International Journal of
Research in Chemistry and Environment
Available online at: www.ijrce.org
ISSN 2248-9649

Research Paper

Synthesis and Characterization 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

Akilandeswari J.[1], Bheeter S. R.[1], *Joseph Selvaraj S.[1], Saravanan D[2]
[1]Department of Chemistry, St. Joseph's College, Tiruchirappalli, Tamilnadu, INDIA
[2]Department of Chemistry, National College, Tiruchirappalli, Tamilnadu, INDIA

(Received 22nd August 2014, Accepted 09th October 2014)

Abstract: The ligand 2-[(5-phenyl-1,3,4-oxadiazole – 2-yl) thio] – N' – [(1E)- (4-methyl-1,3- thiazole-5-yl)methylene] acetohydrazide was synthesized and the complexes with metal chlorides such as Co(II), Mn(II), Ni(II) and metal perchlorate of Cu(II) were synthesized and characterized on the basis of IR and 1H NMR, UV-Visible, molar conductivity, TGA analysis and magnetic susceptibility measurements. Spectral data reveal that ligands chealated with metal through N-atoms. Magnetic susceptibility measurements favour Octahedral coordination for Cu(II), Ni(II), Mn(II) and Tetrahedral co-ordination for Co(II) metal complexes .

Keywords: Transition metal complexes 1,3,4-oxadiazole -2-thiol derivatives, Thiazole.

Introduction

Heterocyclic compounds containing five membered oxadiazole nucleus possess a diverse useful biological effects. In particular compounds bearing the 1,3,4- oxadiazole nucleus are known to have anti oedema and anti inflammatory activities. Differently substituted oxadiazole moieties have also been found to have other interesting activities such as antimicrobial, analgesic, anticonvulsant, viral activities1-5. Five membered ring systems containing nitrogen and sulphur exhibit wide variety of biological activities. These are used in pharmaceuticals and as oxidation inhibitors.

Material and Methods

Instruments

All the chemicals and solvents used were of analar grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. The electronic spectra (in C_2H_5OH) were recorded on Perkin Elemer lambda-35-2B-spectrometer. Molar conductance measurements were conducted using 10-3M solutions of the complexes in Acetonitrile, on Elico CM-82 Conductivity Bridge at room Temperature. Magnetic susceptibility measurements were carried out on a Guoy Balance at room temperature using mercuric tetrathiocyanatocobaltate(II) as the calibrant.

Diamagnetic corrections were applied in compliance with Pascal's constant. FT-IR spectra were recorded in KBr medium on a Perkin Elmer Rx, spectrophotometer in wave number region 400-4000 cm^{-1}. ^{1}HNMR spectra were recorded On Bruker spectrometer employing TMS as internal reference and DMSO-d6 as solvent. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate 10^0C min-1 on TGA Q500 universal V4.5A TA instrument.

Synthesis of 2-[5-phenyl-1,3,4-oxadiazole-2yl)thio]-N'-[(1E)-(4-methyl-1,3-thiazole-5-yl)methylene] acetohydrazide

Anhydrous sodium carbonate (55 mmol) was added to a solution of (5-phenyl-2-mercapto) oxadiazole thiol in acetone (50 ml). To the reaction mixture, ethyl bromo acetate (100 mmol) was added slowly at room temperature under stirring. The progress of a 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 product was concentrated under vacuum to remove acetone and the residual acetone was removed using methanol to give its thioacetate 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 mmol) was added and refluxed. 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 0oc for crystallization. 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-[(5-phenyl-1,3,4-oxadiazole-2-yl)thio]-N'-[(1E)-(4-methyl-1,3-thiazole-5-yl)methylene acetohydrazide]6.

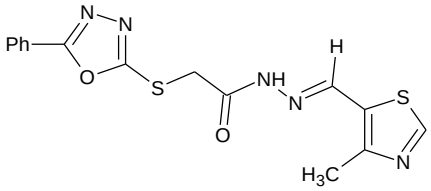
Synthesis of metal complexes

The metal complexes were prepared by the 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 on water bath for 5-9 h. A coloured product appeared on standing and cooling the above solution. The precipitated complex was filtered washed with ether and recrystalised with ethanol several times and dried over anhydrous $CaCl_2$ in a dessicator.

