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RESEARCH PAPER

Solvent-free Synthesis and Characterization of Cu(II), Co(II) and Ni(II) Complexes of 2-(3-phenylallylidene)thiosemicarbazide

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Abstract

Mechanochemical solvent-free synthesis of Cu, Co and Ni complexes of 2-(3-phenylallylidene) thiosemicarbazide is described. The mechanochemical products were characterized on the basis of solubility, melting point, conductivity, FTIR, UV-Visible, GC-MS, ^{1}H-NMR and ^{13}C-NMR. The Schiff base ligand and its metal (II) complexes are coloured stable compounds. The solubility test shows that the compounds are soluble in dimethylsulphoxide, dimethexylformamide; partially soluble in ethanol and insoluble in water. The melting points of the compounds were within the range of 179 ºC to 183 ºC. The UV-Visible electronic spectra data showed the different transfers and transitions in the ligand and metal complexes. The different absorptions in the electronic spectra also predicted the possible structures of the complexes. The ^{13}C-NMR and ^{1}H-NMR showed the different carbon and hydrogen environments in the ligand. The GCMS confirmed the structure of the ligand and exhibited different fragments. The antimicrobial activities of the ligand were enhanced with the metal complexes and the results were very interesting as the complexes showed good antifungal and antibacterial activities.

Keywords: 2-(3-phenylallylidene) thiosemicarbazide; Dimethylsulphoxide; Dimethylformamide; Mechanochemical; Solvent-free

INTRODUCTION

Recent years have witnessed a major drive to increase the efficiency of organic transformations while lowering the amount of waste materials. Many organic solvents are hazardous and can be deleterious to human health. They are volatile and cause an environmental threat by polluting the atmosphere (Tanaka, 2004; Martins et al., 2009). The replacement of volatile organic solvents in organic reaction processes is an important green chemistry goal.

The solvent-free reaction or solid-state reactions are green methods in organic synthesis which have numerous advantages: reduced pollution, low cost and simplicity in process and handling (Tanaka and Toda, 2000; Mikami, 2005). Mechanochemistry can be as simple as grinding two reactants in a mortar and pestle or more complex, as with the use of commercially available ball mills (Schmeyers et al., 1998; Jarrahour and Zarei, 2008). Schiff base ligands contain some heteroatoms such as nitrogen, sulphur and oxygen which affords it the ability to form complexes as these atoms have affinity for transition metals such as copper, manganese, chromium, iron, cobalt, nickel, etc. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behaviours studied.

2-(3-Phenylallylidene) hiosemicarbazide is an analogue of thiosemicarbazide. Thiosemicarbazide have attracted great interest for many years as reagent for synthetic organic chemistry, for its antiviral and antibacterial activities; due to the presence of –NH-C(S)-NH function in the molecule. In the present work we have synthesized new Schiff base, 2-(3-phenylallylidene) thiosemicarbazide and its Co(II), Cu(II) and Ni(II) complexes using mechanochemical solvent-free synthesis.

MATERIALS AND METHODS

Chemicals and reagents

All reagents and chemical were analytical grade and used as obtained from Sigma Aldrich and LOBA without further purification.

Scientific analyses

The electronic spectra of the ligand and complexes were obtained using AQUARIUS CE 7500 series UV/Visible spectrophotometer in DMSO solution in the range of 190-1100 nm. The infrared spectra were recorded on a Burker FTIR in the range of 4000-400 cm^{-1}. Melting point temperature was determined using Gallen kamp 600 melting point equipment. ^{1}H-NMR and ^{13}C-NMR was recorded on Burker 400 MHz spectrophotometer. The conductivity measurement was performed at temperature range of 28.5-33.1 ºC using JENWAY pH/conductivity meter in DMSO solution at a concentration of 10^{-3} mol/dm^{3}. Polar and non-polar solvents were used to determine the solubility of the complex.

Synthesis of 2-(3-phenylallylidene) thiosemicarbazide $C_{10}H_{11}N_3S$ (L)

Thiosemicarbazide (0.91 g, 0.01 mol) and cinnamaldehyde (1.32 g, 0.01 mol) were carefully weighed into a clean ceramic mortar and grinded with a pestle at room temperature for 20 mins to obtain a bright yellow powder. The powder product was removed and stored in the desiccator without further purification.

