World Journal of Applied Chemistry
2016; 1(1): 22-25
http://www.sciencepublishinggroup.com/j/wjac
doi: 10.11648/j.wjac.20160101.14

Synthesis, Characterisation and Biological Activity of Mixed Ligand Complex of Ni(II) with Furfuralurea and Thiourea

Idoko Owoicho*, Emmanuel Stella, Abubakar Salisu, Thomas Sunday Asuquo

Sheda Science and Technology Complex, Sheda, Abuja, Nigeria

Email address:

samuelidoko2015@yahoo.com (I. Owoicho)

*Corresponding author

To cite this article:

Idoko Owoicho, Emmanuel Stella, Abubakar Salisu, Thomas Sunday Asuquo. Synthesis, Characterisation and Biological Activity of Mixed Ligand Complex of Ni(II) with Furfuralurea and Thiourea. *World Journal of Applied Chemistry.* Vol. 1, No. 1, 2016, pp. 22-25.
doi: 10.11648/j.wjac.20160101.14

Received: October 10, 2016; **Accepted**: November 1, 2016; **Published**: November 23, 2016

Abstract: A novel mixed ligand complex of the type $[M(FU)_2A_2]$ where M is Ni(II), FU is furfuralurea and A is thiourea was synthesized, characterized by solubility test, melting point, conductivity measurement, infrared and UV/Vis spectroscopy. The mixed ligand complex of the Ni II was also tested against *Proteus mirabilis, Staphlococus aureus, E. coli, Klebsiella pneumonia* and *Pseudomonas aeriginosa.* The in vitro evaluation of the biological studies of the mixed ligand complex showed greater activity against *Proteus mirabilis* and *Klebsiella pneumonia* at 60 ug/ml/disc with the minimum zone of inhibition of 13mm and 14mm respectively. The conductivity measurement revealed that the complex is a non electrolyte. The different shade of colour of the complex from the ligand, the shift of the band of the carbonyl functional group to a lower wavelength are evidences of coordination between the metal and the ligands. An octahedral geometry was suggested for the complex. The solubility test shows that the complex is soluble in methanol and dimethylsulphoxide.

Keywords: Nickel, Mixed Ligand Complex, Antimicrobial, Furfuralurea, Coordination Compounds

1. Introduction

Developments in the field of coordination chemistry, which is closely bound up with study of mixed and mixed polynuclear complexes have been extensively studied in recent years because of its importance in the field of analytical chemistry [18]. Many naturally occurring metal complexes are mixed ligand complexes containing two or more different ligand molecules or if the ligand is a single macromolecules having two or more different kinds of donor atoms [19]. Coordination complexes have been an important popular area in research due to their simple synthesis, adaptability and different range of applications [20]. Nickel used in this work is an important transition metal normally stable in the +2 oxidation state. This metal is more attracted by the researchers in recent years because of their numerous importance in biological systems [20]. Mixed ligand complexes play key roles in biological, environmental systems and also act as active catalysts in reactions of industrial importance including hydrogenation, hydroformation and oxidative hydrolysis of olefins and carboxylation of methanol [6, 9, 10, 11, 12]. Mixed ligand complexes are characterized by their extreme stability [18]. Many factors that control the mixed ligand complexes formation and determination of the composition and stability of the mixed ligand complexes have been studied. Factors like electronic structure, nature of ligands, geometric structure of complexes have also been studied. Furthermore, mixed ligand complexes are found to be more active biologically than the ligand itself and its binary complexes [9]. From study, it was widely reported that transition metal mixed ligand complexes are used in fighting microbial infections [1, 2, 3, 4, 11]. Furfuralurea used as the primary ligand is a slow release nitrogen fertilizer which releases nitrogen by hydrolysis and microbial activities [12]. The ability of furfuralurea forming a complex with a metal have been investigated [13]. Infectious disease still remains a crucial and challenging problem because of a combination of factors including rising infectious diseases and increasing of multi-drug resistant pathogens. Thus there is still need to

discover new compounds with enhanced antimicrobial activities to combat drug resistance menace [21]. The aim of this work is to synthesise the novel mixed ligand complex, study the spectral properties as well as the antimicrobial activity.

2. Materials and Methods

All reagents and solvents used are analytical grade. The electronic spectra of the complex was obtained using AQUARIUS CE 7500 series uv/vis spectrophotometer in DMSO solution at the range of 190-1100nm. The infrared spectra was recorded on a MATTSON Genesis II FTIR spectrophotometer run in nujol and neat in the range of 4000-500cm^{-1}. Melting point temperature was determined using electrothermal 9100 melting point equipment. The conductivity measurement was performed at temperature range of 28.5–33.1°C 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. The in vitro antimicrobial activity was performed against Proteus mirabililis, Staphlococus aureus, E. coli, Klebsiella pneumonia and Pseudomonas aeriginosa using disc diffusion method.

