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SEMI-EMPIRICAL COMPUTATIONAL STUDY OF THE LIGAND AND ITS METAL COMPLEXES DERIVED FROM 4- AMINOANTIPYRINE AND 2, 4-DIHYDROXY BENZOIC ACID

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Abstract. Theoretical molecular structures of the ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes have been studied using the semi-empirical quantum chemical methods. The experimental IR, electronic and NMR data of the investigated compounds are compared with the computational data. The ESP map and the natural atomic charge of the ligand was calculated to ascertain the reactive sites of the ligand. The experimental data agree well with the computational data.

Keywords: MEP; natural atomic charge; correlation coefficient; AM1; PM3

Introduction

Molecular modelling is an important aspect of computational chemistry because any molecular system which is difficult, dangerous, impossible to handle experimentally can be analysed computationally to get the stability, reactivity and geometrical pictures of the system. Molecular modelling is a quite accurate method in gathering data relating to geometric, electronic structures, vibration frequencies, chemical shifts, bond angles, bond distance (Mahmood et al., 2015). It is also providing information to increase the understanding of various biochemical processes such as enzymatic reactions, photosynthesis. The semi-empirical, ab-initio and DFT methods have been used in recent times successfully in predicting the geometrical, vibrational frequencies and chemical shifts of various chemical systems. It has been reported that the semi-empirical PM3 level of theory has predicted the IR frequencies of complex compounds more closely to experimental data than other methods (Topacli & Topacli, 2003). The structural model of a Al(III) complex has been confirmed due to a close agreement between the experimental and theoretical electronics spectral data (Sirichote et al.,1998).

The present theoretical study is based on the metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) of azo dye ligand derived from 4-Aminoantipyrine and 2, 4-dihydroxy benzoic acid. The synthesis and characterisation of the ligand and its metal complexes has already been reported (Chaulia, 2016). The present study is concentrated on the theoretical study involving MEP study of the ligand, analysis of Mulliken charges of the ligand and comparison of the experimental vibration frequencies, chemical shifts and electronic spectra.

Computational methods

In this work, all the calculations were performed with the MOPAC programme Chem3D Molecular Modelling and Analysis Cambridge soft programme package.$^{1)}$ The structures of the investigated compounds were drawn using the same programme. The structure optimisation of the ligand and its metal complexes were performed by using the PM3 method with the RMS gradient 0.001.

Results and discussion

Natural atomic charge

The distribution of charges in a molecule determines electronic properties such as polarisability and dipole moment (Bejler et al., 1990). Hence, the atomic charges at different sites of the ligand was calculated using BLYP method using 3 – 21(d-p) basis set and summarised in the Table 1. Both oxygen and nitrogen atoms have the most electronegative natural charge but the oxygen atoms are more electronegative than the N atoms. The C6, C8, C10, C11, C12, C13, C19, C21 and C9 are electronegative as they away from the N and O atoms while other carbon atoms are electropositive. All the hydrogen atoms are also electropositive. Therefore, nitrogen atom of the azo group, oxygen atoms of the hydroxyl group(-OH) and carboxy (COOH) can act as the donor atoms. The metal can be coordinated to the ligand through the donor atoms (Figs. 1 and 2).

MEP study of the ligand

The electrostatic potential map(MEP) study of the ligand as given in the Fig. 3 was made to indentify the electrophilic and nucleophilic reactive sites present in the molecule (Politzer & Murray,1991). The map also gives information regarding charge distribution of the molecule. The MEP was calculated using BLYP method using 3 – 21(d-p) basis set. The red colour of the map reflects the reactive sites of electrophilic attack and the blue colour indicates the reactive sites of nucleophilic attack. It was seen from the map that negative region (red colour) is found over nitrogen atoms of the azo group and oxygen atoms of the hydroxyl (-OH) and acidic (-COOH) group. Hence, the metal ion can coordinate with the azo nitrogen and oxygen atoms of the hydroxyl(-OH) and acidic(-COOH) group of the ligand which is supported by the natural atomic charge.

Table 1. Natural atomic charges

Bond	charge	Bond	charge	Bond	charge	Bond	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