Results and Discussion

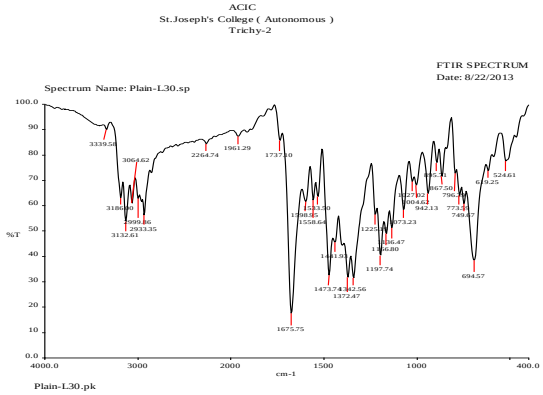
(i)Ligand

Melting point of the ligand 2-[(5-phenyl-1,3,4-oxadiazole-2-yl)-N`-[(1E)-4methyl,(1,3-thiazole-5-yl)methelene] acetohydrazide is 194.5oc and it is soluble in CH3OH, DMSO and in acetonitrile. The structure of the ligand is given below.



IR spectral studies:

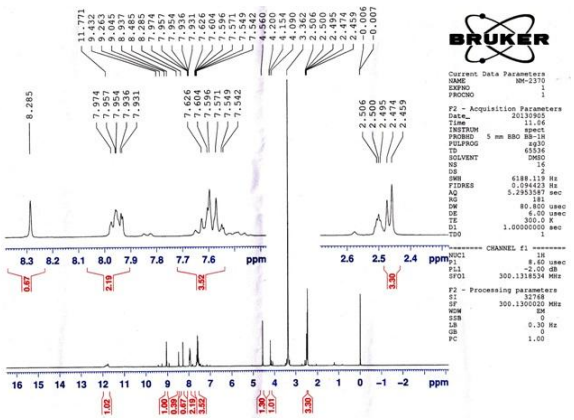
IR spectrum of the ligand exhibits sharp peak at 3339 cm-1 (N-H) stretching, 773 cm-1 (N-H wagging), 619 cm-1 (C-S), 2999 cm-1 (C-Aromatic), 3132 cm-1 (Hetero C-H), 2933 cm-1 (Aliphatic C-H), 1558 cm-1 (C=N), 1225 cm-1 (C-N), 1004 cm1 (N-N), 1197 cm-1 (C-O-C)7.



FTIR Spectrum of Plain Ligand

^{1}H-NMR Spectral data:

NMR spectrum of the ligand showed ^{1}H NMR (∂, ppm) 2.48 (3H, s, CH_3), 4.22 and 4.56 (2H, s, SCH_2), 7.5-7.97 (5H, m, Ar), 8.28 and 8.48 (1H,s,=CH), 9.04 and 9.26 (1H, s, thiazole H), 11.78 and 11.771 (1H, s, NH).The above IR and NMR data of the Schiff base ligand and the complexes were compared, in order to determine the involvement of co-ordination sites in the chealation.