Synthesis of [Cu(L)Cl_2] complex

(0.01 mol, 2.05 g) of 2-(3-phenylallylidene) thiosemicarbazide and (0.01 mol, 0.172 g) of copper chloride was weighed carefully into a mortar. The reactants were grinded for 20 min to obtain a dirty-green powder. The powder was removed from the mortar and stored in a desiccator.

Synthesis of [Co(L)Cl_2] complex

(0.01 mol, 2.05 g) of 2-(3-phenylallylidene) thiosemicarbazide and (0.01 mol, 2.38 g) of cobalt chloride were weighed carefully into a mortar. The reactants were grinded for 20 min to obtain an army-green powder. The powder was removed from the mortar and stored in a desiccator.

Synthesis of [Ni(L)(SO_4)$_2$] complex

(0.01 mol, 2.05 g) of 2-(3-phenylallylidene) thiosemicarbazide and (0.01 mol, 2.63 g) of nickel sulphate were weighed carefully into a mortar. The reactants were grinded for 20 min to obtain a lemon-green powder. The powder was removed from the mortar and stored in a desiccator.

Sensitivity test

The sensitivity tests on the compounds were carried out using agar well diffusion method. The nutrient agar was prepared and poured into Petri dishes to set according to the manufacturer's recommendation. The test organisms *Staphyloccocus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtillis* and *Candida albicans* were cultured. The overnight broth cultures of the test organisms were properly diluted and inoculated on the surface of the agar. The inoculated agar was left for 20 min and holes were bored into it using cork borer. The prepared ligand and complexes were dissolved in DMSO and were then introduced into the agar using sterile swab stick. The innoculated plates were then incubated at 37 ºC for 18 hours thereafter the resultant zones of inhibition were measured and results recorded. Ciprofloxacin and fluconazole which are antibacterial and antifungal agents respectively were used as control drugs.

RESULTS AND DISCUSSION

Physical properties

The Cu(II), Co(II) and Ni(II) complexes of 2-(3-phenylallylidene)thiosemicarbazide were synthesized by reaction of metal salts with 2-(3-phenylallylidene)thiosemicarbazide. The compounds were characterized on the basis of melting point, conductivity, infrared, UV-Visible, GC-MS, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The complexes are generally soluble in polar solvent used (dimethylsulfoxide and dimethylformamide) but insoluble in non-polar solvent. The physical properties of the compounds are shown in Table 1.

All the complexes synthesized were coloured ranging from their parent ligand colour of yellow to lemon-green and dirty green. The complexes are also non-hygroscopic solids with different melting point ranging from 148 ^{o}C to 173 ^{o}C. All complexes have melting points higher than their respective parent ligand. The molar conductance values measured in DMSO solution (10^{-3} M) for the complexes are in 12-28 Ω^{-1} mol^{-1} cm^{2} range. The low conductance value suggests non-electrolytic nature of the complexes.

Table 1. Physical properties of the ligand and complexes.

Compounds	**MW (g/mol)**	**Colour**	**Molar conductivity (Ω^{-1} mol^{-1} cm^{2})**	**MP (^{o}C)**	**Yield (%)**
L*	205	Yellow	-	127-128	87.9
Cu(L)Cl_2	378	Dirty green	18.7	171-173	72.0
Co(L)Cl_2	445	Dark green	28.4	162-163	65.3
Ni(L)(SO_4)$_2$	481	Lemon green	12.7	148-150	63.1

*L- 2-(3-phenylallylidene) thiosemicarbazide; MW: molecular weight; MP: melting point

FTIR analysis

The IR spectrum of the ligand and complexes presented in Figure 1 and Table 2. The spectrum show band between 3411-3414 cm^{-1} for the ligand and complexes corresponding to the NH functional group. The spectra band at 1591-1642 cm^{-1} and 1058-1096 cm^{-1} are due to C=N and C=S respectively. The free ligand has the C=N vibration at 1591cm^{-1} and C=S vibration at 1058 cm^{-1}; therefore the shifting of the bands to higher frequencies as observed in the complexes indicates complexation (Aguzue et al., 2020). The weak bands observed below 600 cm^{-1} are assigned to metal-sulphur, metal-nitrogen and metal-chlorine bonds.

