International Journal on Emerging Technologies **10**(3): 311-317(2019)

ISSN No. (Print) : 0975-8364
ISSN No. (Online) : 2249-3255

Synthesis and Characterisation of Metal Complexes of 2-[(1-methyl-1H-Tetrazole-5-yl)thio]-N'-[(1E)-4-methyl-1,3-thiazole-5 yl) Methylene] Acetohydrazide

Akilandeswari J.[1], Joseph Selvaraj S.[2], and Saravanan D.[3]
[1]Research Scholar, Department of Chemistry, St. Joseph's College, Tiruchirappalli, Tamil Nadu, India.
[2]Associate Professor, Department of Chemistry, St. Joseph's College, Tiruchirappalli, Tamil Nadu, India.
[3]Associate Professor, Department of Chemistry, National College, Tiruchirappalli , Tamil Nadu, India.

(Corresponding author: Akilandeswari J.)

(Received 27 June 2019, Revised 30 August 2019 Accepted 28 September 2019)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: The ligand 2-[(1-methyl-1H-Tetrazole-5yl)thio]–N'-[(1E)-4-methyl-1,3-Thiazole-5-yl) methylene] acetohydrazide Was synthesized and the complexes with metal chlorides such as Co(II), Ni(II) and Metal perchlorates of Co(II) were synthesized by green methods and characterized on the basis of IR, and H^1 NMR , UV-Visible molar conductivity, Cyclic voltammetric analysis and Magnetic susceptibility Measurements. Spectral data reveal that ligands chealated with metal through N-atoms. Magnetic susceptibility measurements favors octahedral coordination for Co(II), Ni(II) metal complexes.

Keywords: Transition metal complexes, Green synthesis, Tetrazole-2-Thiol derivatives, Thiazole.

Abbreviations: FT IR Fourier transform infrared, ^{1}HNMR Proton Nuclear magnetic resonance, DMSO Dimethyl sulphoxide, TMS tetramethyl silane.

I. INTRODUCTION

Transition metal ions play an important role in a number of chemical and biological reactions. The metal complexes of heterocyclic ligands having azomethine group such as oximes, thiosemicarbazones, semi carbazones, hydrazones were reported [1-3]. Hydrazones are characterized by the presence of triatomic grouping >C=N-N<. These can be considered as Schiff bases derived from acid hydrazides. These Schiff base metal complexes have been studied extensively for years due to the synthetic flexibilities of these ligands and their selectivity as well as sensitivity towards transition metal ions [4]. Biological resemblance of Schiff bases is due to the structural resemblance of peptide bonds in protein [5]. Hydrazide and hyrdrazones occupy a special place due to their chealating capability, Structural flexibility and interesting electrical as well as magnetic properties [6]. The metal complexes with these ligands exhibit many types of applications like catalysis [7], Pharmaceuticals [8] and molecular based materials [9].

II. MATERIALS AND METHODS

All the chemicals and solvents used were of analar grade. All the reagents used for the preparation of Schiff bases were obtained from sigma Aldrich. The electronic spectra in Ethanol were recorded on perkin elmer lambda 35-2B-spectrometer. Molar conductance measurements were conducted by using 10^{-3} M solutions of the complexes in acetonitrile, on Elico 82-33 conductivity bridge at room temperature. Magnetic susceptibility measurements were carried out on a guoy balance at room temperature using mercuric thiocyanato cobaltate (II) as the calibrant. Dia-magnetic corrections were applied in compliance with Pascal`s constant. FT-IR spectra are recorded in KBr medium on a Perkin Elmer spectro photometer in wave Spectrometer number region 400 cm^{-1} – 4000 cm^{-1}, H1 NMR spectra were recorded on Bruker spectrometer employing TMS as internal reference and DMSO –d_6 as solvent.

Syntheses of 2-[(1-methyl-1H-Tetrazole-5-yl)thio]-N`-[(1E)-(4-methyl-1.3-thiazole-5yl) methylene] acetohydrazide

Anhydrous sodium carbonate (55 m mol) was added to a solution of [(1-methyl-5-mercapto-Tetrazole) Thiol] in acetone (50 ml). To the reaction mixture, ethyl bromo acetate (100 m mol) and few drops of freshly prepared lemon juice was added slowly at room temperature under stirring. The progress of the reaction was monitored by thin layer chromatography using a mixture of ethyl acetate and n-hexane (3:7) as eluent. The by product sodium bromide was removed by filtration. The mother liquor containing the products was concentrated under vacuum to remove acetone and residual acetone was removed using methanol to give its thio acetate derivative. The residue was used for next step as such the residue thus collected was dissolved in methanol (30 ml), to the clear solution Hydrazine hydrate (200 m mol) was added and refluxed in a microwave oven. The progress of the reaction was monitored by thin-layer chromatography using a mixture of chloroform and methanol (9:1) as eluent. The reaction mass was cooled to 0 degree centigrade for crystallisation. On filtration and washing with chilled methanol acylated hydrazine derivative of heterocyclic compound was synthesised by the following procedure disclosed above, use of 4-Methyl-1, 3-Thiazol-5-carbaldehyde yielded 2-[(1-methyl-1H-Tetrazole-5yl) methylene] acetohydrazide.