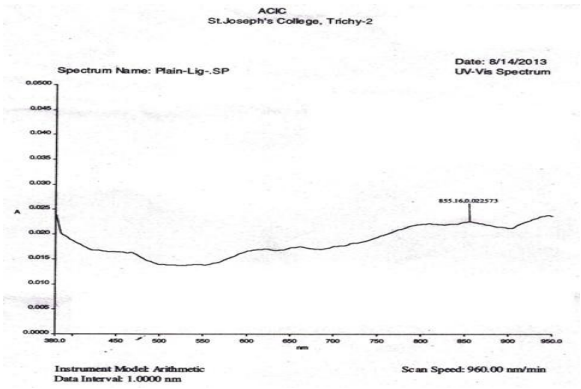


NMR Spectrum of Plain Ligand

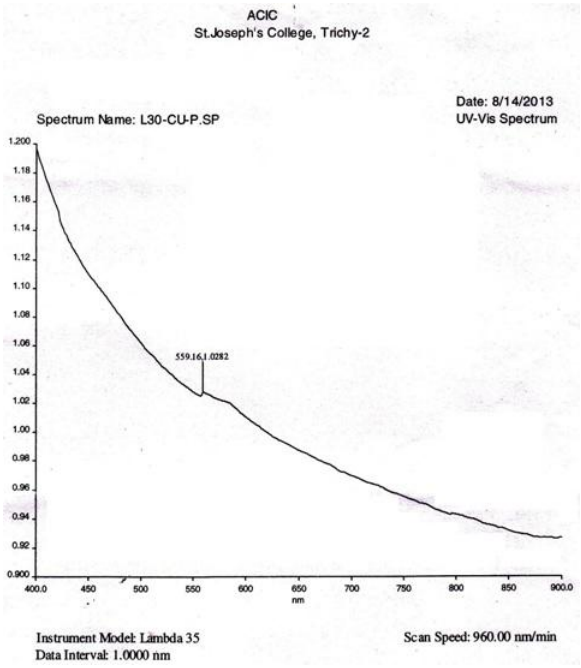
(ii) Metal complexes

Conductance study shows that the chloride complexes of Ni(II), Mn(II) and perchlorate complex of Cu(II) are all of 1: 6 stoichiometry and the chloride complex of Ni(II) is a non electrolyte[8]. The magnetic moments of the complexes are in consistent with the expected values for the given geometries of complexes. The blue colour of cobalt chloride complex and strong absorption at 15,220 cm^{-1} suggests $4A_2 \rightarrow 4T_1(P)$, transition of tetrahedral geometry. The conductance study again shows that Co(II) is electrolytic in nature and four ligands are co-ordinated to the Metal atom. The appearance of broad band at 17,890 cm^{-1} and magnetic moment of 1.55 BM suggests distorted octahedral geometry for copper perchlorate

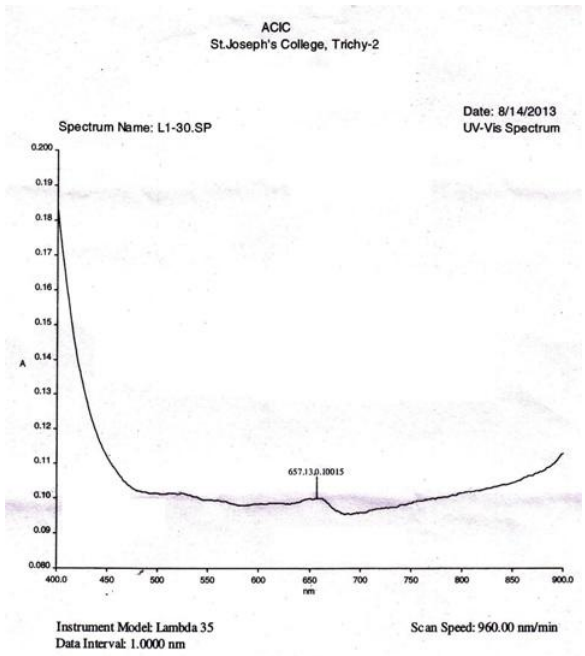
complex .The pale green colour of the Nickel complex and a broad strong band at 13,717 cm^{-1} and 25,000 cm^{-1} assigned to $3A_{2g} \rightarrow 3T_{2g}(F)$ and $3A_{2g} \rightarrow 3T_{1g}.(P)$ transitions suggesting octahedral geometry for the nickel complex[9].The light yellow coloured Mn(II) complex shows band at 25,000 cm^{-1} which is assigned to CT transition. Because of strong CT transition the weak d-d transition are over shadowed. The effective magnetic moment 5.93 BM and analytical data are in consistent with the octahedral geometry of Mn(II) complex[10-15].