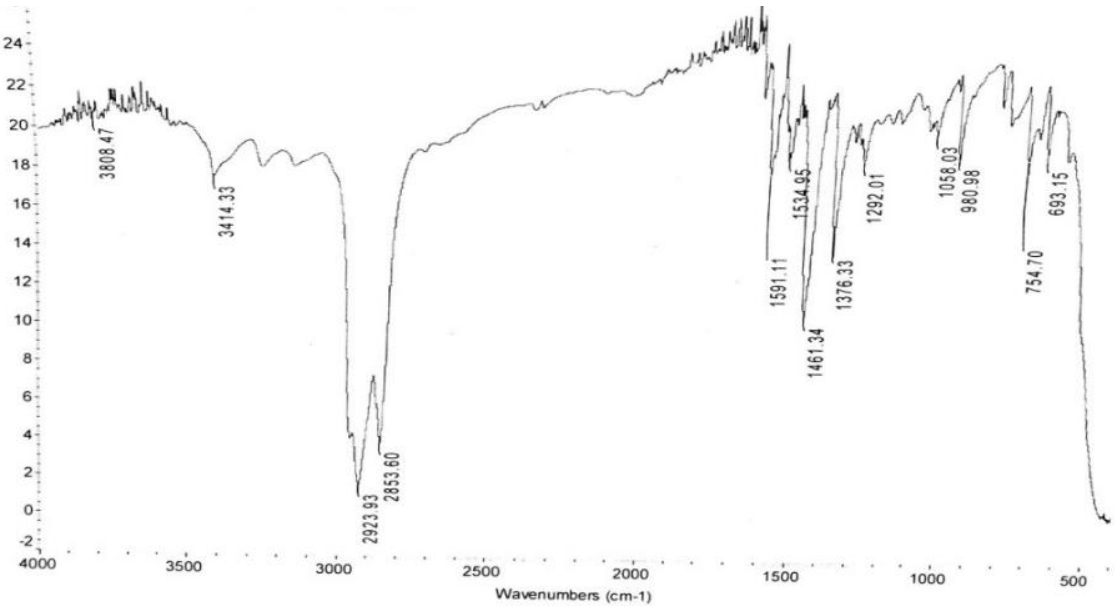

Figure 1. The FTIR spectrum of LCo (a representative spectrum for the complexes).

Table 2. The FTIR spectra data for the ligand and its complexes (cm^{-1}).

Compound	N-H stretch	=CH/Ar	C=N	C=S	M-S	M-N	M-Cl
L	3414	2923	1591	1058	-	-	-
LCu	-	2955	1642	1096	589	505	442
LNi	3411	2980	1623	1083	543	443	399
LCo	3411	2969	1640	1087	546	488	425

UV-Visible analysis

From Table 3, the UV/visible electronic spectra of the ligand L and its complexes. The ligand exhibited absorptions at 350nm and 291 nm. These absorptions resulted from intra-ligand charge transfer (ILCT) and were assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the phenyl bonds. The Cu(II) complex LCu showed a single absorption band at 287 nm characteristic of a tetrahedral geometry and was due to $^2T_2 \rightarrow {}^2E_2$ transition. The LCo showed three absorption bands at 675 nm, 612 nm and 386 nm. The bands which have tail in the visible region suggest an octahedral geometry. The transitions were due to MLCT (metal-ligand charge transfer) or LMCT (ligand-metal charge transfer) (Elemike et al., 2011). The transitions were therefore assigned the following Mulliken symbols $^4T_{1g}\rightarrow{}^4T_{2g}$ (F), $^4T_{1g}\rightarrow{}^4T_{1g}$(P), and $^4T_{1g}\rightarrow{}^4A_{2g}$ (Nwabueze et al., 2007). The Ni(II) complex exhibits a single band at 466nm and an octahedral geometry has been suggested for this band.