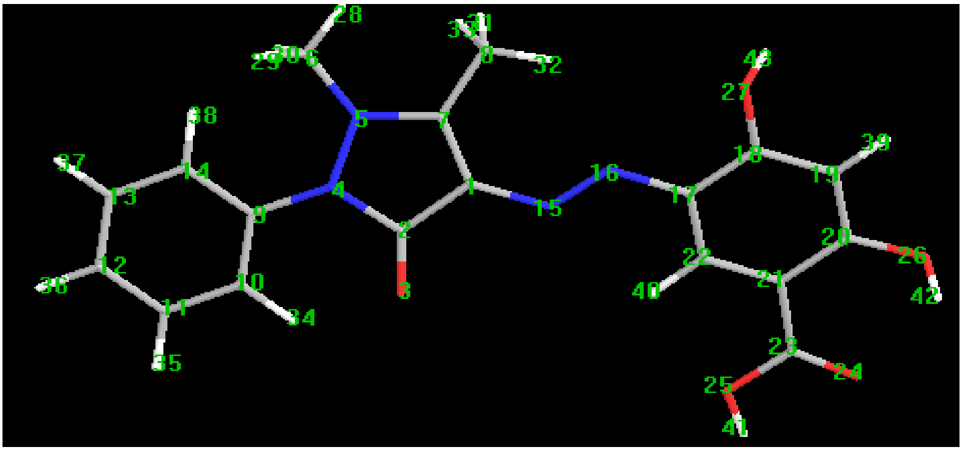

Figure 1. Optimised geometry of the ligand

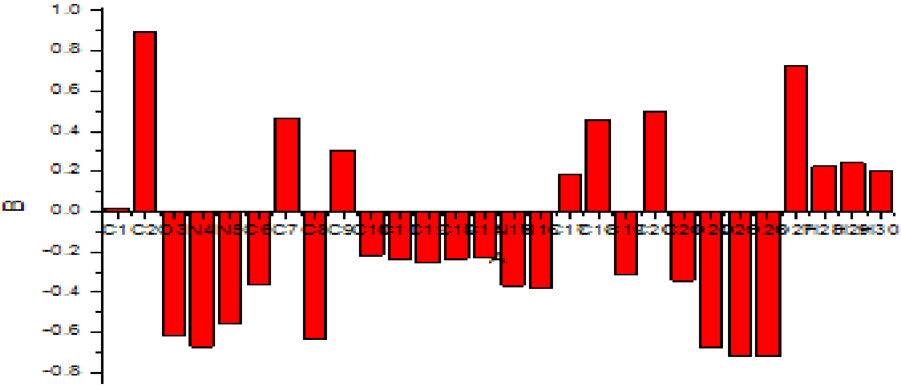

Figure 2. Histogram of Mullikan charge of the ligand

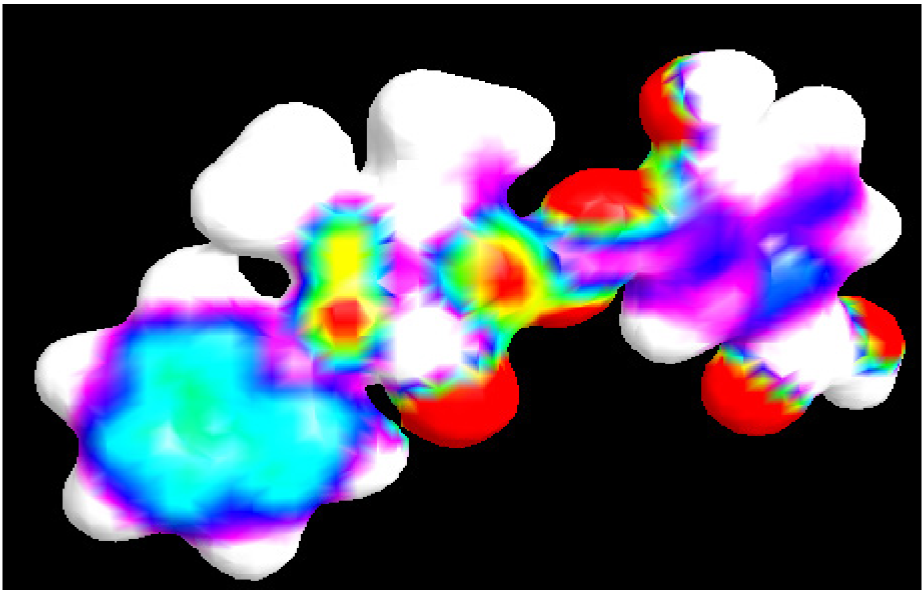

Figure 3. MEP of the ligand

IR study

The IR study the ligand and its metal complexes were undertaken in our previous study to characterise the investigated compounds, but in this study attempts has been made to compare the experimental vibration data with the computational data. Here semi-empirical study has been made using the force field AM1 (Dewar et al.,1985) and PM3 (Stewart, 1989) because semi-empirical models are less expensive and less time consuming and are providing the better results (Cornard & Merlin, 2003).

