrogen atoms. This observation suggests that the nitrogen and oxygen atoms are rich source of electrons, and the metal ions is coordinating with the ligand through the azo nitrogen and oxygen atoms of the ligand as given in the Fig.3

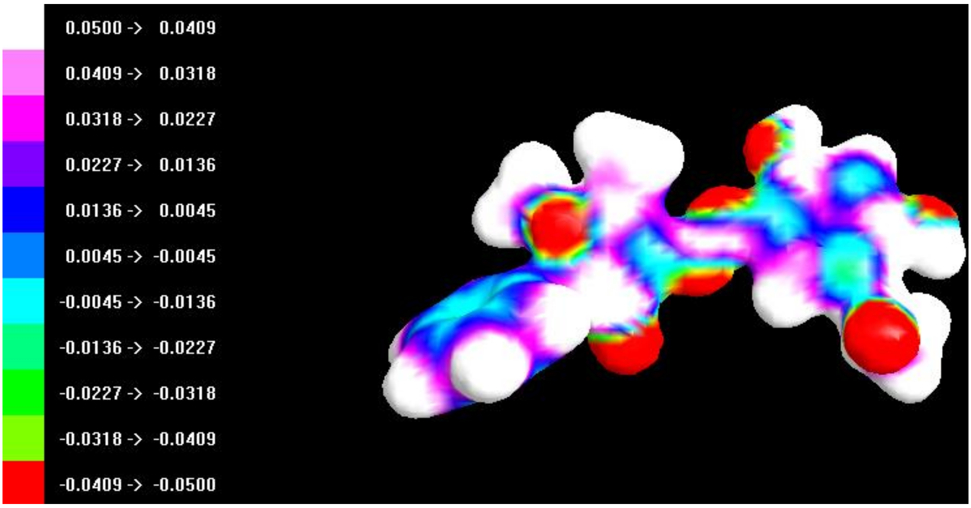
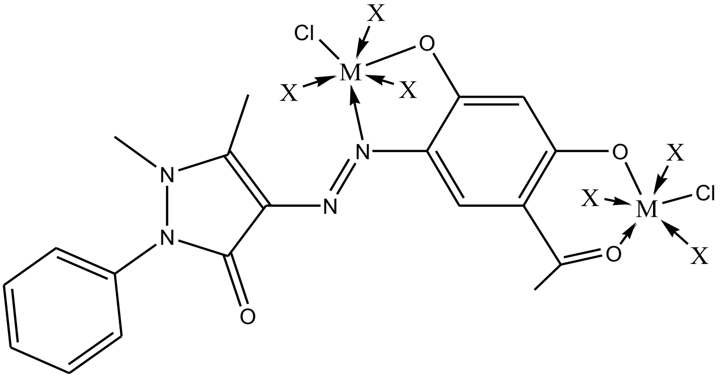


Figure 3. Electrostatic potential map of the ligand



X=H_2O for Co, Ni, Cu &X=nil for Zn

Figure 4. Structure of metal complexes

IR spectra

The IR spectra of the ligand and its metal complexes were recorded and the experimental spectral data were compared with the computationally generated spectral data and presented in the fig 5, 8 and table 2 and 3. The IR spectrum of the ligand gives a band at 1270 cm^{-1} corresponding (C-O) vibration but the AM1 (Dewar et al. 1985) predicts it at 1262 cm^{-1} and the PM3 (Stewart 1989)predicts it at 1257 cm^{-1}. The experimental frequency for the vibration of (N=N) appeared at 1493 cm^{-1} but the AM1 predicts it at 1479 cm^{-1} and the PM3 predicts it at 1491 cm^{-1}. The computational study indicates the vibrational frequency for (C=O) is at 1708 cm^{-1} according to AM1 and at 1642 cm^{-1} according to PM3 but experimental study indicates it at 1639 cm^{-1}. The correlation coefficient of experimental and computational vibration frequency calculated using AM1 and PM3 is 0.999 as given in fig 6 and 7.

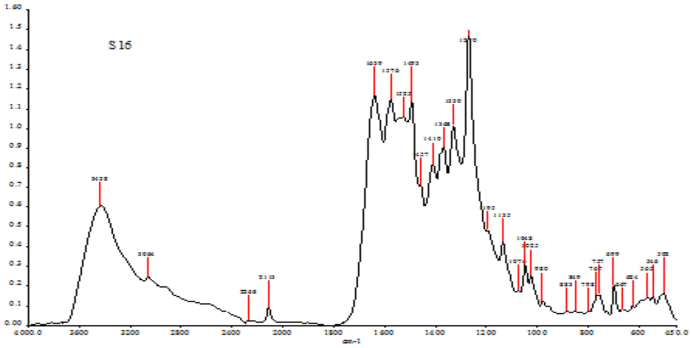


Figure 5. IR spectrum of the ligand(experimental)

Table 2. Experimental and computational vibration frequency data of the ligand

Band	EXPT	AM1		
	v/cm^{-1}	v/cm^{-1}	Intensity	v/cm^{-1}
(C-O)	1270	1262	3	1257
(N=N)	1493	1479	50	1491
(O-H)	3434	3609	47	3877
(C=O)	1639	1708	49	1642