Table 3. UV/visible spectra of the ligand and its complexes (λ nm).

Compounds	λ nm	λ nm	λ nm
L	350	291	-
LCu	287	-	-
LNi	466	-	-
LCo	675	612	386

GC-MS analysis

The molecular ion peak at (*m/z*) 206[M+1] corresponds to the molecular weight of the Schiff base under investigation while the base peak appeared at (*m/z*) 56 with several other peaks 26, 41, 55, 83, 107, 121, 135, 173,191 and 206. Some of the fragments could be represented as shown in Figure 2.

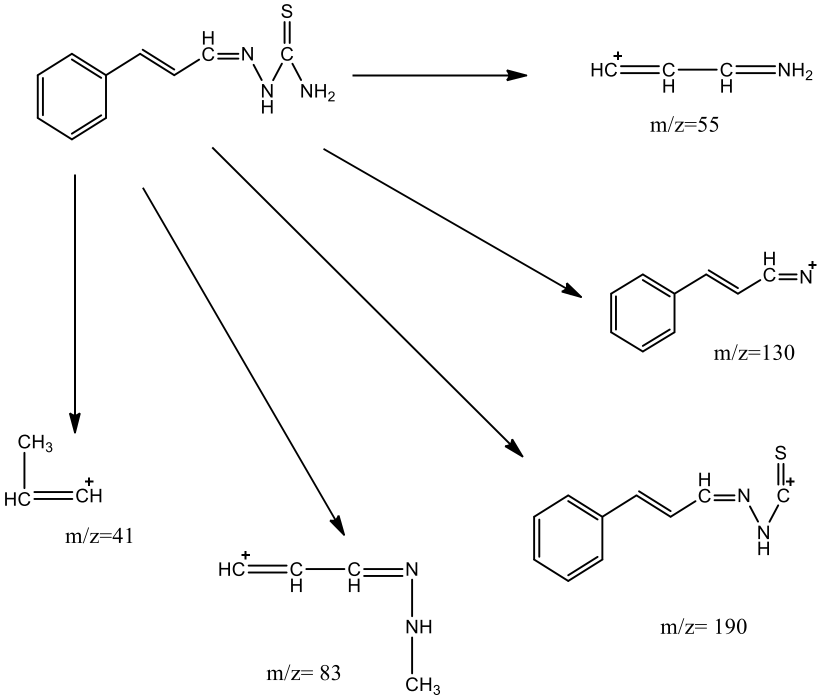

Figure 2. GC-MS fragmentation of the ligand.

^{1}H-NMR AND ^{13}C-NMR analyses

From the ^{1}HNMR data (Figure 3(a)), there appeared four proton environments. The aromatic protons appeared within the range of 6.83-7.58 ppm and were not affected by chelation (Neelakantan et al., 2010; El-Ajail et al., 2006; Olagboye et al., 2013). The signal at 11.26 ppm is assigned to amine proton N-NH. The α-NH_2 signal appeared at 7.83 ppm and the azomethine proton occurred at 8.03 ppm. In ^{13}C-NMR (Figure 3(b)), the TMS and d6-DMSO was represented at 0 and

40 ppm respectively. The C=S peak resonated at 145 ppm and the aromatic carbon peaks appeared between 125- 136 ppm. The azomethine carbon peak was observed at 139 ppm.