The IR spectrum of the ligand as given in the Fig. 4 shows a broad band at 3434 cm^{-1} due to the O-H stretching vibration. That band is missing from the spectra of the metal complexes as given in the Fig. 5 and Tables 2 and 3. The AM1 and PM3 force fields indicate vibrational frequencies at 3440 cm^{-1} and 3444 cm^{-1} respectively. The (C-O) vibration frequency of the ligand is observed at 1270 cm^{-1} but AM1 force field predicts it at 1279 cm^{-1} and PM3 force field indicates at 1257 cm^{-1}. This (C-O) frequency is shifted to ~ 1236 cm^{-1} in metal complexes, the computational study for the Co(II) metal complex reveals it at 1199 cm^{-1} and 1226 cm^{-1} under the AM1 and PM3 force fields respectively, this fact confirms deprotonation of the phenolic(OH) group and the bonding between the metal ions and oxygen atoms. In the spectrum of the ligand, a band is seen at 1493 cm^{-1} due to (N=N) vibration but

AM1 and PM3 force fields predicts at 1497 cm^{-1} and 1457 cm^{-1}. This band is shifted to ~ 1456 cm^{-1} but computational study of Co(II) indicates at 1465 cm^{-1} under AM1 and PM3 force fields suggesting bonding between azo nitrogen and metal ions. The monodentate nature of –COOH group is confirmed from the band at 1411 cm^{-1} due to $(COO^-)_{sym}$ vibration and at 1632 cm^{-1} due to $(COO^-)_{asym}$ vibration. The AMI force field indicates at 1406 cm^{-1} and 1633 cm^{-1} and PM3 for predicts at 1366 cm^{-1} and 1579 cm^{-1} for to $(COO^-)_{sym}$ and $(COO^-)_{asym}$ vibrations. These bands observed in the spectra of metal complexes at ~1386 cm^{-1} due to $(COO^-)_{sym}$ stretching and at ~1621 cm^{-1} due to $(COO^-)_{asym}$ stretching. The AM1 force field for the Co(II) complex predicts it at 1364 cm^{-1} and at 1634 cm^{-1} for $(COO^-)_{sym}$ and$(COO^-)_{asym}$ respectively, However, the PM3 force field for it indicates at 1366 cm^{-1} and 1579 cm^{-1}. All these observations confirm the bonding between the metal ions and oxygen atom of the carboxyl group.

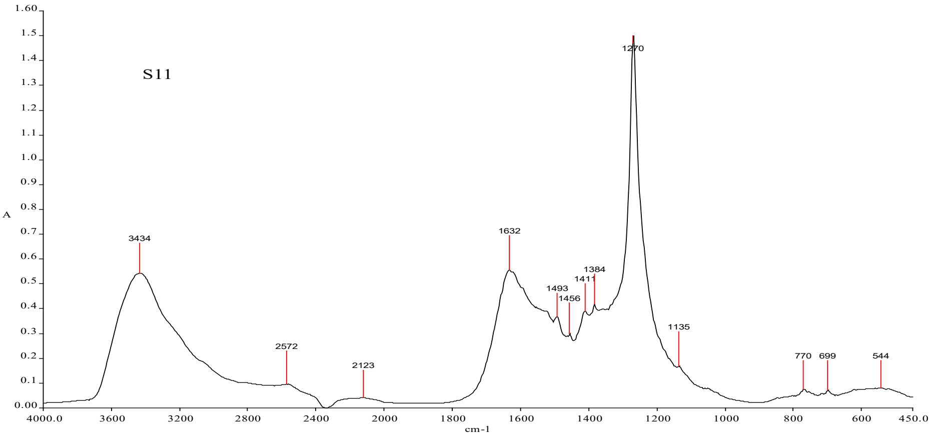

Figure 4. IR spectrum of the ligand

Table 2. IR data of the investigating compounds

compound	υ(C-O) cm^{-1}	υ(N=N) cm^{-1}	υ(COO-)sym cm^{-1}	υ(COO-)asym cm^{-1}	υ(M-O) cm^{-1}	υ(M-N) cm^{-1}
1	1270	1493	1411	1632	-	-
2	1236	1456	1386	1621	606	585
3	1234	1456	1385	1588	605	585
4	1235	1455	1385	1587	604	584
5	1236	1454	1384	1586	604	585

1-ligand, 2- Co(II) complex, 3-Ni(II)complex, 4- Cu(II) complex and 5- Zn(II) complex

Table 3. Experimental and computational vibration frequency data of the ligand

Band	EXPT		AM1		PM3
	v/cm^{-1}	v/cm^{-1}	Intensity	v/cm^{-1}	Intensity
(C-O)	1270	1279	3.414	1257	0.519
(N=N)	1493	1497	18.669	1457	25
(O-H)	3434	3440	12.341	3444	26
$(COO-)_{sy}$	1411	1406	20.933	1366	5
$(COO-)_{asym}$	1632	1633	119.984	1579	75