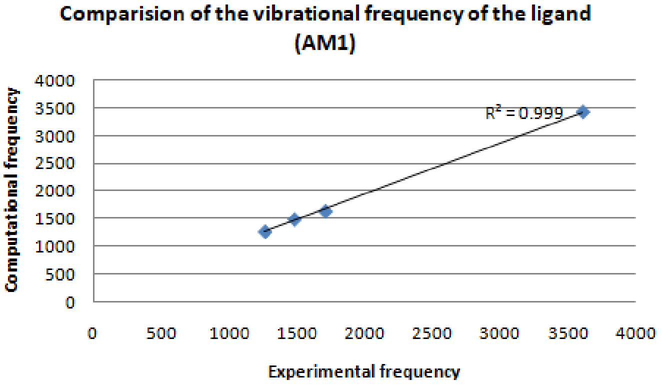


Figure 6. Correlation graph of the ligand

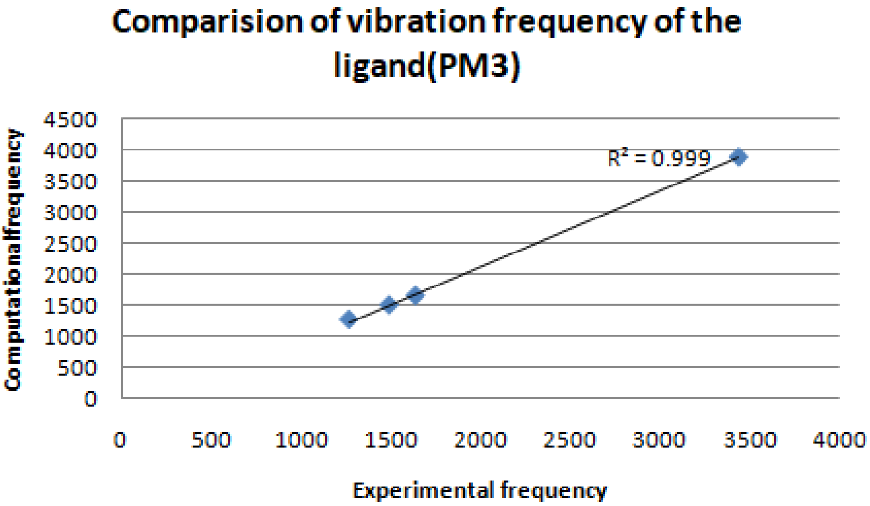


Figure 7. Correlation graph of the ligand

The IR spectrum of metal complex shows a band at ~1219 cm^{-1} but in the free ligand, it was at 1270 cm^{-1} and missing of peak at ~3434 cm^{-1} in the metal complexes that indicates deprotonation of -OH group and formation of bond by the metal atom or ion with the oxygen atom of the -OH group. However, the computational study predicts it at 1262 cm^{-1} according to AM1 force field and at 1283 PM3 force field. The spectrum of the complex also shows peak at ~1454 cm^{-1} but it was at 1493 cm^{-1} in the free ligand indicating formation of bond with one of the nitrogen atoms of the azo group(-N=N-) with the metal atom or ion. The computational generated spectrum indicates this peak at 1492 cm^{-1} and 1490 cm^{-1} corresponding to AM1 and PM3 force fields. The (C=O) stretching vibrational frequency of the free ligand is at 1639 cm^{-1} but IR spectrum of the complex shows at 1610 cm^{-1} that suggests formation of bond of carbonyl oxygen with the metal ion or atom. The computer-generated spectrum data indicates the vibrational frequency at 1647 cm^{-1} according to AM1force field but at 1644 cm^{-1} according to PM3 force field. The bonding between the metal ion and oxygen atom of the (-OH) group is confirmed by the appearance of peak at 536 cm^{-1} in the IR spectrum of the complex[7] but according to AM1 force field it is at 561 cm^{-1} but PM3 predicts it at 581 cm^{-1}. The bonding between the metal ion and nitrogen atom of the (-N=N-) group is confirmed by the appearance of peak at 536 cm^{-1} in the IR spectrum of the complex but according to AM1 force field it is at 556 cm^{-1} but PM3 predicts it at 522 cm^{-1}. (Sirichote et al. 1998). The correlation coefficient of experimental and computational vibration frequency calculated using AM1 and PM3 is ~ 0.997 as given in fig 9 and 10.

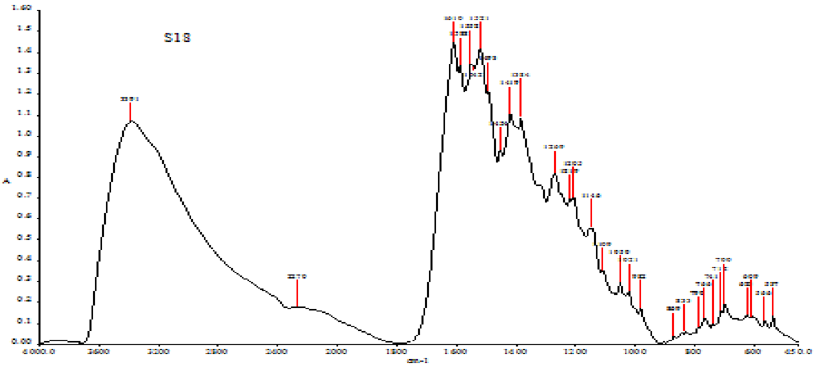


Figure 8. IR spectrum of the ligand(experimental)

Table 3. Experimental and computational vibration frequency data of the Co(II) complex

Band	EXPT	AM1		
	v/cm^{-1}	v/cm^{-1}	Intensity	v/cm^{-1}
(C-O)	1219	1262	3	1283
(N=N)	1454	1492	54	1490
(M-O)	565	561	9	581
(C=O)	1639	1647	54	1644
(M-N)	536	556	53	522