2.1. Synthesis of Furfuralurea

In a 250ml flat-bottomed flask fitted with a thermometer, 40ml of furfuraldehyde, 40g of urea and 10ml of distilled water was added. The mixture was heated on a water bath until the temperature rose to 60°C. Then 1ml of NaOH solution was added and the heating continued for 20mins. The mixture was cooled in iced water and the precipitate was filtered. The precipitate was then washed with n-haxane and recrystalised from methanol. The crystals was dried at 50°C in the oven [11].

2.2. Synthesis of the Mixed Ligand Complex

To an aqueous solution of furfuralurea, 10.4g of $Ni(NO_3)_2.6H_2O$ was added and boiled with stirring on a hot plate. The mixture was filtered and the filtrate refluxed. 20g of thiourea was added stirred and reflux further. The mixture was cooled and precipitate recrystalised with ethanol. It was dried in the oven at 50°C. The general equation for the formation of the complex is shown below:

$$MX_2.6H_2O + 2Fu + 2A \rightarrow [M(Fu)_2A_2] + (NO_3)_2 + 6H_2O$$

Where M = Ni (II), X = NO_3, Fu = Furfural-urea, A = Thiourea

2.3. Preparation of Turbidity Standard

A 0.5McFarland standard was prepared as described by [18]. 0.5ml of barium chloride was added to 1% sulfuric acid solution and mixed well. A small volume of those turbid solutions was transferred to a storage bottle and stored in the dark at room temperature until require for use.

2.4. Standardization of Inoculums

Using inoculating loop, enough material from an overnight culture of the test organisms were transferred into a tube containing about 2.0ml normal saline, until the turbidity of the suspension matched the turbidity standard 0.5McFarland [16].

2.5. Disc Preparation

Whatman No.1 filter paper disc of (6mm in diameter) were punched and placed in Bijour bottles, which were sterilized by autoclaving at 121°C for 15mins and kept in a refrigerator until require for use.

2.6. Disc Antimicrobial Activity Testing

Agar diffusion method as modified and adopted from [17] was employed. The freshly prepared Mueller-Hilton agar plates were dried on a dryer for about 15mins to remove surface moisture. The plates were aseptically inoculated uniformly with test organism by streaking methods. With the help of a sterile forceps, impregnated paper discs (Whatman No.1 filter paper) containing the extract at different concentration (60, 30, and 15ug/disc) were arranged in three ddirection and pressed firmly unto the inoculated agar surface to ensure even contact including positive control at the centre of the plate and negative control on the other side. Each disc was sufficiently spaced out and kept at least 15mm from the edge of the plate and 25mm from disc to disc to prevent overlapping of zones. The plates are incubated at 37°C for 24hrs. The zone diameter of the semi-confluent growths were measured with the aid of meter rule to the nearest millimeter.

Table 1. *Physical properties of the complex and ligand.*

Complex/ligand	Colour	Melting point(°C)	Conductivity (Ms/m)
FU	Light brown	167 – 169	--
[M(FU)2A2]	Dirty green	160	0.0875

FU-Furfuralurea

The physical properties of the complex and ligand was shown in Table 1. The various shade of colour exhibited by the complex and ligands was as a result of a charge transfer band or an internal transition in the ligand [4]. The melting of the complex is 160°C lower than the primary ligand between 167–169°C. The primary ligand is more stable compared to the complex. The solubility test shows that the complex is soluble in methanol and dimethylsulfoxide. The low conductivity value for the complex is indication that it is non-electrolyte [7].

Table 2. *Electronic spectra data for the complex and ligand.*

Complex/ligand	wave nos (cm^{-1})	electronic transition
FU	39292 – 35587	π - π*, n - π
	29895	Charge transfer
[M(FU)2A2]	11166	3A2g(F) – 3T1g(P)
	9965	3A2g(F) – 3T1g(F)
	9492	3A2g(F) – 3T2g(F)

FU- Furfuralurea

Table 2 shows the electronic spectra data for the complex and ligand. The band within the region of 11166 – 9483cm^{-1} for the complex corresponds to $^3A_{2g}(F) - {}^3T_{1g}(P)$, $^3A_{2g}(F) - {}^3T_{1g}(F)$ and $^3A_{2g}(F) - {}^3T_{2g}(F)$ transitions typical of a d^8 configuration with an octahedral environment around Ni(II) ion(3,5,21). The band at 29895cm^{-1} indicates charge transfer between the ligands and metal [3]. The primary ligand has a band between 39292-35587cm^{-1} which could be attributed to $\pi - \pi^*$ and $n - \pi^*$ electronic transitions.