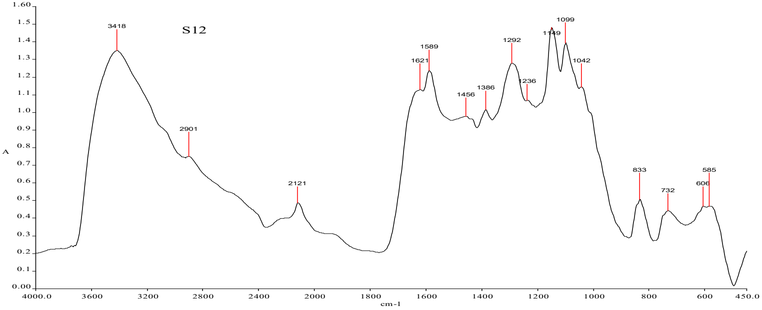

Figure 5. IR spectrum of the Co(II) complex

The calculated and experimental vibration frequencies of the ligand have been compared as provided in the Figs. 6 and 7. The correlation coefficient between the vibration frequency calculated by AM1 method and the experimental data is 1, whereas the correlation coefficient between the vibration frequency calculated by PM3 method and the experimental data is 0.998 while the percentage variation in both the methods is less than 5.

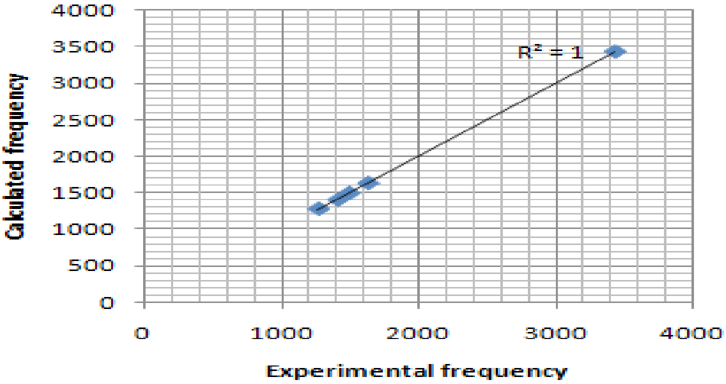

Figure 6. Correlation Graph between experimental and calculated frequency

(AM1) of the ligand

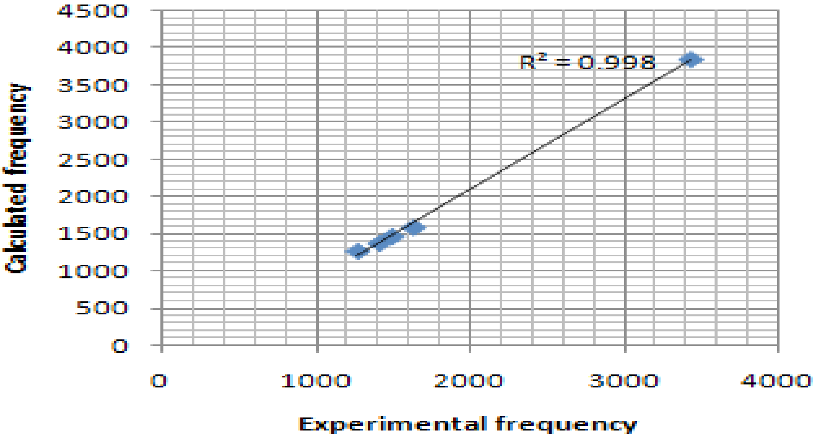

Figure 7. Correlation Graph between experimental and calculated frequency (PM3) of the ligand

Table 4. Experimental and computational vibration frequency data of the Co(II) complex

Band	EXPT		AM1		PM3
	v/cm^{-1}	v/cm^{-1}	Intensity	v/cm^{-1}	Intensity
(C-O)	1236	1199	54.12	1226	0.519
(N=N)	1456	1465	462.272	1465	25
(O-H)	3418	3494	25.167	3882	26
(COO-)$_{sy}$	1386	1364	3.285	1348	5
(COO-)$_{asym}$	1621	1634	116	1647	75
M-O	606	629	21	595	5
M-N	585	546	11	544	4

The comparison between the experimental and calculated vibration frequency of the Co(II) has been made and it provides the correlation coefficient 0.999 and 0.996 for the AM1 and PM3 methods respectively (Figs. 8 – 11) and percentage variation for both methods is less than 5. It has been established from the experimental and calculated data that the ligand has been coordinated with the metal ions through azo nitrogen atom, oxygen atoms of the aromatic hydroxy and carboxylate group (Fig. 12).

