



ISSN 2248-9649

International Journal of
Research in Chemistry and Environment

Available online at: www.ijrce.org



Research Paper

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

J. Akilandeswari¹, * S. Joseph Selvaraj¹, S.R. Bheeter¹, D. Saravanan²
¹Department of Chemistry, St. Joseph's College, Tiruchirappalli, (Tamilnadu), INDIA
²Department of Chemistry, National College, Tiruchirappalli, (Tamilnadu), INDIA

(Received 14th July 2017, Accepted 12th September 2017)

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 and characterized on the basis of IR, and ¹H NMR, UV-Visible molar conductivity, Cyclic voltammetric analysis and Magnetic susceptibility Measurements. Spectral data reveal that ligands chelated with metal through N-atoms. Magnetic susceptibility measurements favors octahedral coordination for Co(II), Ni(II) metal complexes.

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

© 2017 IJRCE. All rights reserved

Introduction

Heterocyclic compounds containing five membered Tetrazole nucleuses possess a diverse useful biological effects. In particular compounds bearing the Tetrazole nucleus are known to have anti-inflammatory and anti-oedema activities¹⁻⁵. Five membered ring systems containing Nitrogen and sulphur exhibit wide variety of biological activities. Similarly 1,5 substituted tetrazoles have long been known as stimulants or anti-depressants. These are used in pharmaceuticals and also as an oxidation inhibitors.

Material and Methods

Instruments

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 10⁻³M 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 400cm⁻¹-4000 cm⁻¹, ¹H NMR spectra were recorded on Bruker spectrometer employing TMS as internal reference and DMSO -d₆ 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 mmol) was added to a solution of [(1-methyl-5-mercapto-Tetrazole) 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 the reaction was monitored by thin layer chromatography using a mixture of ethyl acetate and n-hexane (3:7) as eluent.

The byproduct 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 (30ml), 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 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-5-yl)methylene]acetohydrazide]⁶.

Synthesis of metal complexes

The metal complexes were prepared by mixing of (50ml) ethanolic solution of metal salts with the 50ml ethanolic solution of Schiff bases in 1:6 (metal: ligand) ratio. The resulting mixture was refluxed on water bath for 5-9 hours. 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 CaCl₂ in a dessicator.

Results and Discussion

Ligand

Melting point of the ligand is 297.36⁰C and it is soluble in methanol, DMSO and in aceto nitrile. The structure of the ligand is given below.

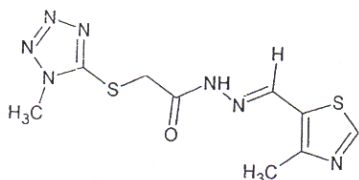


Figure 1: Structure of the ligand

IR spectral studies: 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), 1528cm⁻¹(C=N), 1201 cm⁻¹(C-N), 1015 cm⁻¹ (N-N), 1411 cm⁻¹ (aliphatic CH₃ deformation)⁷.

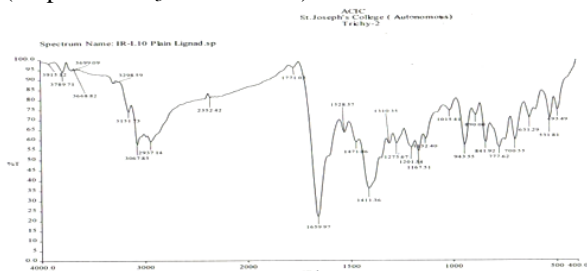


Figure 2: FT-IR Spectrum of plain ligand

¹H-NMR spectrum data

NMR spectrum of ligand showed ¹H-NMR 2.47 (3H,S,Thiazole,CH₃), 3.98 (3H,S,NCH₃), 4.16 and 4.51 (2H,S,SCH₂), 8.28 and 8.46 (1H,S,=CH), 9.06 (1H,S,thiazole,CH), 11.763 (1H, S, NH)

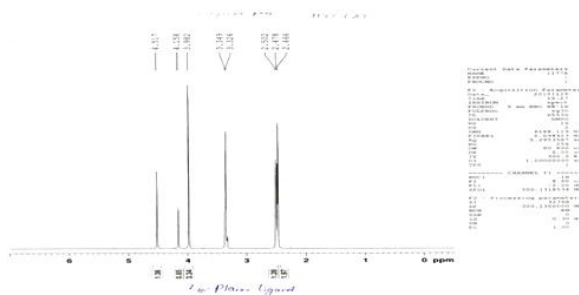
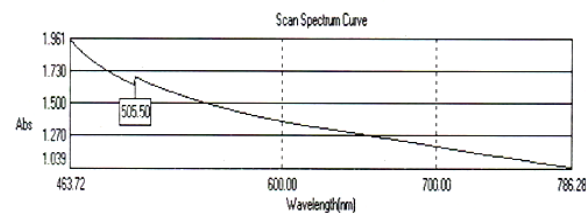


Figure 3: NMR spectrum of plain ligand

Metal complexes

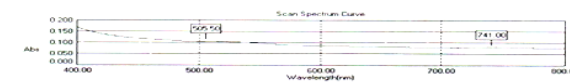
Conductance studies shows that the chloride complexes of Ni(II),Cu(II),Co(II) are all non electrolytes⁸. The magnetic moments of the complexes are in consistent with the expected values for the given geometries of complexes .The purple colour of cobalt chloride complex and strong absorption at 15361cm⁻¹ suggests 4T1g(F) -> 4T1(g)(P) transition of octahedral geometry⁹. 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 complexes¹⁰⁻¹⁵. The magnetic moment of 2.9 BM confirms the above geometry.