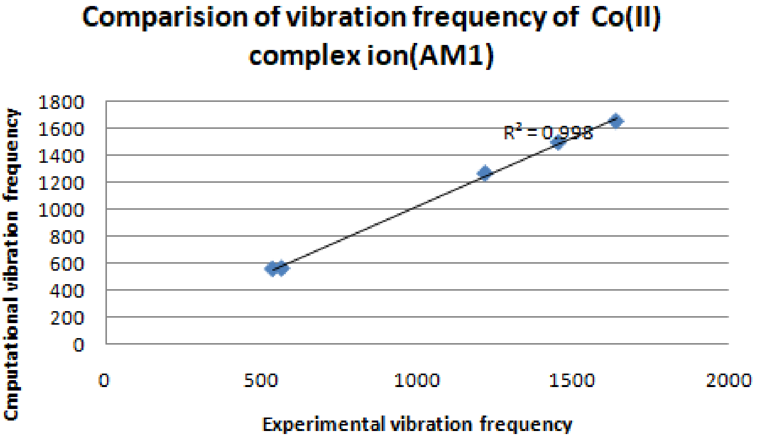


Figure 9. Correlation graph of the Co(II) complex

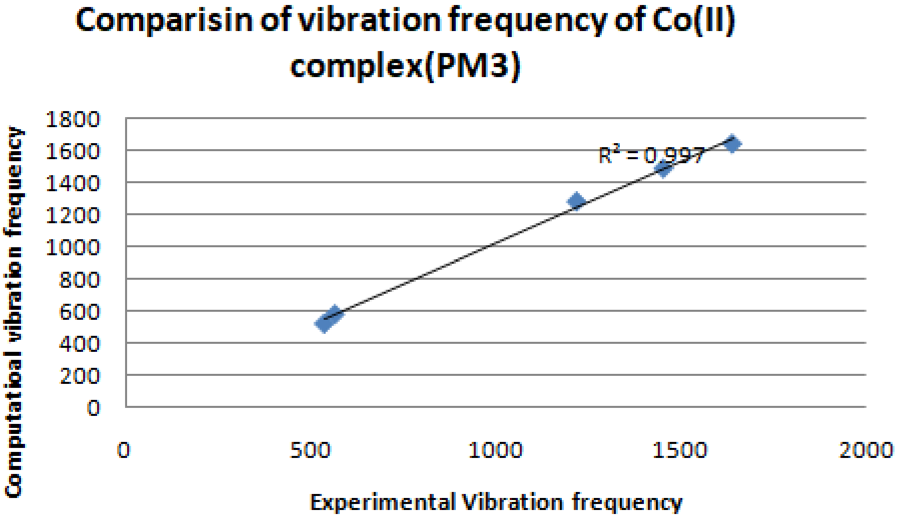
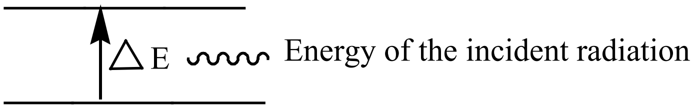


Figure 10. Correlation graph of the Co(II) complex

Electronic spectra

The semi empirical quantum chemical method find uses in calculating excited states hence to predict UV spectra of chemical compounds effectively. The single point energy calculations were carried out at semi empirical level to predict UV spectra. The computational electronic spectral bands of the ligand and its Co(II), Ni(II), Cu(II) complexes were calculated. The spectral bands of the investigated compounds were calculated by using the ZINDO programme (Zerner 1991).

The ligand and its metal complexes were also characterised by the Electronic spectra. The absorption bands are observed in the UV-Visible region of the electromagnetic spectrum due to transition of electrons between two electronic energy levels when energy difference between two electronic energy levels matches the energy of the incident photon[1].



$$\Delta E = \frac{hc}{\lambda}\, where\ h = \ plank's\ constant, c = \ velocity\ of\ light, \lambda = wavelength\ of\ the\ radiatio$$

n

The semi empirical quantum chemical method find uses in calculating excited states hence to predict UV spectra of chemical compounds effectively. The single point energy calculations were carried out at semi empirical level to predict UV spectra. The computational electronic spectral bands of the ligand and its Co(II), Ni(II), Cu(II) complexes were calculated and given in table. The spectral bands of the investigated compounds were calculated by using the ZINDO programme (Zerner 1991).

The computational study of the Co(II)complex predicts spectral bands at 12987 cm, 16393 cm, 22727 cm corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$. The theoretical spectral bands were compared with the experimental spectral bands which were found at 14492 cm^{-1}, 20449 cm^{-1} and 25575 cm^{-1} respectively as given in table 4. Both experimental and computational values were compared, and the correlation coefficient was found to be 0.954 given in fig 11.

Table 4. Experimental and calculated wavelength of the ligand and its metal complexes

compound	Expt wavelength(cm)	Calcd wavelength(cm)	assignment
Ligand	275	377	n-$\pi*$
	245	318	
$[Co_2LCl_2(H_2O)_6]$	12987	14492	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	16393	20449	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	22727	25575	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
$[Ni_2LCl_2(H_2O)_6]$	13157	14084	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	16528	18552	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	23255	24271	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[Cu_2LCl_2(H_2O)_2]$	15350	13642	${}^2E_g \rightarrow {}^2T_{2g}$

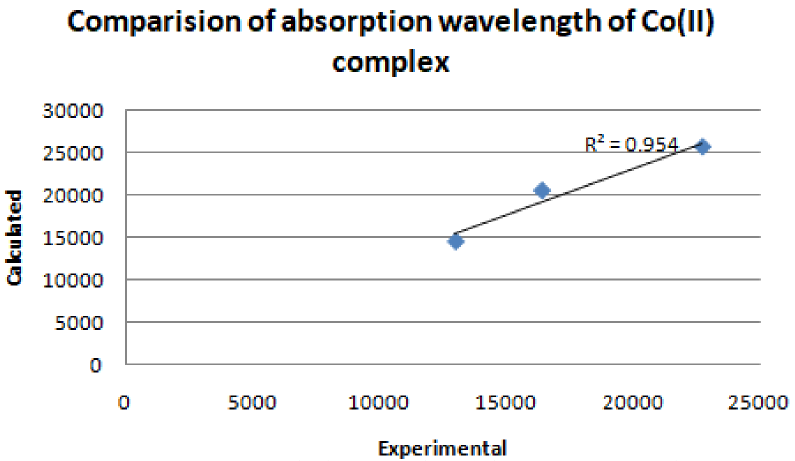


Figure 11. Correlation graph of the Co(II) complex

Similarly, Ni(II) complex predicts spectral bands at 13157 cm^{-1}, 16528 cm^{-1} and 23255 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The computational study indicated it at 14084 cm^{-1}, 18552 cm^{-1} and 24271 cm^{-1}. A good correlation was obtained between the experimental and calculated data ($R^2 = 0.954$) given in fig 12 and percentage variation is less than 5.