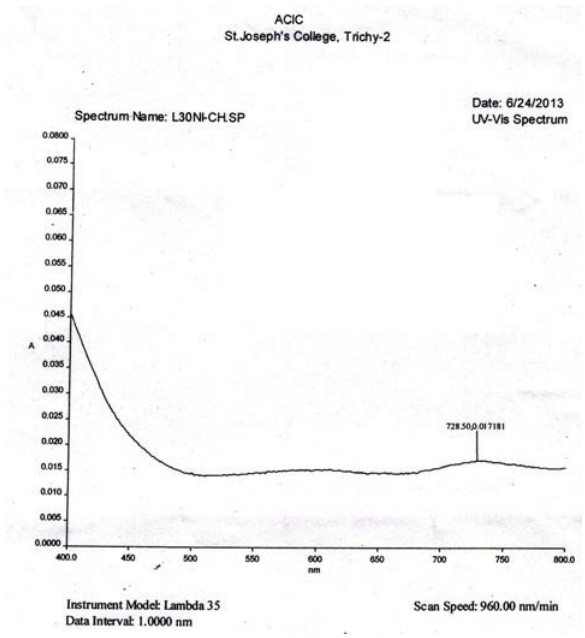
Electronic Spectrum of Plain Ligand



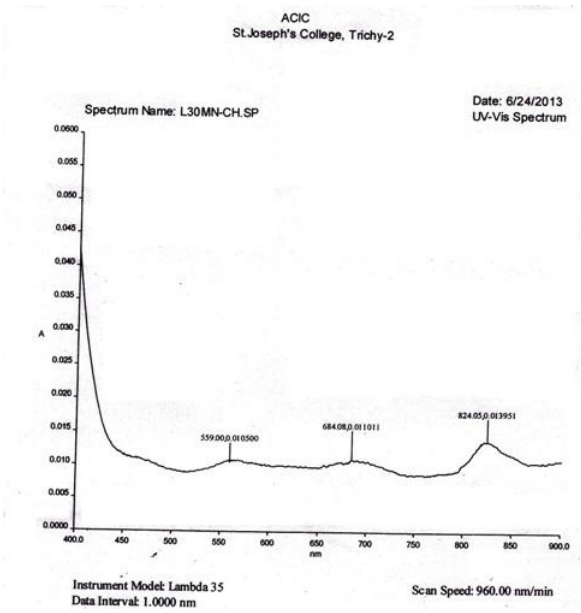
Electronic Spectrum of Copper per Chlorate Complex



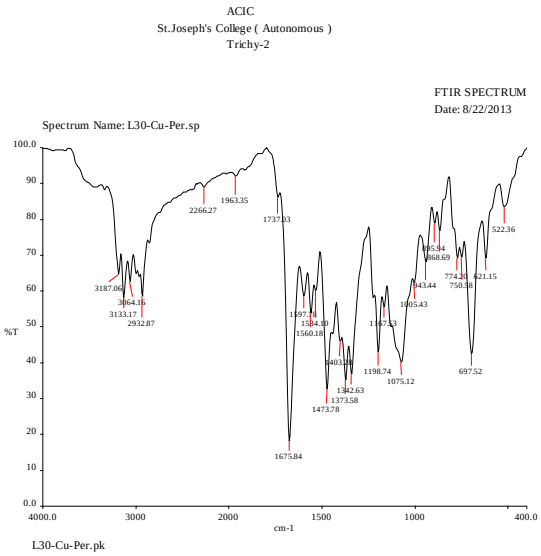
Electronic Spectrum of Cobalt chloride Complex



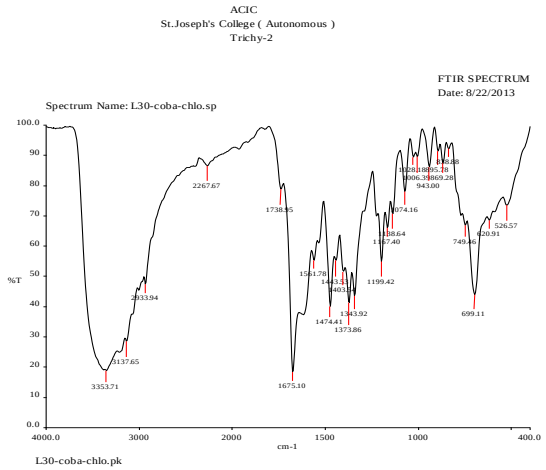
Electronic Spectrum of Nickel chloride Complex