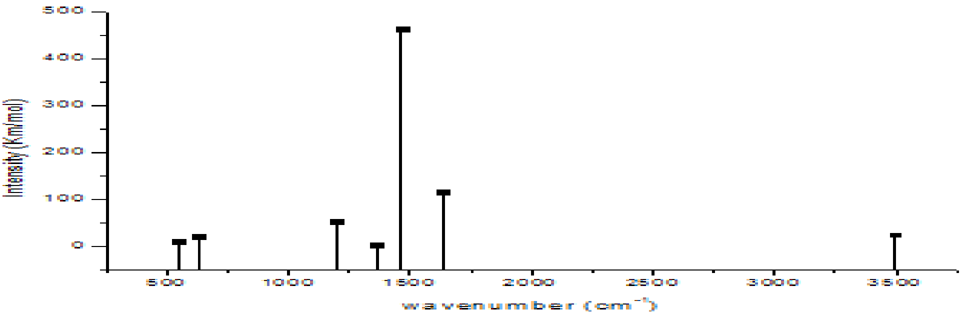

Figure 8. Calculated vibration frequency of the Co(II) complex by AM1 method

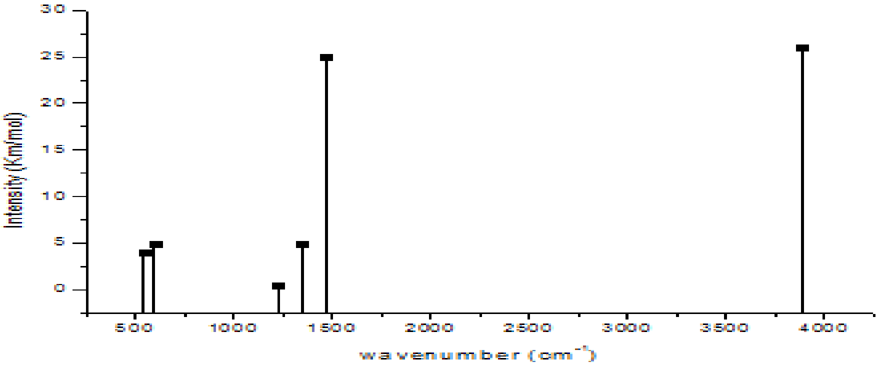

Figure 9. Calculated vibration frequency of the Co(II) complex by PM3 method

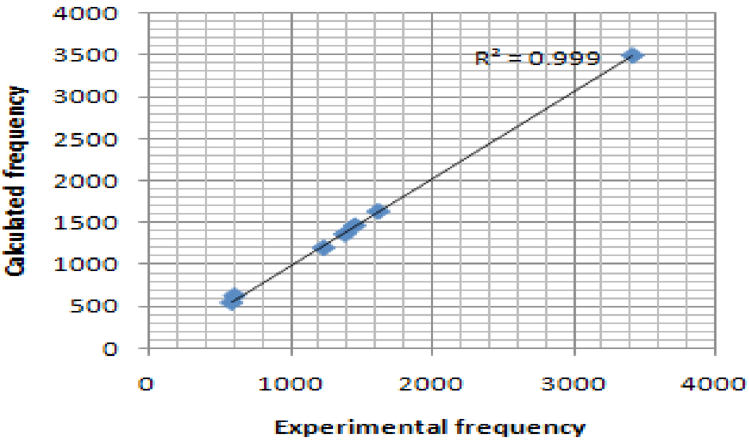

Figure 10. Correlation Graph between experimental and calculated frequency(AM1) of the Co(II) complex

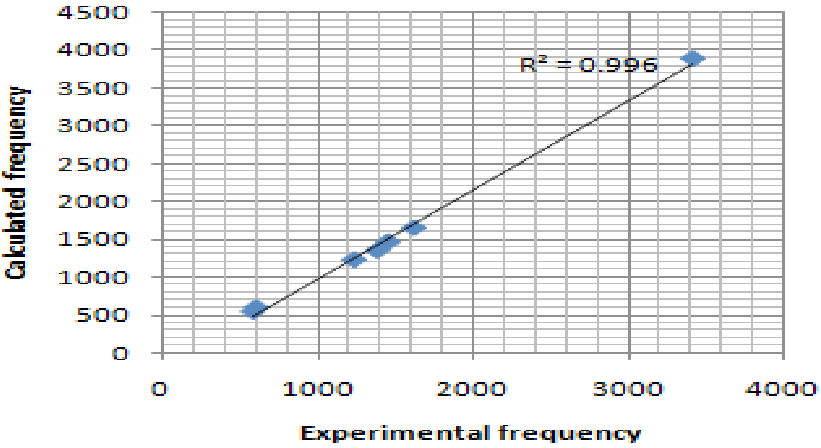

Figure 11. Correlation Graph between experimental and calculated frequency(PM3) of the Co(II) complex