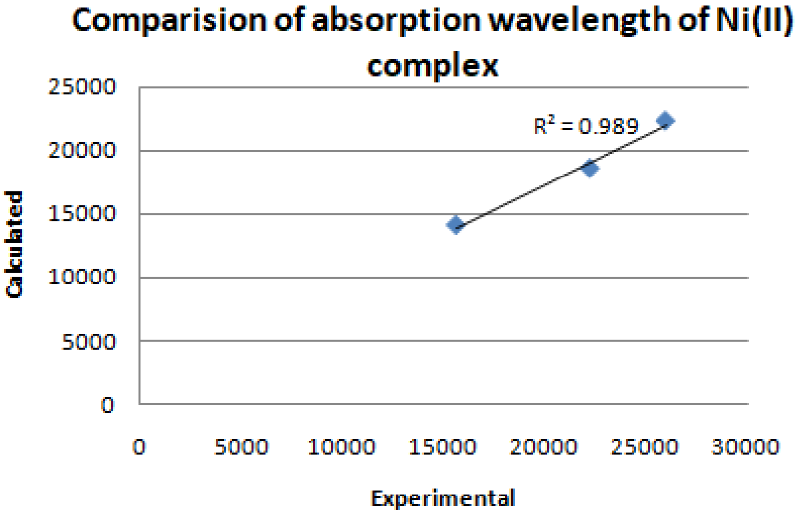


Figure 12. Correlation graph of the Ni(II) com

The electronic parameters of the Co(II) metal complex were calculated by using the following relations and presented in the table no 5

$$Dq = v2 - v1/10 \text{ ....} Equation\ 1$$

$$B = v2 + v3 - 3\ v1/15 \text{........} Equation\ 2$$

$$\beta 35 = B/\ 971 \qquad \text{........} Equation\ 3$$

$$\beta 35\% = (1 - \beta 35) \times 100 \text{ ... .} Equation\ 4$$

Similarly, the electronic parameters of Ni(II) metal complex were also calculated by using the following relations and presented in the table no 5

$$Dq = v1/10 \text{........} Equation\ 5$$

$$B = v2 + v3 - 3\ v1/15 \text{........} Equation\ 6$$

$$\beta 35 = B/1041 \text{........} Equation\ 7$$

$$\beta 35\% = (1 - \beta 35) \times 100 \text{ ....} Equation\ 8$$

It has been seen that the electronic parameters such as B, β_{35} and υ_2/υ_1 calculated from the computational $\boldsymbol{v1, v2}$ ***and*** $\boldsymbol{v3v1, v2}$ ***and*** $\boldsymbol{v3}$ values for Co and Ni as given in table 6 gives good correlation with the electronic parameters calculated from experimental its values as compared to $[Co_2LCl_2(H_2O)_6]$ metal complex.

Table 5. Experimental electronic parameter of the complexes

compound	B	Dq	β_{35}	% of β_{35}	υ_2/υ_1
$[Co_2LCl_2(H_2O)_6]$	23.93	548	0.705	29.5	1.62
$[Ni_2LCl_2(H_2O)_6]$	20.8	1275	0.038	96.2	1.25
$[Cu_2LCl_2(H_2O)_6]$	-		-	-	-

Table 6. computational Electronic parameter of the complexes

compound	B	Dq	β_{35}	% of β_{35}	υ_2/υ_1
$[Co_2LCl_2(H_2O)_6]$	170	595	0.175	82.5	1.41
$[Ni_2LCl_2(H_2O)_6]$	30.8	2044	0.029	97.1	1.31
$[Cu_2LCl_2(H_2O)_6]$	-		-	-	-

Nuclear magnetic spectra

The Nuclear magnetic resonance spectroscopy has been used for structure elucidations of various complex molecules. The use of experimental and computational data offers powerful techniques to interpret and predict the structure of bulky molecules (Torda & Gunsteren 1992). The gauge independent atomic orbital method has been used for calculating the NMR chemical shifts (Wolinski et al. 1990)

The ^{1}H NMR spectra of the ligand as given in fig 13 and its Zn(II) given in fig 14 complex were recorded experimentally separately. The computational chemical shifts values of the ligand and metal complexes are also collected as given in fig 15 and 16 and these chemical shifts values (δexp) were compared with the computational ($\delta calc$)$\delta calc$) values. The correlation coefficient of both the values was found to be 0.828 as given in fig 17.