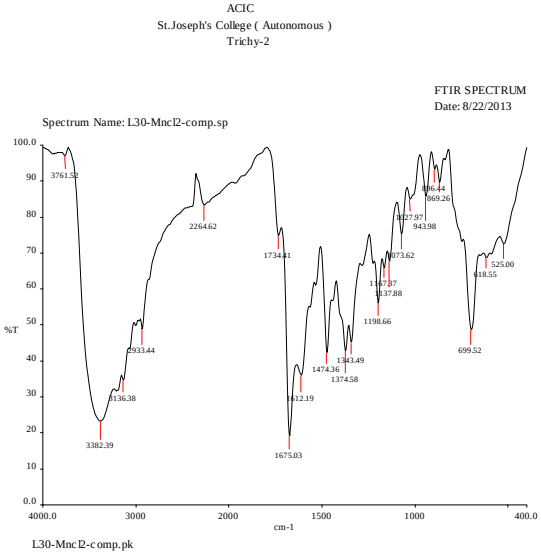
Electronic spectrum of Manganese chloride complex



FTIR spectrum of copper per chlorate complex



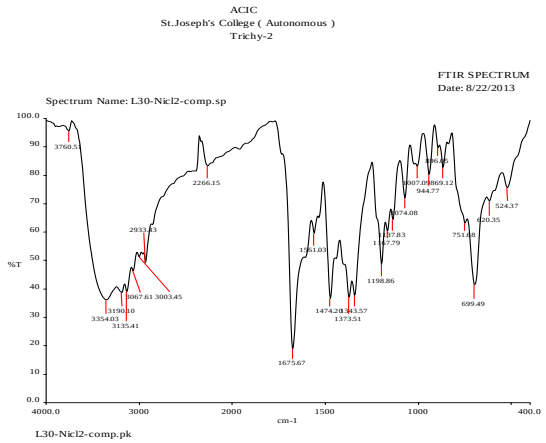
FTIR spectrum of cobalt chloride complex



FTIR spectrum of manganese chloride complex

IR Spectra

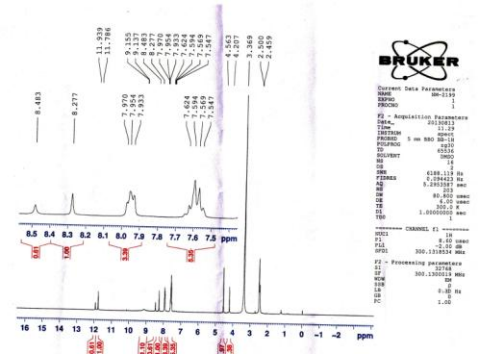
Comparison of the IR spectrum of the ligand with the IR spectra of the complexes suggest the co-ordination of the peptide linkage N with metal ion. The positive shift of amide (I) band (-NH stretch) suggest that co-ordination of the peptide linkage `N` with the metal ion and the oxygen of the peptide linkage is not involved in the co-ordination. The negative shift of the ligand in the form of feeble vibration in the NH bending 1598 cm^{-1} and the negative shift of (C-N) stretch at 1225 cm^{-1}-1250 cm^{-1} confirm the coordination of peptide linkage N with the metal ion. The stretch in between 590 cm^{-1} and 593 cm^{-1} which is found only in the IR spectra of complexes are assigned to M-N stretch[16]. In the perchlorates the stretch of perchlorate ion are found at 1100 cm^{-1} and 900 cm^{-1} without splitting, suggesting that the presence of ClO_4^{2-} ions and it is not involved in co-ordination with metal ion, and it is confirmed by conductance studies also. The other stretches are not very much affected in the spectra of complexes in comparison with that of ligand.