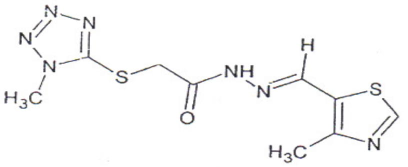
Synthesis of metal complexes

The metal complexes were prepared by mixing of (50 ml) ethanolic solution of metal salts with the 50 ml ethanolic solution of Schiff bases in 1:6 (metal: ligand) ratio . The resulting mixture was refluxed in microwave oven for 5-10 minutes. A coloured product appeared on standing and cooling the above solution. The precipitated complex was filtered and washed with ether and recrystallised with ethanol several times and dried over anhydrous $CaCl_2$ in a dessicator [10].

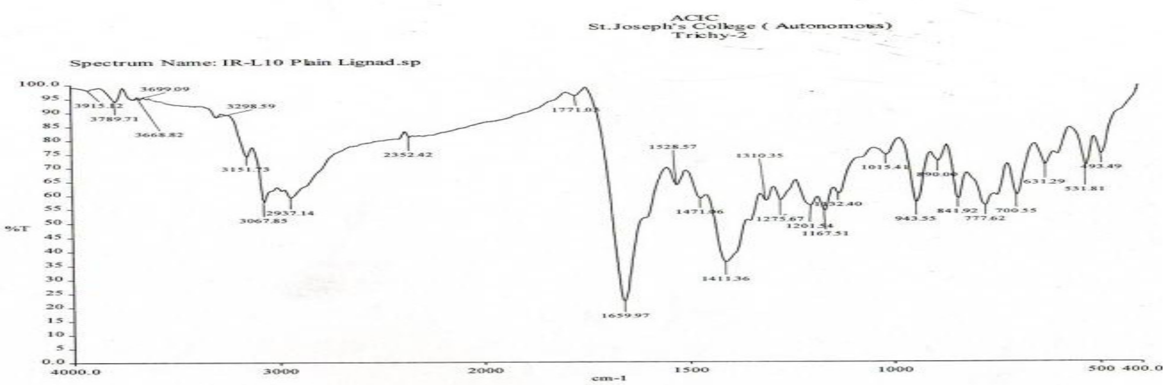
III. RESULTS AND DISCUSSION

Ligand

Melting point of the ligand is 297.36℃ and it is soluble in methanol, DMSO and in acetonitrile. The structure of the ligand is given below.



FTIR spectrum of plain ligand



IR spectrum of the ligand exhibits sharp peak at 3298 cm^{-1} (NH-stretching), 773 cm^{-1} (NH wagging), 631 cm^{-1} (C-S), 2937cm^{-1} (aliphatic C-H), 1659 cm^{-1} (Amide (I) band), 1528 cm^{-1} (C=N), 1201 cm^{-1} (C-N), 1015 cm^{-1} (N-N), 1411 cm^{-1} (aliphatic CH_3 deformation)

NMR spectra:

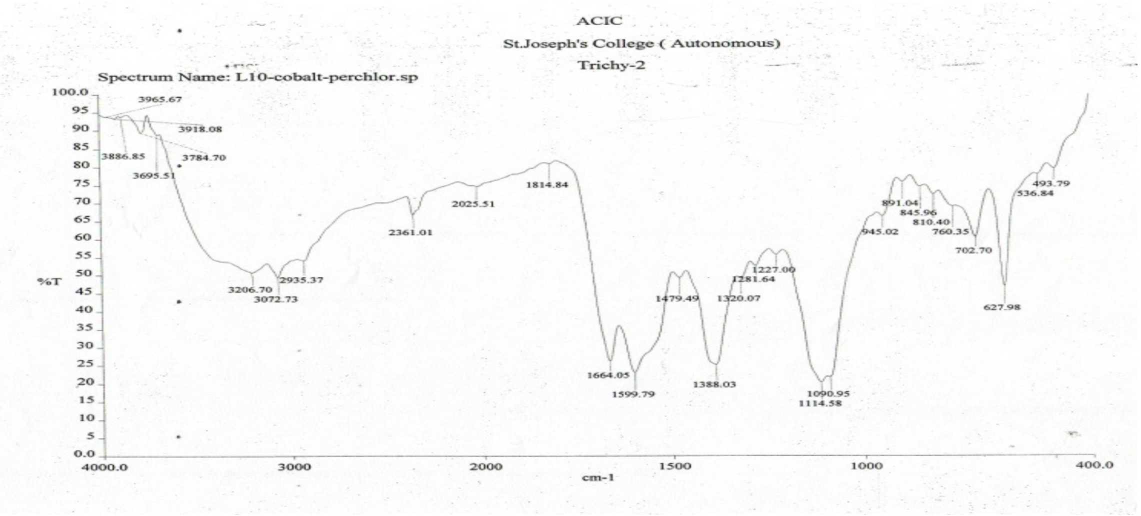
NMR spectrum of ligand showed ^{1}H-NMR 2.47 (3H,S, Thiazole, CH_3), 3.98 (3H, S, NCH_3), 4.16 and 4.51 (2H, S, SCH_2), 8.28 and 8.46 (1H,S,=CH) ,9.06 (1H,S, thiazole, CH), 11.763 (1H , S , NH)

Molar conductance and UV spectra.

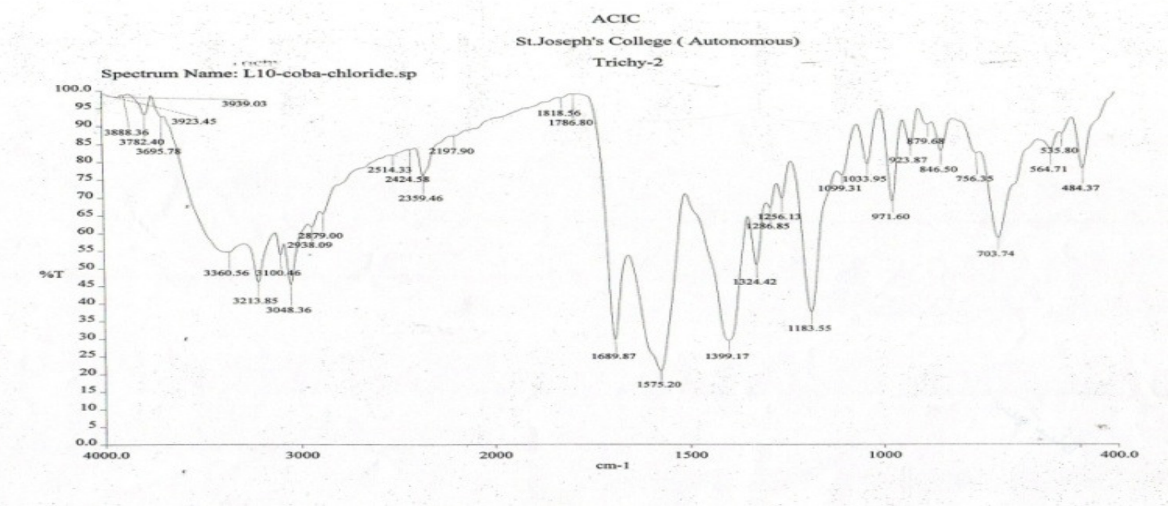
The molar conductance of the complexes were found to be ranging from140-ohm^{-1} cm^2 mol^{-1} to 22 ohm^{-1} cm^2 mol^1. This evidences non electrolytic behaviour of the complexes. No change in the conductance is observed when determined in various solutions this further substantiates the non electrolytic nature of these three chloride complexes of Ni(II), Cu(II), Co(II) are all non-electrolytes. The magnetic moments of the complexes are in consistent with the expected values for the given geometries of complexes. The purple colour of cobalt chloride complex and strong absorption at 15361 cm^{-1} suggests 4T1g (F) -> 4T1(g) (P) transition of octahedral geometry. In metal complexes the appearance of broad band at 23,866 cm^{-1} showed the transition of 3A2(g) -> 3T1(g) (P) suggesting octahedral geometry and another transition of 13793 cm^{-1} favours 3A2(g) -> 3T1(g) (F) strongly favours octahedral structure for nickel chloride complexes.