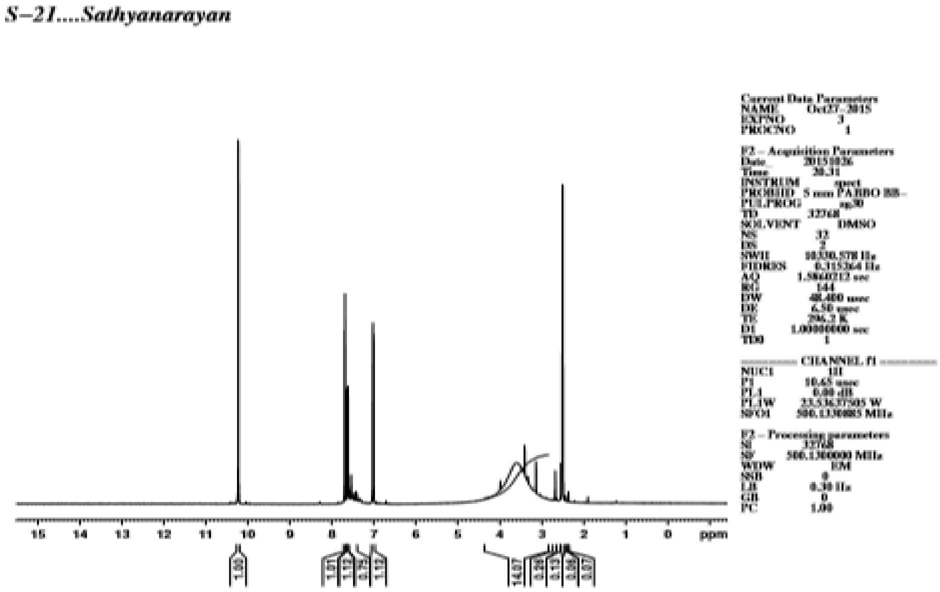
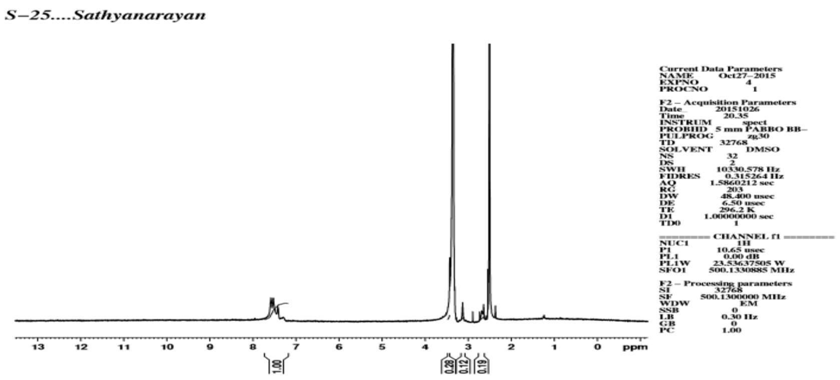


Figure 13. Experimental 1H NMR Spectrum of the ligand



```
Current Data Parameters
NAME        Oct27–2015
EXPNO              4
PROCNO             1

F2 – Acquisition Parameters
Date_       20151026
Time           20.35
INSTRUM         spect
PROBHD   5 mm PABBO BB–
PULPROG         zg30
TD          32768
SOLVENT         DMSO
NS              32
DS              2
SWH        10330.578 Hz
FIDRES      0.315264 Hz
AQ        1.5860212 sec
RG             203
DW          48.400 usec
DE           6.50 usec
TE           296.2 K
D1       1.00000000 sec
TD0              1

======== CHANNEL f1 ========
NUC1            1H
P1          10.65 usec
PL1          0.00 dB
PL1W      23.53637505 W
SFO1     500.1330885 MHz

F2 – Processing parameters
SI          32768
SF       500.1300000 MHz
WDW             EM
SSB              0
LB           0.30 Hz
GB               0
PC            1.00
```

Figure 14.