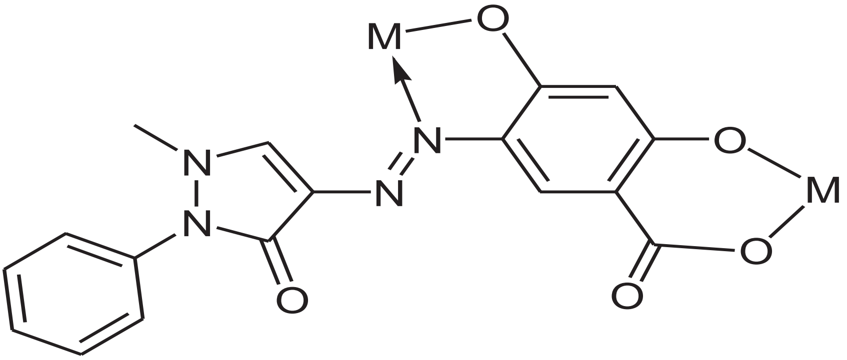

Figure 12. Structure of the ligand with the metal ions

NMR spectra

The computational NMR study of the ligand and its Zn(II) complexes were undertaken to predict the ^1H chemical shifts (δ *ppm*) and the computational data were correlated with the experimental data (Torda & Van Gunsteren, 1992]. The gauge independent atomic orbital method has been used for calculating the NMR chemical shifts (Wolinski et al.,1990). The results predict the experimental NMR data are in good agreement with the calculated data of the ligand and its Zn(II) complex. A good correlation between the calculated and experimental chemical shifts was obtained with R^2 = 0. 989 which is depicted in the Fig. 15.