Magnetic susceptibility

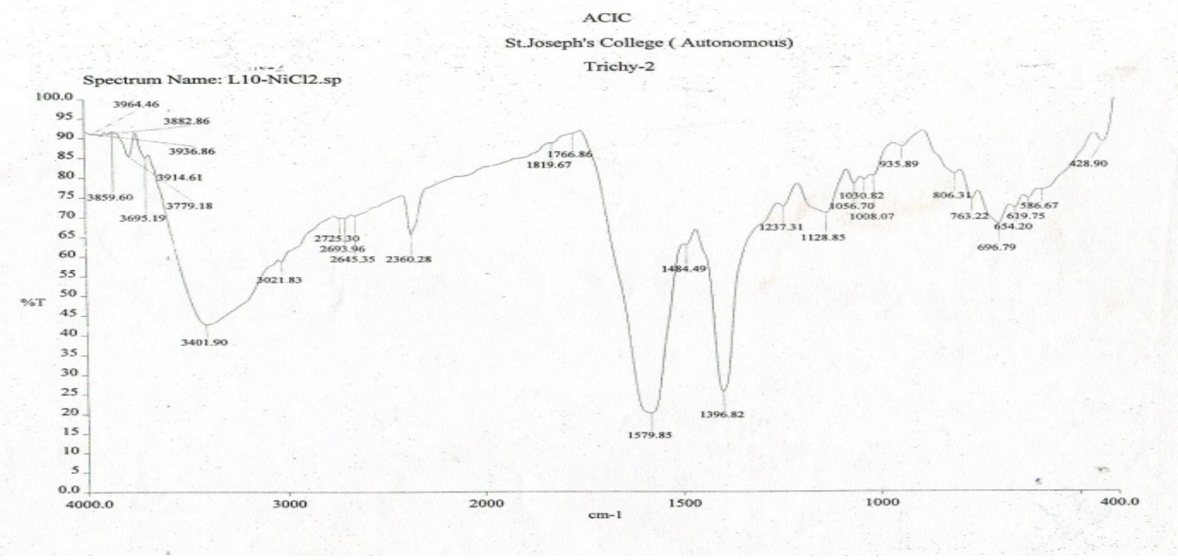
Magnetic susceptibility was measured by using guoy balance. The guoy method [11] was used to determine the magnetic susceptibilities of the complexes at room temperature. The tube was filled uniformly with the powdered sample up to the mark and suspended vertically by means of an aluminium chain from the pan of a sem micro one pan mettler balance in such a way that the bottom of the tube was at the centre of the pole faces. The mark at the top of the tube was essentially out of the magnetic field. Under this condition when the field was on, the cylindrical sample experienced magnetic gradient causing an apparent change in the weight of the sample. Mercury Tetra thiocyanato cobaltate (II) was used as the calibrant. The weights of the sample in the presence and in the absence of magnetic fields were taken. After determining the apparent change in the weight of the sample, its gram susceptibility(χ_g) and magnetic moment μ_{eff} was calculated by using the formulae $X_{g\,=}$ ($\alpha + \beta$ F') / W and μ_{eff} = 2.84 $(\chi_m\ T)^{1/2}$ where χ_g is gram susceptibility α and β are constants for a particular tube F' is the total pull on the specimen in mgm and W is the weight of the sample and μ eff is magnetic moment and T is the temperature on the absolute scale**.** The magnetic moment thus calculated as 2.9 BM confirms the octahedral geometry.