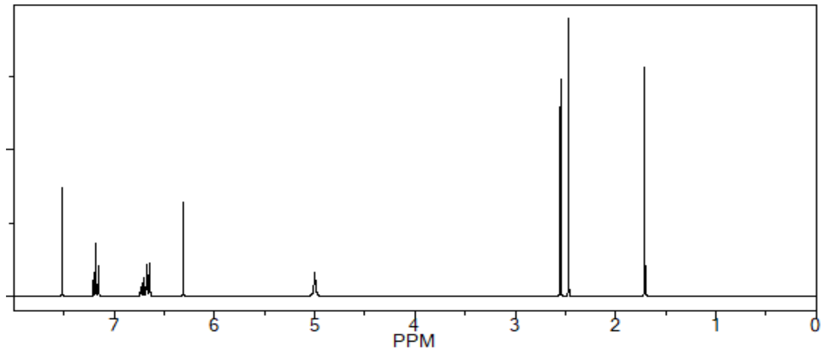


Figure 15. Calculated 1H NMR Spectrum of the ligand

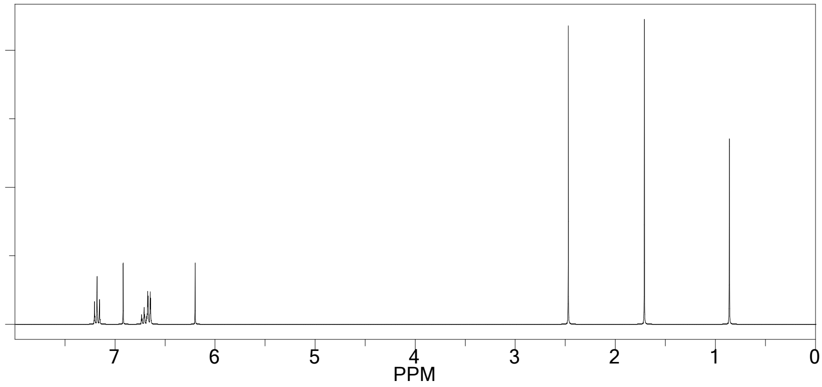


Figure 16. Fig 16. Calculated 1H NMR Spectrum of the Zn(II) complex

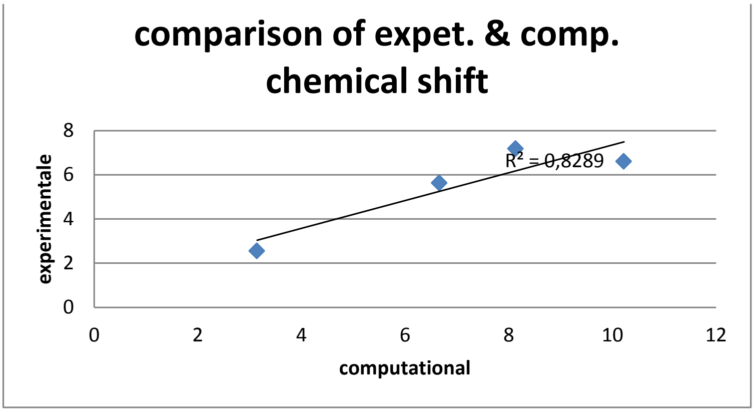


Figure 17. Correlation graph of the ligand

The 1H NMR computational data gathered for the ligand are given below

```
Protocol of the H-1 NMR Prediction:

Node      Shift     Base + Inc.    Comment (ppm rel. to TMS)

 CH3       2.47         0.86       methyl
                        1.61       1 alpha -N
 CH3       1.71         0.86       methyl
                        0.85       1 alpha -C=C
  CH       6.66         7.26       1-benzene
                       -0.60       1 -N-N
  CH       7.18         7.26       1-benzene
                       -0.08       1 -N-N
  CH       6.71         7.26       1-benzene
                       -0.55       1 -N-N
  CH       7.18         7.26       1-benzene
                       -0.08       1 -N-N
  CH       6.66         7.26       1-benzene
                       -0.60       1 -N-N
  CH       6.3          7.26       1-benzene
                         ?         1 unknown substituent(s)
                       -0.53       1 -O
                       -0.53       1 -O
                        0.11       1 -C(=O)C
                                   -> 1 increment(s) not found
  CH       7.5          7.26       1-benzene
                         ?         1 unknown substituent(s)
                       -0.17       1 -O
                       -0.17       1 -O
                        0.60       1 -C(=O)C
                                   -> 1 increment(s) not found
 CH3       2.55         0.86       methyl
                        1.69       1 alpha -C(=O)-1:C*C*C*C*C*C*1
  OH       5.0          5.00       aromatic C-OH
  OH       5.0          5.00       aromatic C-OH
```

The 1H NMR computational data obtained for the Zn(II) complex are given below

```
Protocol of the H-1 NMR Prediction:

Node      Shift    Base + Inc.   Comment (ppm rel. to TMS)

 CH3      2.47        0.86       methyl
                      1.61       1 alpha -N
 CH3      1.71        0.86       methyl
                      0.85       1 alpha -C=C
  CH      6.66        7.26       1-benzene
                     -0.60       1 -N-N
  CH      7.18        7.26       1-benzene
                     -0.08       1 -N-N
  CH      6.71        7.26       1-benzene
                     -0.55       1 -N-N
  CH      7.18        7.26       1-benzene
                     -0.08       1 -N-N
  CH      6.66        7.26       1-benzene
                     -0.60       1 -N-N
  CH      6.2         7.26       1-benzene
                       ?         1 unknown substituent(s)
                     -0.53       1 -O
                     -0.53       1 -O
                       ?         1 unknown substituent(s)
                                 -> 2 increment(s) not found
  CH      6.9         7.26       1-benzene
                       ?         1 unknown substituent(s)
                     -0.17       1 -O
                     -0.17       1 -O
                       ?         1 unknown substituent(s)
                                 -> 2 increment(s) not found
 CH3      0.9         0.86       methyl
                       ?         1 unknown alpha substituent(s)
                                 -> 1 increment(s) not found
OH2+       ?          n.a.       not estimated
OH2+       ?          n.a.       not estimated
```

The ^{13}C NMR computational study of the ligand and Zn(II) complex was undertaken to study the nature of bonding between metal ion and donor atoms of the ligand as given in the fig 18 and 19.