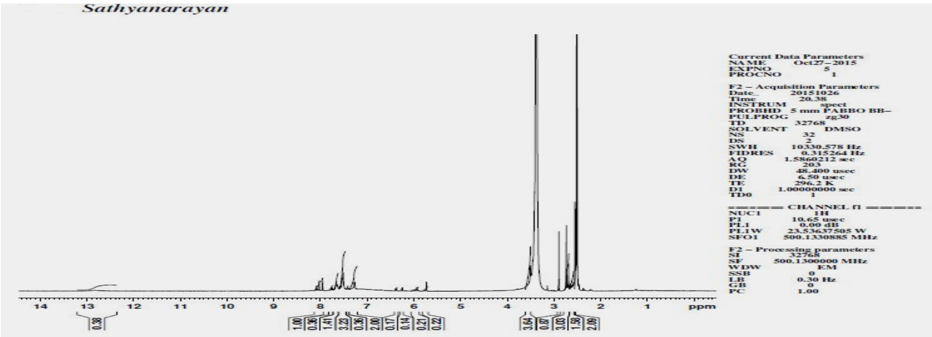

Figure 13. Experimental NMR spectra of the ligand

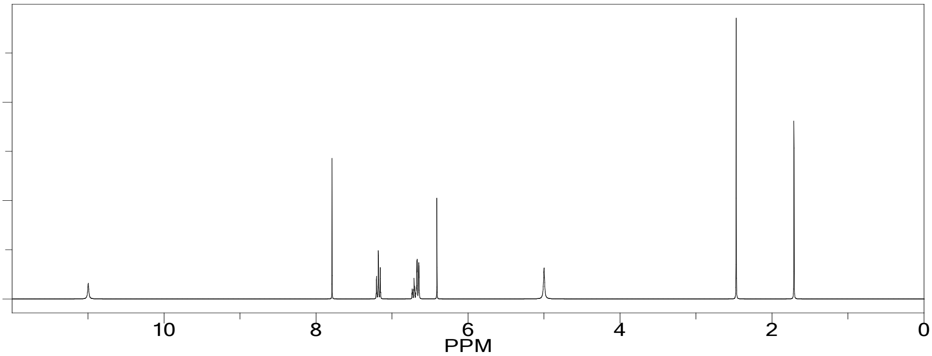

Figure 14. Calculated NMR spectra of the ligand

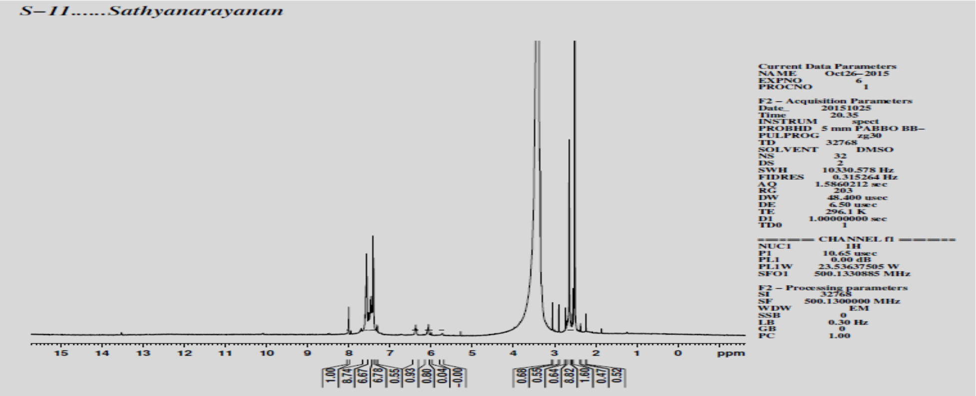

Figure 15. Experimental NMR spectra of the Zn(II) complex

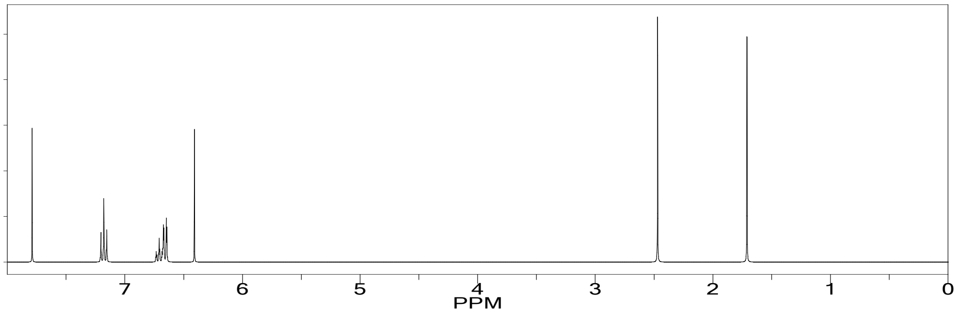

Figure 16. Calculated NMR spectra of the Zn(II) complex

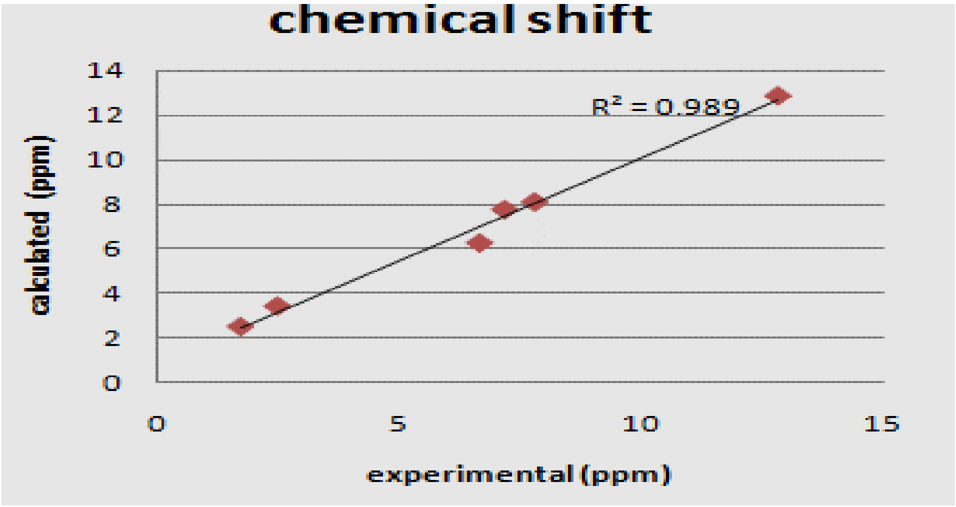

Figure 17. Correlation graph between calculated and experimental chemical shifts of the ligand

Electronic spectra

The semi empirical methods have been used to calculate excited states and hence to predict UV spectra. 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 computational study of the Co(II)complex predicts spectral bands at 13850 cm^{-1}, 18867 cm^{-1}, 24271 cm^{-1} and 39370 cm^{-1} corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$,

$^4T_{1g}(F) \rightarrow \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$and CT transition bands. The theoretical spectral bands were compared with the experimental spectral bands and the correlation coefficient was found to be 0.985 and percentage variation is less than 5.

Similarly, Ni(II) complex predicts spectral bands at 13280 cm^{-1}, 20161 cm^{-1}, 29096 cm^{-1} and 33670 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and CT band transition bands. A good correlation was obtained between the experimental and calculated data ($R^2 = 0.954$) and percentage variation is less than 5.