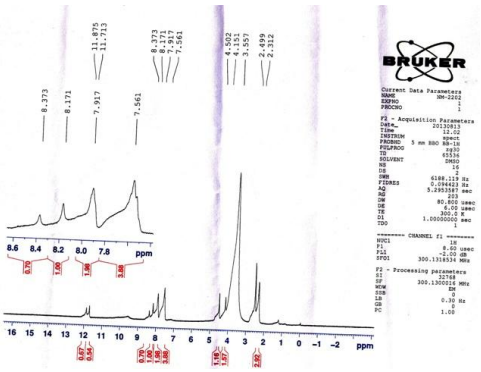
FTIR spectrum of nickel chloride complex

^{1}H NMR spectra:

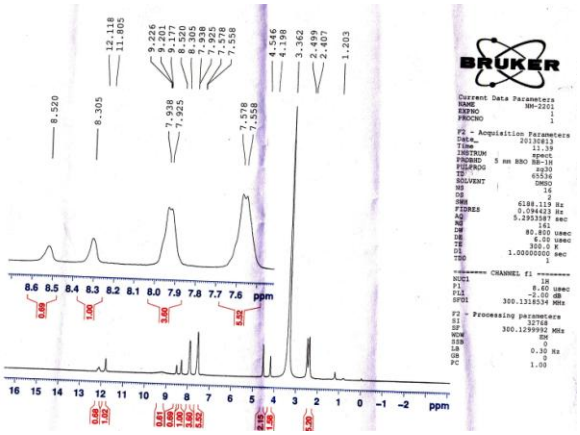
The complex exhibited ^{1}H NMR signals besides the signals of aromatic protons 7.5-7.97 *ppm* and thiazole 9.04, 9.26 *ppm*. The downfield shifts in NMR frequencies from 11.771 to 11.875, 11.713 *ppm* for Co(II) 11.771 to11.939, 11.786 *ppm* in Cu(II), 11.771 to12.118, 11.805 *ppm* in Ni(II) and 11.771 to 12.118 *ppm* Zn(II) complexes confirms NH co-ordination.



NMR spectrum of copper per chlorate complex



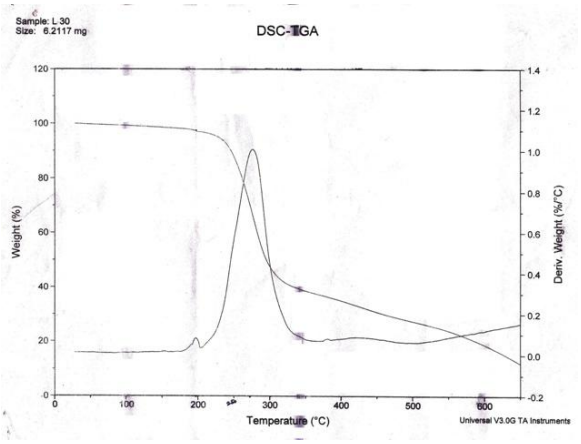
NMR spectrum of cobalt chloride complex



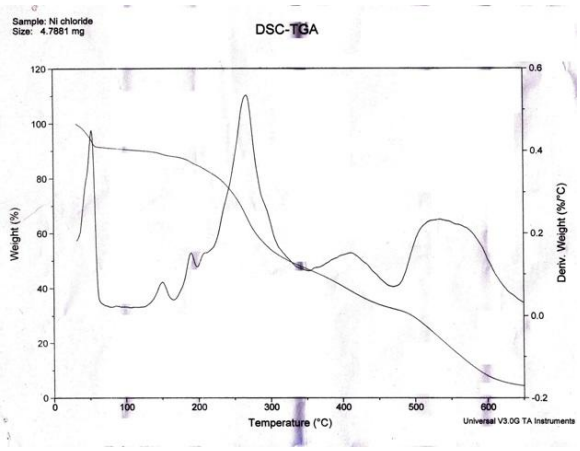
NMR spectrum of nickel chloride complex

TGA

The ligand melts at 194.5^{0}C and decomposes above 500^{0}C.The TGA curve of the Ni(II) complex is exhibiting four endo peaks, above 330^{0}C showing the decomposition and pyrolysis of the product as metal oxides[16].