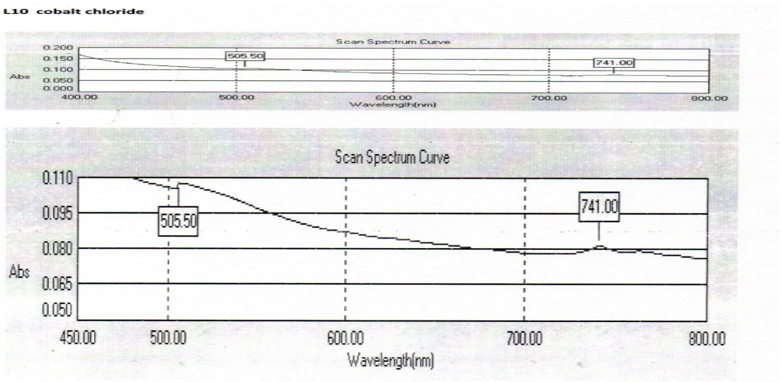


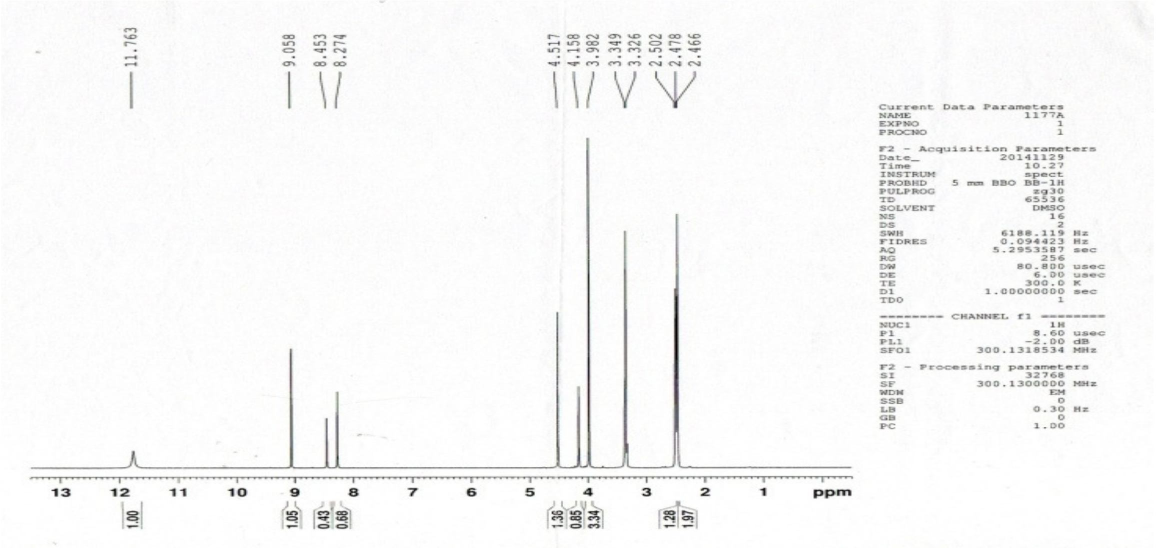
Electronic spectra of metal complexes



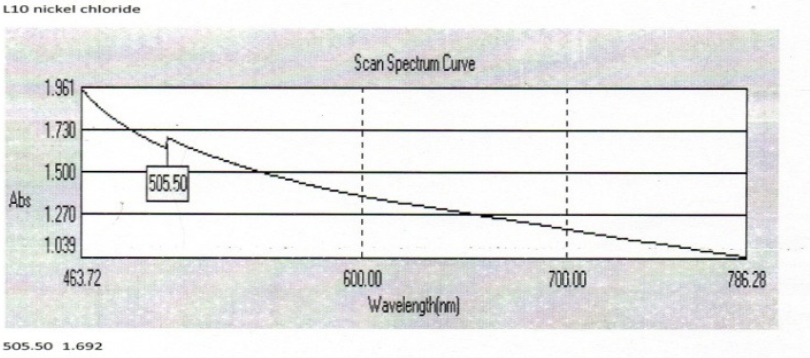
FT-IR, NMR and Electronic spectra of Metal Complexes:







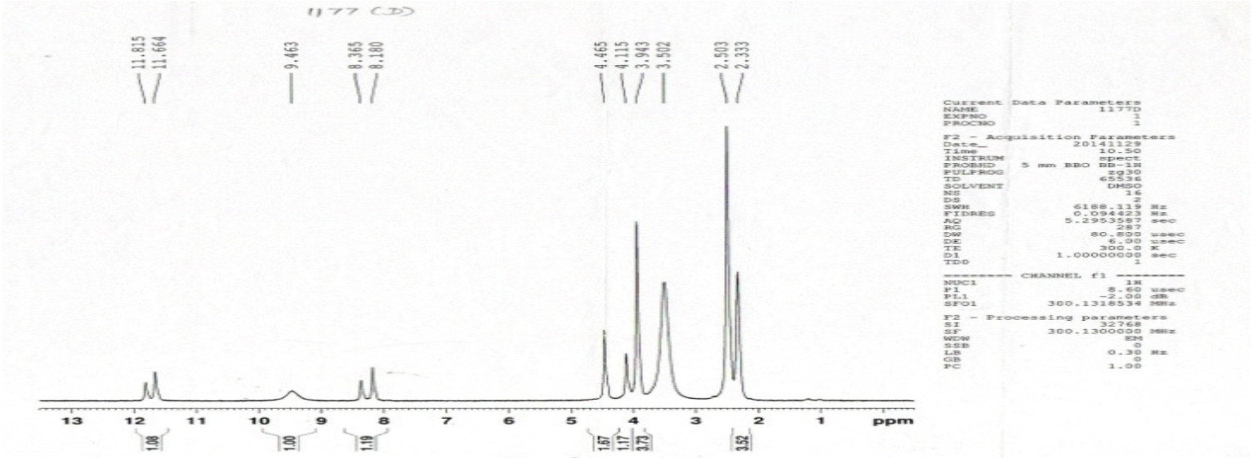
```
Current Data Parameters
NAME                  1177A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141129
Time                  10.27
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES             0.094423 Hz
AQ                5.2953587 sec
RG                      256
DW                   80.800 usec
DE                     6.00 usec
TE                    300.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.60 usec
PL1                   -2.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



Comparison of the IR spectrum of the ligand with IR spectra of the complexes suggest that the co-ordination of the, peptide linkage N-with metal ion. The positive shift of amide (I) band (-NH stretch) suggest the co-ordination of the peptide linkage` N` with the metal ion and the oxygen of the peptide linkage is not involved in the co-ordination. The negative shift of the ligand in the form of feeble vibration in NH bending 1528 cm^{-1} and the negative shift of C-N stretch at 1201 cm^{-1} –1225 cm^{-1} confirms the co-ordination of peptide linkage N- with the metal ions. The stretch in between 536 cm^{-1} – 540 cm^{-1} which is found only in the IR spectra of complexes are assigned to M-N stretch. The other stretches are not very much affected in the spectra of complexes in comparison with that of ligand [12].

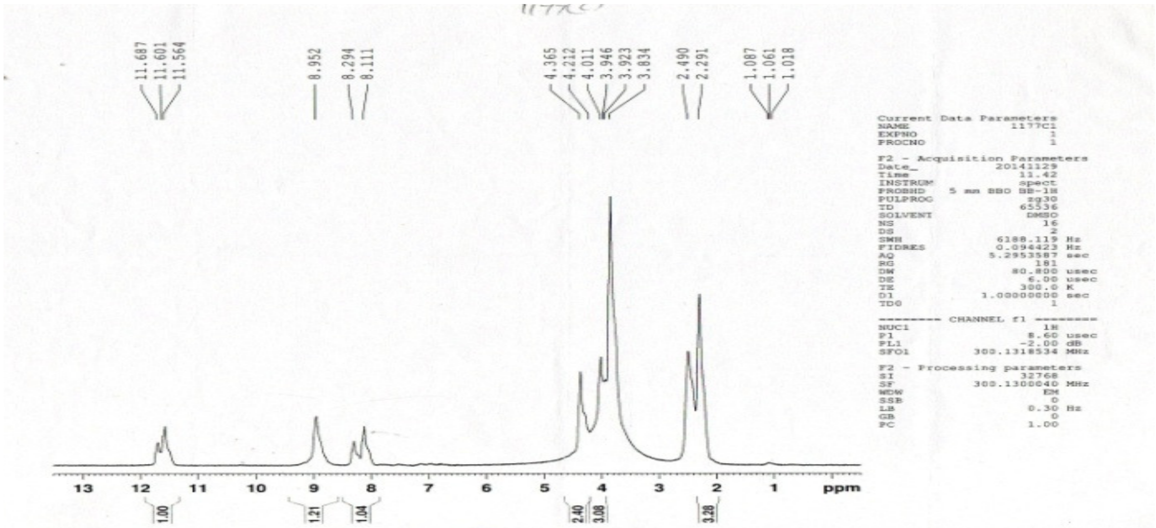
H^1 NMR spectra of cobalt (II) complexes

The complex exhibited ~H NMR signals besides the signals of aromatic protons 7.5-7.97 ppm and Thiazole protons 9.04-9.26 ppm. The downfield shifts of 11.763 to 11.815 in the case of cobalt chloride and shift of 11.763-11.687 ppm in the case of cobalt perchlorate complex confirms –NH co-ordination [13-23].



```
Current Data Parameters
NAME              1177D
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20141129
Time              10.50
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ            5.2953587 sec
RG                  287
DW               80.800 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.60 usec
PL1               -2.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