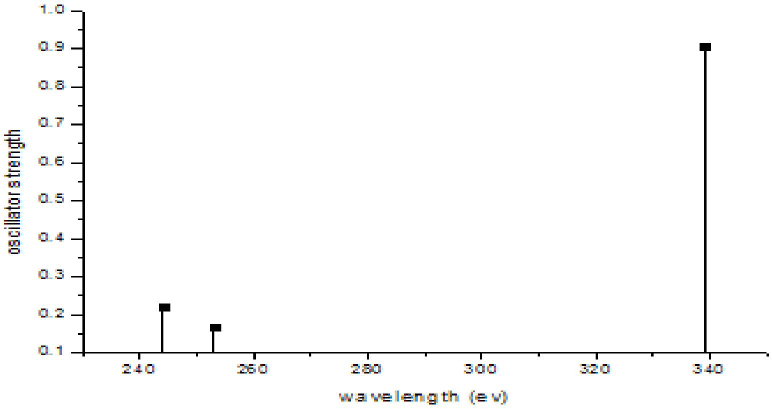

Figure 17. Calculated electronic spectrum of the ligand

Table 5. Experimental and calculated wavelength of the ligand and its metal complexes

compound	Expt wavelength(nm)	Calcd wavelength(nm)	assignment
Ligand	275 245	339 253	n-π*
$[CoL_2(H_2O)_2]$	12820 16447 22739 32258	13850 18867 24271 39370	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F \rightarrow {}^4T_{2g}(P)$ CT
$[NiL_2(H_2O)_2]$	15625 22220 25967 32786	13280 20161 29096 33670	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ CT
$[CuL_2(H_2O)_2]$	15350	13642	$^2E_g \rightarrow {}^2T_{2g}$

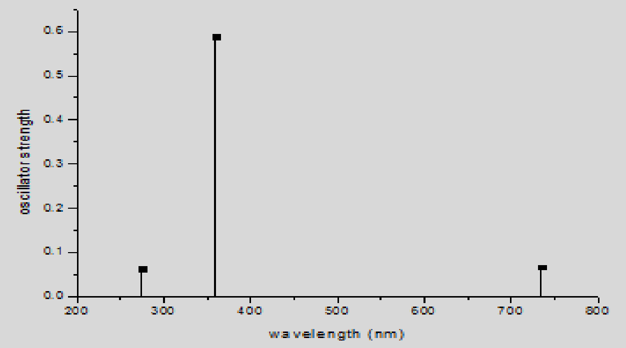

Figure 18. Calculated electronic spectrum of the Cu(II) complex

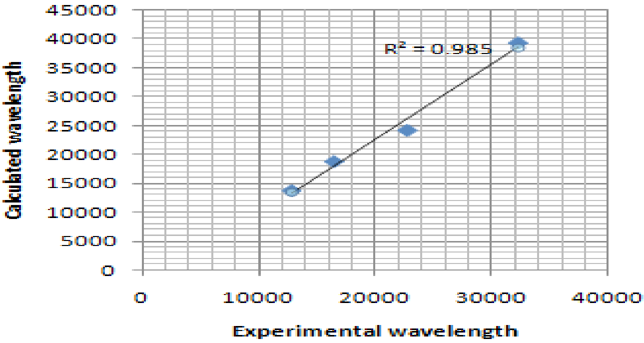

Figure 19. Correlation graph between calculated and experimental wavelength of Co(II) complex

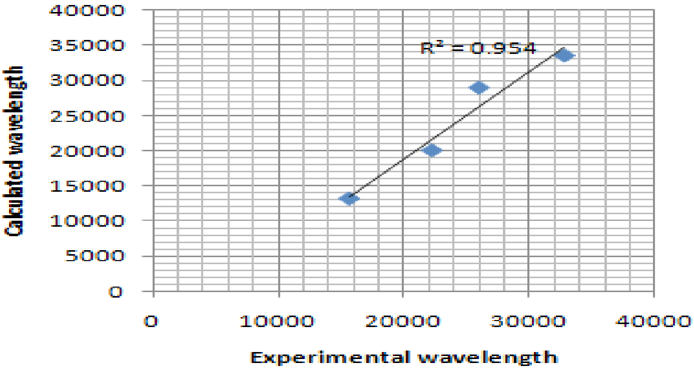

Figure 20. Correlation graph between calculated and experimental wavelength of Ni(II) complex

Conclusion

The MEP study and the natural atomic charge study of the ligand confirm the tetradentate nature of the ligand with azo nitrogen, oxygen atoms of the aromatic hydroxyl group and oxygen atom of the carboxylate 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. The NMR computational study of ^{1}H spectrum of the ligand and its Zn(II) complex predicts the chemical shifts $(\delta calc)$ $(\delta calc)$ and compared with the experimental $\delta expt \delta expt$ spectral data. The ZINDO program has been used to predict the molecular electronic spectra of Co(II) and Ni(II) and the comparison study of the vibration frequencies indicates good correlation coefficient. The percentage variation between the experimental and computational results is very less. As azo dyes and their complexes find application in the dye sensitised solar cells, the investigated compounds may be examined in future.

NOTES

1. http://www.cambridgesoft.com/support/DesktopSupport/Documentation/Manuals/files/chem3d_9_english.pdf

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