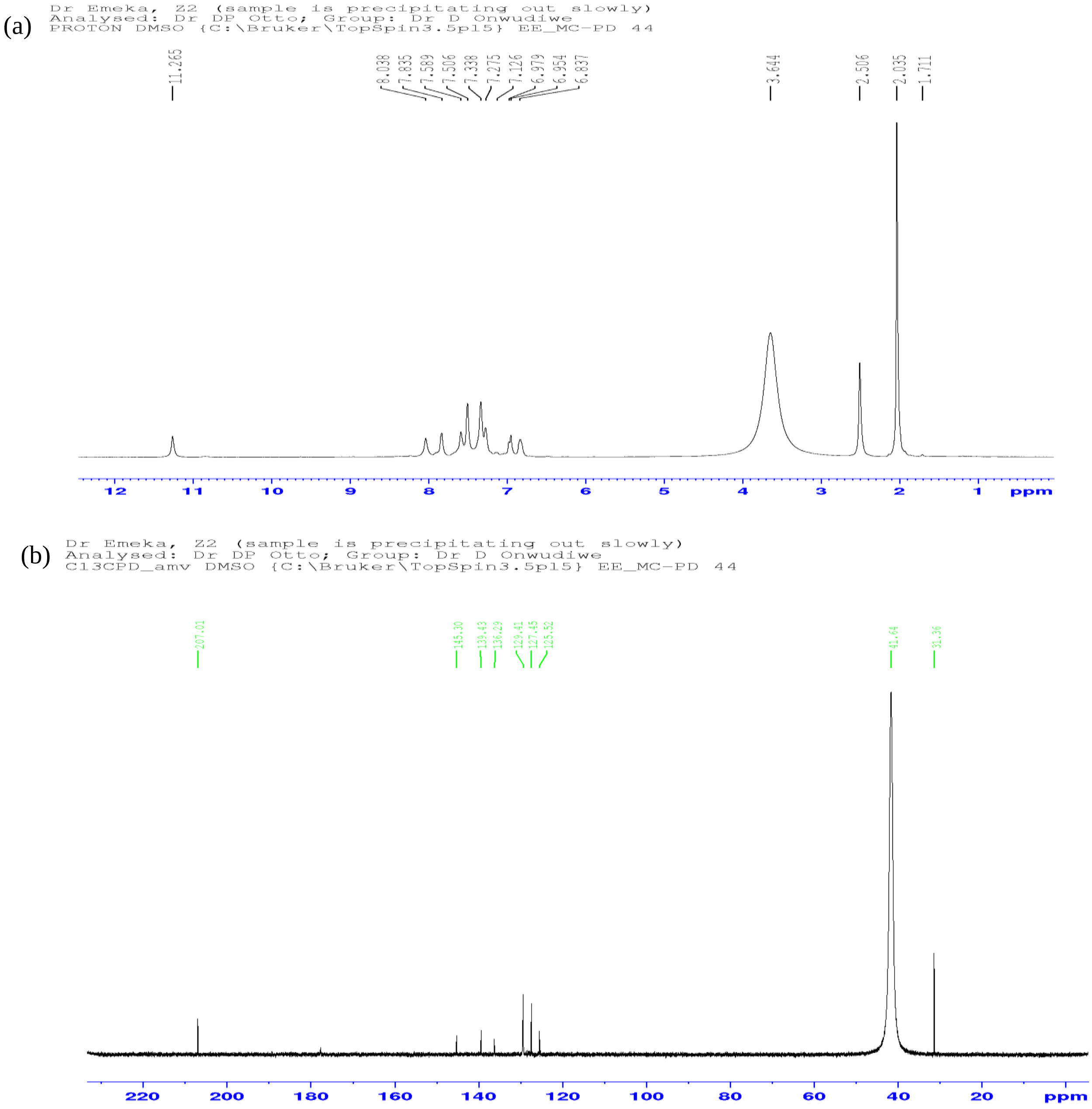

Figure 3. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of the ligand.

Antimicrobial test

The synthesized compounds were screened against some microbes and the results are presented in Table 4. All the values are in cm (zones of inhibition measured with a meter rule). The control drugs used were ciprofloxacin and fluconazole. The ligand was active against some of the microbes especially the fungi but activities were increased upon chelation with metal ions. The Co, Ni, and Cu complexes exhibited great antifungal than antibacterial activities. The antimicrobial test showed that the synthesized compounds especially the complexes are active chemotherapeutic agents and have shown great antibacterial and antifungal activities. A further study is therefore encouraged as these types of complexes are promising.

Table 4. Antimicrobial test result.