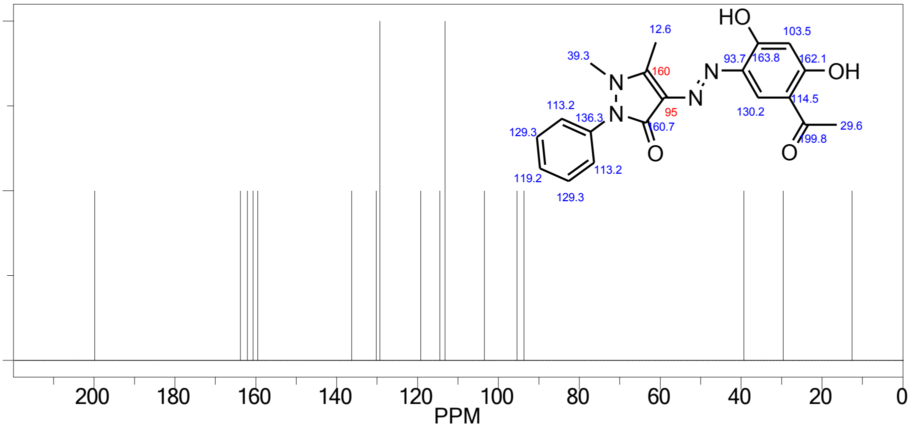


Figure 18. ^{13}C NMR spectrum of the ligand

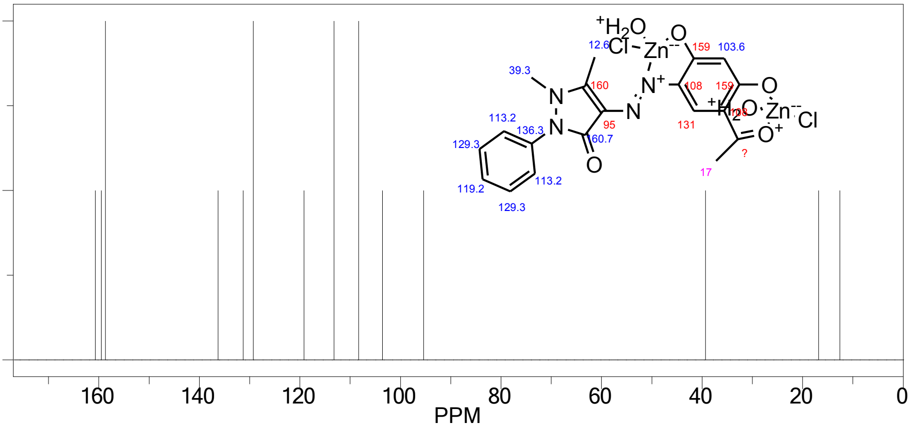


Figure 19. ^{13}C NMR spectrum of the Zn(II) complex

The ^{13}C NMR computational data gathered for the ligand are given below

```
Protocol of the C-13 NMR Prediction:
Node     Shift    Base + Inc.   Comment (ppm rel. to TMS)
   C      95         123.3      1-ethylene
                       7.5      1 -C(=O)N
                        ?       1 unknown substituent(s)
                      -7.4      1 -C
                     -28.0      1 -N
                                -> 1 increment(s) not found
   C     160.7       165.0      1-amide
                       2.6      1 -C=C-C
                      -4.5      1 -1:C*C*C*C*C*C*1 from N-amide
                      -2.4      1 -N from N-amide
 CH3      39.3        -2.3      aliphatic
                      28.3      1 alpha -N
                       6.9      1 beta -C=C
                      11.3      1 beta -N
                      -2.6      1 gamma -1:C*C*C*C*C*C*1
                      -2.7      1 gamma -C=O
                      -2.5      1 gamma -C
                       0.0      1 delta -N
                       2.9      general corrections
   C     160         123.3      1-ethylene
                       5.8      1 -C(=O)N
                        ?       1 unknown substituent(s)
                       9.4      1 -C
                      21.0      1 -N
                                -> 1 increment(s) not found
 CH3      12.6        -2.3      aliphatic
                      19.5      1 alpha -C=C
                      11.3      1 beta -N
                      -3.2      1 gamma -C(=O)-N
                      -2.5      1 gamma -C
                      -5.1      1 gamma -N
                       0.3      1 delta -1:C*C*C*C*C*C*1
                       0.0      1 delta -N
                      -5.4      general corrections
   C     136.3       128.5      1-benzene
                      13.7      1 -N-N
                      -5.9      general corrections
  CH     113.2       128.5      1-benzene
                     -16.5      1 -N-N
                       1.2      general corrections
  CH     129.3       128.5      1-benzene
                       0.5      1 -N-N
                       0.3      general corrections
  CH     119.2       128.5      1-benzene
                      -9.6      1 -N-N
                       0.3      general corrections
  CH     129.3       128.5      1-benzene
                       0.5      1 -N-N
                       0.3      general corrections
  CH     113.2       128.5      1-benzene
                     -16.5      1 -N-N
                       1.2      general corrections
   C      93.7       128.5      1-benzene
                        ?       1 unknown substituent(s)
                     -12.8      1 -O
                      -7.4      1 -O
                      -0.1      1 -C(=O)-C
                     -14.5      general corrections
                                -> 1 increment(s) not found
   C     163.8       128.5      1-benzene
                        ?       1 unknown substituent(s)
                      28.8      1 -O
                       1.4      1 -O
                       4.4      1 -C(=O)-C
                       0.7      general corrections
                                -> 1 increment(s) not found
  CH     103.5       128.5      1-benzene
                        ?       1 unknown substituent(s)
                     -12.8      1 -O
                     -12.8      1 -O
                      -0.1      1 -C(=O)-C
                       0.7      general corrections
                                -> 1 increment(s) not found
   C     162.1       128.5      1-benzene
                        ?       1 unknown substituent(s)
                       1.4      1 -O
                      28.8      1 -O
                       0.1      1 -C(=O)-C
                       3.3      general corrections
                                -> 1 increment(s) not found
```

```
   C      199.8       193.0      1-carbonyl
                       -3.0      1 -1:C*C*C*C*C*C*1
                        6.5      1 -C
                        3.3      general corrections
  CH3      29.6        -2.3      aliphatic
                       29.3      1 alpha -C(=O)-C
                       -4.2      2 gamma -C*C
                        0.3      1 delta -O
                        6.5      general corrections
```