TGA of plain ligand



TGA of Nickel chloride complex

Conclusion

The formation of these complexes were confirmed by analytical, IR, UV-Visible, ^{1}H NMR spectral data, magnetic moments and thermal analyses. The probable geometries for Cu(II),Ni(II)and Mn(II) complexes are octahedral and Co(II) complex is Tetrahedral.

References

1. Adamac J., Waisser K., Kunes J., Kauston J., A note on the antitubercular drugs, *Molecules***, 15**, 1732-1752**, (2007)**

2. Alisagarar J., Kalihi D., Clercq E.D., Salmi C., Brusel J.M., Synthesis, antibacterial antifungal and antiviral activity evaluation of some new bis-schiff bases of isatin and their derivatives. *Molecules*, **21**, 1720-1730**, (2007)**

3. Ali M.A., Saharyar M., Oxadiazole mannich bases, synthesis and antimycobacterial activity, *Bio-org. Med. Chem*. Lett., **17**, 3314-3316 **(2007)**

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

5. Bachar S.C., Lahiri S.C., Synthesis chloro and bromo substituted 5-(indane-1'-1yl) tetrazolor and 5(indan-1'-yl) methyl tetrazoles as possible analgesic agents, *Die Pharmazic-int. J. Pharm. Sci*. **, 59**, 435-438 **(2004)**

6. Saravanan P., Joseph selvaraj S., Saravanan D., Copper (II) complexes of 2-(2`-pyridyl)benzimidazole : Synthesis characterization and Biological studies, *Res. J. Chem. Environ*., **18 (2) (2014)**

7. Synthesis and antimicrobial studies of a novel series of 2-{[4-(5ethyl pyridine-2-yl) ethoxy] phenyl}-5-substituted-1,3,4-oxadiazoles, *European J. Med. Chem*., **41**, 841-846 **(2006)**

8. Kumar P., Narasiman B., Sharma D., Analysis of substituted benzoicacid, benzylidene/furan-2-Yl methylene hydrazides as antimicrobial agents, *Eur. J. Med. Chem*, **44**, 1853-1863**(2009)**

9. Saravan Bhava P., Tharmaraj P., Synthesis, spectral characterization, biological screening and DNA studies of 2-(5-mercapto-1,3,4-oxadiazol-2-yl) phenol transistion metal complexes, *International Journal of Science and Engineering*, **2(12)**, 16-25 **(2010)**

10. Joule J.A. and Mills K., *Heterocyclic chemistry*, 5th edition, John Wiley & sons publications, P569, (**2010)**

11. Galal S.A., Abdelsamie A.S., Radriguez L., Kerwin S.M. and H.I.EI-Diwan, *Eur. J. chem*, **1(2),** 67-72 **(2010)**

12. Herr R.J., 5-substituted-1-H Tetrazoles as carboxylic acid isosteres, Medicinal Chemistry and Synthetic methods, *Bioorg Med. Chem*, **10**, 3379-3393**(2002)**

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

14. Mohan S., Anandan S., Murugan K.R., *J. Pharm. sci. Res*.,**9**,391-398**(2010)**

15. Karabasanagowda T., Adhikari A.V., Ramgopal D. and Parameshwarappa G., Syntheses of some New 2-(4-alkyl thio phenoxy)-S-substituted-1,3-thiazoles as possible anti inflammatory and anti microbial agents, *Indian J. chem*, **4 (2008)**

16. Abbs T.F., Reji F., Devi SKC, Thomas K.K., Sreeja Lakshmi K.G., Manju S.L., Francis M., Philip S.K., Bharathan A. and Rajasekaran K.N., Syntheses and cytotoxicity studies of Thiazole analogs of the anti cancer drugs, *Indian J. Chem*., **47B**, 1145-1150 **(2008)**