Compounds	***Escherichia coli***	***Pseudomonas aeruginosa***	***Bacillus subtilis***	***Staphylococcus aureus***	***Candida albicans***
L*	-	-	12 cm	-	15 cm
CoL	15 cm	24 cm	18 cm	21 cm	15 cm
NiL	13 cm	17 cm	23 cm	16 cm	17 cm
CuL	-	12 cm	18 cm	17 cm	11 cm
Control	14 cm	10 cm	15 cm	-	13 cm

CONCLUSION

The solvent-free synthesis and characterization of Cu(II), Co(II), and Ni(II) Complexes of 2-(3-Phenylallylidene) Thiosemicarbazide has been studied. A Schiff base ligand 2-(3-phenylallylidene) Thiosemicarbazide have been synthesized by the mechanochemical solvent-free reaction of Thiosemicarbazide and Cinnamaldehyde. Its divalent complexes of Co, Cu, and Ni were also synthesized. The ligands and complexes have been characterized by FTIR, UV-Visible, GC-MS, ^{1}H-NMR, and ^{13}C-NMR. The ligand behaved as a bidentate donor by using its S and azomethine N as binding sites for the metals. Of the five microbes tested (four bacteria and a fungi species), the ligand showed low activity for only two and no activity to the other three microbes. But the complexes were remarkably active against the bacteria and fungi species.

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REFERENCES

Aguzue, O., Oviawe, A.P., Adebiyi, A. (2020). Mechanochemical synthesis and potentiation of the antimicrobial activity of 4-[3-(4-methoxyphenyl) allylideneamino]-1,5-dimethyl-2-phenylpyrazol-3-one by metal chelation. *Journal of Science and Mathematics Letters*, 8(2), 15-21.

El-Ajaily, M.M., Maihub, A.A., Hudere, S.S., Ben-Saber, S.M. (2006). Nickel (II) Chelate of Schiff base derived from 4-dimethyl-amino-benzaldehyde with cysteine. *Asian Journal of Chemical Society*, 18 (4), 2427-2430.

Elemike, E.E., Oviawe, A.P., Otuokere I.E. (2011). Potentiation of the antimicrobial activity of 4-benzylimino-2,3-dimethyl-1-phenylpyrazal-5-one by metal chelation. *Research Journal of Chemical Sciences*, 1(8), 6-11.

Jarrahour, A., Zarei, M. (2008). Solid-solid phase and solvent-free oxidative removal of N-(4-ikoxyphenyl) groups of monocyclic β-lactams with ceric ammonium nitrate as a cheap, simple and efficient method. *Synthetic Communications*, 38, 1837-1845.

Martins, M.A.P., Frizzo, C.P., Moreira, D.N., Buriol, L., Machado, P. (2009). Solvent-free heterocyclic synthesis. *Chemistry Reviews*, 109, 4140-4182.

Mikami, K. (2005). Green Reaction Media in Organic Synthesis, Blackwell, Oxford.

Neelakantan, M.A., Esakkiammal, M., Mariappan, S.S., Dharmaraja, J., Jeyakumar, T. (2010). Synthesis, characterization and biocidal activities of some Schiff base metal complexes. *Indian Journal of Pharmaceutical Sciences*, 72(2), 216-222.

Nwabueze, J.N., Salawu, O.W. (2007). Complexes of Ni(II) and Cu(II) sulphates with hydrazone derived from nicotinic and isonicotinic acids. *Journal of Chemical Society of Nigeria*, 32(2), 254-259.

Olagboye, S.A., Okoronkwo, A.E., Lajide, L. (2013). Synthesis, characterization and antimicrobial evaluation of mixed ligand complexes of Ni(II) and Co(II) 1,2,3-Triazole with thiocyanate. *Research and Reviews: Journal of Chemistry*, 2(1), 25-31.

Schmeyers, J., Toda, F., Boy, J., Kaup, G. (1998). Quantitative solid-solid synthesis of azomethines. *Journal of the Chemical Society, Perkin Transactions 1*, 2, 989-994.

Tanaka, K. (2004). Solvent-free Organic Synthesis, Wiley-VH, Weinheim.

Tanaka, K., Toda, F. (2000). Solvent free Organic synthesis. *Chemistry Reviews*, 100, 1025-1074.