The ^{13}C NMR computational data gathered for the Zn(II) are given below

```
Protocol of the C-13 NMR Prediction:
Node      Shift     Base + Inc.   Comment (ppm rel. to TMS)
   C       95         123.3      1-ethylene
                        7.5      1 -C(=O)N
                          ?      1 unknown substituent(s)
                       -7.4      1 -C
                      -28.0      1 -N
                                 -> 1 increment(s) not found
   C      160.7       165.0      1-amide
                        2.6      1 -C=C-C
                       -4.5      1 -1:C*C*C*C*C*C*1 from N-amide
                       -2.4      1 -N from N-amide
  CH3      39.3        -2.3      aliphatic
                       28.3      1 alpha -N
                        6.9      1 beta -C=C
                       11.3      1 beta -N
                       -2.6      1 gamma -1:C*C*C*C*C*C*1
                       -2.7      1 gamma -C=O
                       -2.5      1 gamma -C
                        0.0      1 delta -N
                        2.9      general corrections
   C      160         123.3      1-ethylene
                        5.8      1 -C(=O)N
                          ?      1 unknown substituent(s)
                        9.4      1 -C
                       21.0      1 -N
                                 -> 1 increment(s) not found
  CH3      12.6        -2.3      aliphatic
                       19.5      1 alpha -C=C
                       11.3      1 beta -N
                       -3.2      1 gamma -C(=O)-N
                       -2.5      1 gamma -C
                       -5.1      1 gamma -N
                        0.3      1 delta -1:C*C*C*C*C*C*1
                        0.0      1 delta -Np
                       -5.4      general corrections
   C      136.3       128.5      1-benzene
                       13.7      1 -N-N
                       -5.9      general corrections
  CH      113.2       128.5      1-benzene
                      -16.5      1 -N-N
                        1.2      general corrections
  CH      129.3       128.5      1-benzene
                        0.5      1 -N-N
                        0.3      general corrections
  CH      119.2       128.5      1-benzene
                       -9.6      1 -N-N
                        0.3      general corrections
  CH      129.3       128.5      1-benzene
                        0.5      1 -N-N
                        0.3      general corrections
  CH      113.2       128.5      1-benzene
                      -16.5      1 -N-N
                        1.2      general corrections
   C      108         128.5      1-benzene
                          ?      1 unknown substituent(s)
                      -12.8      1 -O
                       -7.4      1 -O
                          ?      1 unknown substituent(s)
                                 -> 2 increment(s) not found
   C      159         128.5      1-benzene
                          ?      1 unknown substituent(s)
                       28.8      1 -O
                        1.4      1 -O
                          ?      1 unknown substituent(s)
                                 -> 2 increment(s) not found
  CH      103.6       128.5      1-benzene
                          ?      1 unknown substituent(s)
                      -12.8      1 -O
                      -12.8      1 -O
                          ?      1 unknown substituent(s)
                        0.7      general corrections
                                 -> 2 increment(s) not found
```

```
   C      159          128.5      1-benzene
                          ?       1 unknown substituent(s)
                        1.4       1 -O
                       28.8       1 -O
                          ?       1 unknown substituent(s)
                                  -> 2 increment(s) not found
   C      108          128.5      1-benzene
                          ?       1 unknown substituent(s)
                       -7.4       1 -O
                      -12.8       1 -O
                          ?       1 unknown substituent(s)
                                  -> 2 increment(s) not found
  CH      131          128.5      1-benzene
                          ?       1 unknown substituent(s)
                        1.4       1 -O
                        1.4       1 -O
                          ?       1 unknown substituent(s)
                                  -> 2 increment(s) not found
   C        ?           n.a.      no substructure found
 CH3       17           -2.3      aliphatic
                         9.1      1 alpha -C
                         9.3      1 beta -1:C*C*C*C*C*C*1
                          ?       1 unknown beta substituent(s)
                          ?       1 unknown gamma substituent(s)
                        -0.5      1 delta -Cl
                         0.3      1 delta -O
                          ?       1 unknown delta substituent(s)
                         0.9      general corrections
                                  -> 3 increment(s) not found
```

Conclusion

The tetradentate nature of the ligand is confirmed from the MEP study and the natural atomic charge study of the ligand. The donor atoms of the ligand are found to be azo nitrogen, oxygen atoms of the aromatic hydroxyl group and oxygen atom of the ethanoyl group. The vibration frequencies of various groups of the ligand and its Co(II) complex have been computed under the force fields AM1 and PM3 and the comparison study of the vibration frequencies indicates good correlation coefficient.. The ZINDO program has been used to predict the molecular electronic spectra of Co(II) and Ni(II). The percentage variation between the experimental and computational electronic spectra data is very less. The NMR computational study of ^{1}H spectrum of the ligand and its Zn(II) complex predicts the chemical shifts $(\delta calc)$ and compared with the experimental $\delta expt$ spectral data. The ^{13}C NMR spectra of the ligand and its Zn(II) complex are also predicted. All experimental data relating to IR, NMR and electronic agree well with computational generated data of IR, NMR and electronic spectra.

REFERENCES

Bejler, B. H., Merz, K. M., Kollman, P. A., 1990. Atomic charges derived from semi empirical methods. *Journal of computational chemistry,* **11**, 431 – 439.

Chaulia, S. N., 2016. *Der pharmacia Letter,* **8**(21), 55 – 74.

Chem3D Ultra Molecular modelling and Analysis, Cambridge soft Corporation, 1985 – 2003.

Cornard, J. P., Merlin, J. C., 2003. Complexes of Al(III)with isoquercitrin: Spectroscopic characterisation and quantum chemical calculation. *Polyhedron,* **21**, 2801 – 2810.

Dewar, M. J. S, Zoebisch, E. J., Healy, E. F., Stewart, J. J. P., 1985. AM1; A new general purpose quantum mechanical model. *Journal of the American Chemical Society,* **107**, 3902 – 3909.

Leach, Andrew R., 2009. *Molecular Modelling Principles and applications*. Pearson.

Politzer, P., Murray, J. S., 1991. Molecuar Electrostatic potentials and Reactivity. *Reviews in Computational chemistry,* New York: VCH Publisher, 273 – 312.

Ramachandran, K. I., Deepa, G., Namboori, K. 2008. *Computational Chemistry and Molecular Modelling.* Springer.

Sirichote, O. Hansongnern, K., Sudkeaw, P., 1998. Vibrational frequencies and structure of estragole using semiempirical calculations. *Journal of sci. Soc. Thai.*, **24**, 65 – 71.

Stewart, J. J. P., 1989. Optimisation of parameters for Semi-empirical Methods I. *Journal of computational Chemical Chemistry,* **10**, 209 – 220.

Torda, A. E. & Gunsteren, W. F., 1992. *Molecular modelling using NMR data, Reviews in Computational chemistry,* **2**. New York: VCH Publisher, 143 – 172.

Wolinski, K., Hinton, J. F., Pulay, F., 1990. Efficient implementation of the gauge atomic orbital method for NMR chemical shifts calculation. *J. of Am. Chem. Soc.,* **112**, 8251 – 8260.

Zerner, M. C., 1991. *Semi-empirical Molecular orbital methods, Reviews in Computational chemistry,* **2**. New York: VCH Publisher, 313 – 366.

✉ **Satya Narayan Chaulia (corresponding author)**
ORCID iD: 0000- 0001-5699-1892
Rajendra (Auto) College
Balangir
767002 Odisha, India
E-mail: satyanarayanchaulia@gmail.com