L10 nickel chloride



(a)

L10 cobalt chloride



(b)

Figure 4: Electronic spectra of metal complexes

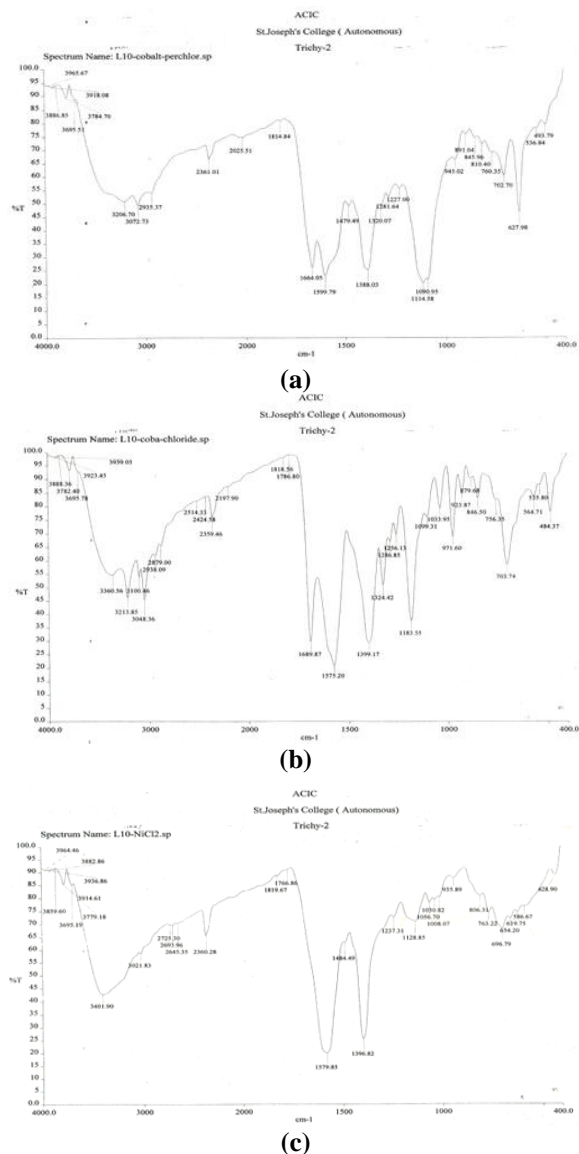


Figure 5: IR Spectra of Metal Complexes:

IR spectra

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 ion. 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 stretch¹⁶.The other stretches are not very much affected in the spectra of complexes in comparison with that of ligand .

¹H NMR spectra

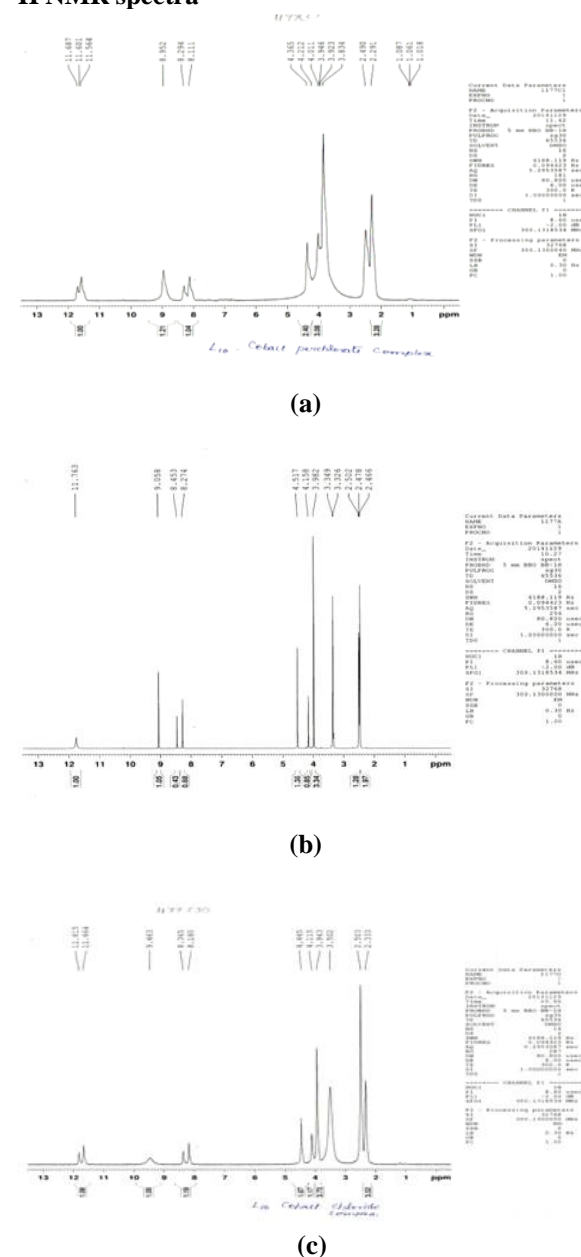


Figure 6: ¹H NMR spectra of cobalt (II) complexes

The complex exhibited ¹H 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^{17,18}.