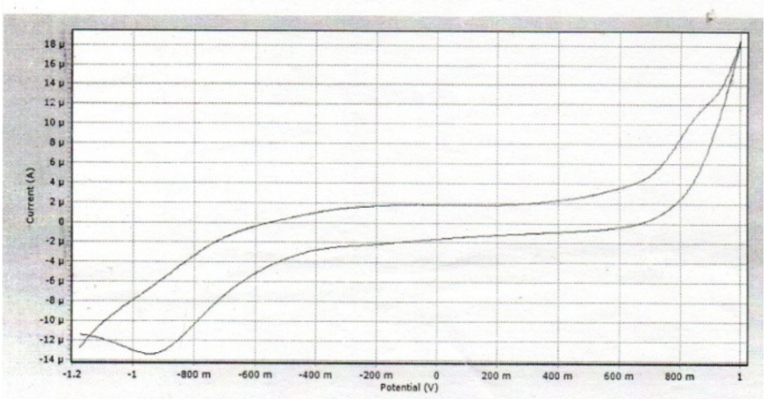
L_{10}-Cobalt chloride complex



```
Current Data Parameters
NAME             1177C1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20141129
Time              11.42
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ            5.2953587 sec
RG                  181
DW               80.800 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.60 usec
PL1               -2.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300040 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

L_{10}-Cobalt perchlorate complex.

Cyclic Voltammetry



Cyclic Voltammogram of cobalt chloride complex. The electrochemical data of metal complexes indicates the nature of metal complexes. The cyclic voltammogram of Cobalt chloride reveals the reversible nature of the metal complex in the catalytic reactions. During the formation of Cobalt chloride complex one electron transfer is involved and it is reversible in nature [24].

IV. CONCLUSION

In this paper a simple and convenient route is adopted for the synthesis of mixed ligand of Tetrazole and thiazole metal complexes. The reaction time is very much reduced compared with the conventional method. Microwave assisted synthesis with green trend reduced the reaction time from hours together to few minutes with better yield compared to classical synthetic methods [25]. The formation of the Schiff base complexes were confirmed by analytical, IR, UV-Visible, ^{1}HNMR spectral data, Magnetic moments and cyclic voltammetry analyses . The probable geometries for Co (II), Ni (II) are octahedral and in the formation of Cobalt Chloride complex one electron transfer is involved and it is reversible

V. FUTURE SCOPE

To obtain a single crystal for the above Schiff base ligands and its trasition metal metal complexes and to explore the crystal structures.

To impregnate the synthesized Schiff base ligands and its complexes in to Zno nano particles and investigate their antimicrobial and anti-bacterial, and DNA cleaving Nature for anti cancer studies.

ACKNOWLEDGEMENTS

The authors express their gratitude to instrumentation centre of St. Joseph's college, Tiruchirappalli for recording UV, FT-IR and Cyclic voltammogram. CARISM, Sastra university, Tanjore for recording H^1-NMR spectral data. .

Conflict of Interest. The authors declare that they have no conflict of interest.

REFERENCES

[1]. Pattanayak, P., Parua, S. P., Patra, D., Pratihar, J. L., Brandao, P., & Felix, V. (2014). Synthesis, Characterisations and structure of ortho metallated Part (II) and (IV) complexes: *Polyhedron,* Vol. *70,* pp. 1-5.

[2]. Paul, N. D., Samanta, S., Mondal, T. K., & Goswami, S. (2011). Examples of reductive azo cleavage and oxidative azo bond formation on Re2 (CO)10 template*: Inorg. Chem*., Vol. *50*, pp. 7886-7893.

[3]. Abou-Melha, K. S., & Faruk, H. (2008). (Synthesis, spectral and antimicrobial studies of rare earth metal complexes with Schiff base hydrazone containing quinoline moiety) *J. Co. ord. chem*., Vol. *61*(12) pp. 1862-1874.

[4]. Walcourt, A., Loyevsky, M., Lovejoy, D. B., Gordeuk, V. R., & Richardson, D. R. (2004). Novel aroylhydrazone and thiosemicarbazone iron chelators with anti-malarial activity against chloroquine-resistant and-sensitive parasites. *The international journal of biochemistry & cell biology*, *36*(3), 401-407.

[5]. Adamac, J., Waisser, K., Kunes, J., & Kauston, J. (2007). A note on the antitubercular drugs. *Molecules,* Vol. *15*, pp.1732-1752**.**

[6]. Jarrahpour, A., Khalili, D., De Clercq, E., Salmi, C., & Brunel, J. (2007). Synthesis, antibacterial, antifungal and antiviral activity evaluation of some new bis-Schiff bases of isatin and their derivatives. *Molecules*, *12*(8), 1720-1730.

[7]. Ali, M. A., & Saharyar, M. (2007). Synthesis and anti-mycobacterial activity, *Bio-org.med. chem. Lett*., Vol. *17,* pp. 3314-3316.

[8]. Amir, M., Kumar, S. (2007). Synthesis and evaluation of anti-inflammatory, analgesic, ulcerogenic and lipid peroxidation properties of ibuprofen derivatives, *Actaphar,* Vol. *57*, pp. 31-45.