Cyclic voltammetry

Cyclic voltammogram of cobalt chloride

The cyclic voltammogram recorded for the ligand cobalt chloride complex shows an oxidation peak at 630mv and a reduction peak at 1100mv. The presence

of single peak indicates the electron transfer and as the difference between oxidation and reduction peaks are very small it is confirmed that one electron transfer is involved and it is reversible.

Conclusion

The formation of these complexes was confirmed by analytical, IR, UV-Visible, H NMR 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.

References

- Adamac J., Waissner K., Kunes J., Kauston J., A note on the antitubercular drugs. *Molecules*, **15**: 1732-1752 (2007)
- 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)
- Ali M.A., Saharyar M., Synthesis and antimycobacterial activity, *Bio-org. med. chem. Lett.*, **17**: 3314-3316 (2007)
- Amir M., Kumar S., Synthesis and evaluation of anti-inflammatory, analgesic, ulcerogenic and lipid peroxidation properties of ibuprofen derivatives, *Actaphar* , **57**: 31-45 (2007)
- Bachar S.C., Lahiri S.C., Synthesis of chloro and bromo substituted 5-(indane-1'-yl) methyl tetrazolar and 5 -(indan-1yl) methyl tetrazoles as possible analgesic agents, *Die Pharmazic- Int. J. pharm. sci.*, **59**: 435-438 (2004)
- Akilandeswari J., Bheeter S.R., Joseph Selvaraj S., Saravanan D., 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, *Int. J. Res. Chem. Environ.*, **5**: 38-43 (2015)
- Saravanan P., Joseph Selvaraj S., Saravanan D., copper (II) complexes of 2-(2'-pyridyl) benzimidazole : Synthesis charecterization and Biological studies. *Res. J. Chem. Environ.*, **18**(2): (2014)
- Synthesis and antimicrobial studies of a novel series of 2-[[4-(5-ethylpyridine-2-yl)ethoxy]Phenyl]-5-substituted -1,3,4-oxadiazoles. *European J. Med. Chem.*, **41**: 841-846(2006)
- Kumar P., Narasiman B., Sharma D., Analysis of substituted benzoic acid, benzylidene/furan-2-yl methylene hydrazides as anti microbial agents. *European J. Med. Chem.*, **44**: 1853-1863 (2009)
- Joule J.A. and Mills K., *Heterocyclic chemistry*, 5th edition, John Willey & sons publications, P569 (2010)
- Galal S.A., Abdelsamie A.S., Radriguez L., Kerwin S.M. and I.EI-Diwan H., Synthesis and studying the antitumor activity of novel 5-(2-methylbenzimidazol-5-yl)-1,3,4-oxadiazole-2(3H)-thiones. *European J. Chem.*, **1**(2): 67-72 (2010)
- Herr R.J., 5-substituted-1H-Tetrazoles as carboxylic acid isosteres, Medicinal chemistry and synthetic methods, *Bio-org Med. Chem.*, **10**: 3379-3393 (2002)
- Mohan S., Anandan S., Murugan K.R., *J. Pharm.sci. res.*, **9**: 391-398 (2010)
- Basava K.M., Somasekhar B. and Appalaraju S., Synthesis and biological activity of some 2-[3-substituted-2-thione-1,3,4-thiazole-5 yl]amino benzo Thiazoles, *Indian J. of Heterocyclic Chem.*, **18**: 69-72 (2008)
- 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. and Rajasekaran K.N., Synthesis and cytotoxicity studies of Thiazole analogs of anti cancer drugs. *Indian J. Chem.*, **47B**:1145-1150 (2008)
- Karabasanagowda T., Adhikari A.V., Ramgopal D. and Parameshwarappa G., Synthesis of some New 2-(4-alkyl thio phenoxy)-S-substituted-1,3-thiazoles as possible anti inflammatory and antimicrobial agents. *Indian J. chem.*, **47B**: 144-152 (2008)
- Siddiqui N., Ahuja P., Ahsan W., Pandeya S.N. and Alam M.S., Thiadiazoles: Progress report on biological activities. *J. Chem. Pharm. Res.*, **1**: 19-30 (2009)
- Upadhyaya R.S., Jain S., Sinha N., Kishore N., Chandra R. and Arora S.K., Synthesis of novel Substituted tetrazoles having anti-fungal activity. *Eur. J. Med. Chem.*, **39**: 579-592 (2004).