[9]. Bachar, S. C., & Lahiri, S. C. (2004). Synthesis of chloro and bromo substituted 5-(indane-1'-1 yl) methyl tetrazolar and 5 –(indan-1yl) methyl tetrazoles as possible analgesic agents, Die Pharmazic *international J. pharm. Sci*., Vol. *59*, pp. 435-438.

[10]. Akilandeswari, J., Bheeter, S. R., Joseph, Selvaraj, S., & Saravanan, D. (2015). Synthesis and charecterizations of Metal complexes of 2-[5-Phenyl (1, 3, 4-oxadiazole-2-yl) thio]-N'-[(1E)-(4-Methyl-(1, 3-Thiazole-5-yl) methylene)] acetohydrazide, *International Journal Res. chem. Environ*., Vol. *5*, pp. 38-43.

[11]. Figgis, B. N., & Lewis, J. (1960). Interscience, *Modern coordination chemistry*, Vol. *1*, 321.

[12]. Saravanan, P., Joseph, Selvaraj S., & Saravanan D. (2014). Copper (II) complexes of 2-(2'-pyridyl) benzimidazole: synthesis charecterization and Biological studies, *Res. J. Chem. Environ.*,Vol. *18*(2), pp. 8-16.

[13]. Kumar, P., & Narasiman (2006). Synthesis and antimicrobial studies of a novel series of 2-{[4-(5-ethyl pyridine-2-yl) ethoxy] Phenyl}-5-substituted -1,3,4-oxadiazoles, *European J. Med. Chem*., Vol. *41*, pp. 841-846.

[14]. Kumar, P., Narasimhan, B., Sharma, D., Judge, V., & Narang, R. (2009). Hansch analysis of substituted benzoic acid benzylidene/furan-2-yl-methylene hydrazides as antimicrobial agents. *European journal of medicinal chemistry*, *44*(5), 1853-1863.

[15]. Joule, J. A., & Mills, K. (2010). *Heterocyclic chemistry*, 5th edition, *John willey & sons publications*, Vol. *1*, p. 569.

[16]. Galal, S. A., Abdelsamie, A. S., Radriguez, L., Kerwin, S. M., & H., I.El-Diwan. (2010) *European J. Chem*., Vol. *1*(2), pp. 67-72.

[17]. Herr, R. J. (2002). 5-substituted -1H-Tetrazoles as carboxylic acid isosteres. Medicinal chemistry and synthetic methods. *Bio-org Med. Chem*., Vol. *10,* pp. 3379-3393.

[18]. Mohan, S., Anandan, S., & Murugan, K. R. (2010). *J. Pharm. Sci. Res*., Vol. *9*, pp. 391-398.

[19]. Basava, K. M., Somasekhar, B., & Appalaraju, S. (2008). Synthesis and biological activity of some 2-[3-substituted-2-thone-1, 3, 4-thiazole-5 yl] amino benzo Thiazoles, *Indian J. of Heterocyclic. Chem*., Vol. *18*, pp. 69-72.

[20]. Abbs, T. F., Reji, F., Devi, S. K. C., Thomas, K. K., Sreejalakshmi, K. G., Manju, S. L., Francis, M., Philip, S. K., Bharathan, A., & Rajasekaran, K. N. (2008) Synthesis and cytotoxicity studies of Thiazole analogs of anti cancer drugs. *Indian J. Chem*., Vol. *47B,* pp. 1145-1150.

[21]. Karabasanagowda, T., Adhikari, A. V., Ramgopal, D., & Parameshwarappa, G. (2008). Synthesis of some New 2-(4-alkyl thio phenoxy)-S-substituted-1,3-thiazoles as possible anti-inflammatory and anti-microbial agents, *Indian J. Chem*., Vol. *4*, pp. 7-14.

[22]. Sadimengo, A. P., & Basson, S. S. (1996). Organo metallic complexes of heterocyclic, *Complexes of Pyrazole, Coordination Chemistry Reviews*, Vol. *1*, pp, 147-297.

[23]. Saravanan, P., Joseph, Selvaraj, S., & Saravanan, D. (2014). Syntheses and characterization of copper complexes of quinoline derivatives. *Research Journal of Chemistry and Environment*, Vol. *1*, pp. 6-11.

[24]. Usha, S., & Palaniandavar, M. (1994). Influece of Chealate ring size and number of sulfur donor atoms on spectra and redox behavior of copper (II) bis benzimidazoyl – tetra-and- pentathio ether complexes. *J. Chem. Soc. Dalton. Trans.*, Vol. *15*, pp. 2277-2283.

[25]. Kodge, S., Shiv Prasad K. H., & Kodge, A. K. (2016). Microwave aided synthesis and biological screening of drug based Schiff base complexes of silver. *International Journal on Emerging Technologies*, Vol. *7*(2), pp. 143-147.

How to cite this article: Akilandeswari J., Joseph Selvaraj S., and Saravanan, D. (2019). Synthesis and Characterisation of Metal Complexes of 2-[(1-methyl-1H-Tetrazole-5-yl)thio]-N’-[(1E)-4-methyl-1,3-thiazole-5 yl) Methylene] Acetohydrazide. *International Journal on Emerging Technologies*, **10**(3): 311–317.