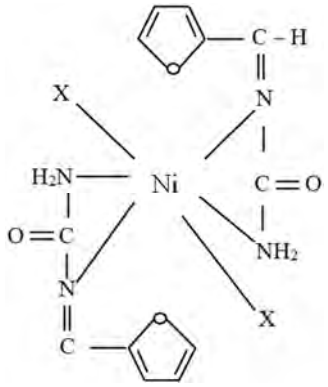
Table 3. *Infrared spectra of the complex and ligand.*

Complex/ligand	NH_a (cm^{-1})	NH_S (cm^{-1})	C=N	C=O	C=S
FU	3444.40	3299.62	1592.92	1666.20	-
Thio	3376.76	-	-	-	1079.94
$[M(FU)_2A_2]$	3376.76	3276.48	-	1610.28	1083.80

FU- Furfuralurea, Thio- Thiourea

The infrared spectra of the complex and ligand presented in Table 3 shows bands between 3444.40-3174.27cm^{-1} for the complex and ligands corresponding to the NH functional groups. The spectra band at 1592.92cm^{-1} of the furfuralurea corresponds to C=N. The band at 1666.20cm^{-1} of the primary ligand indicates C=O which shifted to a lower wavelength upon complexation. The absence of C=N in the complex could be as a result of coordination involving the azomethine nitrogen. The presence of NH in the ligand and complex could provide a good evidence for the ligand coordination around Ni (II) ion through the thione sulphur atom of the thiourea and azomethine nitrogen of the furfuralurea [15]. The band at 1079.94cm^{-1} seen in the spectra of the thiourea shifted to higher wavelength upon coordination. This band could be attributed to the C = S of the thiourea.

suggested structure



X = Sulphur atom of the thiourea.
[M(Fu)2A2]

Table 4. *Antimicrobial activity of the complex.*

Complex	Test Organisms	Concentration µg/ml/disc			+ve control CHP (60µg/ml/disc)
		15	30	60	
		Zone of inhibition (mm)			
$[M(Fu)_2A_2]$	proteus mirabilis	NA	10	13	21
	staphylococcus aureus	NA	NA	10	23
	E. coli	7	7	10	21
	klebsiella pneumonia	13	13	14	21
	pseudomona aeriginosa	NA	9	11	21

Table 4 shows the antimicrobial activity of the complex. It was carried out in dimethylsulfoxide solution at concentrations of 15, 30 and 60ug/ml/disc. The positive control was chloranphenicol at 60ug. The complex shows appreciable activity against all the test organisms at 60ug/ml/disc. The highest zone of exhibition which was 14mm was seen against *Klebsiella pneumonia* compared to 21mm inhibition of the control. The complex showed activity against *E. Coli* and *Klebsiella pneumonia* at all the concentrations used. The complex is active against *Staphylococcus aureus* at the concentration of 60 ug/ml/disc while it showed no activity against *Proteus mirabilis* and *Pseudomona aeriginosa* at 15ug/ml/disc. The higher the concentration, the higher the zone of inhibition.

3. Conclusion

As seen in this work, a novel mixed ligand complex of Ni (II) with furfuralurea and thiourea was synthesized. The shades of colour, infrared and electronic spectra indicates that there is coordination between the metal ion and ligands. An octahedral geometry was suggested. The complex shows appreciable activity against all the test organisms especially *Klebsiella pneumonia* at 60ug.

References

[1] Sangita S, Jayesh R, Jasmin B, Neha P, Khusubu T, et. al (2011) Synthesis, characterization and antimicrobial activity of some transition metal complexes (Mn, Co, Zn, Ni) with L-proline and Kojic acid. Advances in Applied Science Research, 2 (4): 374-382.

[2] Fayad NK, Taghreed HA Ghanim FH(2012) Synthesis, characterization and antibacterial activities of Manganese II CoII, IronII, NickelII Zn II and CadmiumII mixed ligand complexes containingamino acid (L-Valine) and saccharin. Advance in Physics Theories and Applications. 9: 1-4.

[3] Yosuva SM, Sabastiyan A (2012) Synthesis, characterization and antimicrobial activity of Cobalt II, and Nickel II complexes with a novel mannich base 2-(diethylaminomethyl)isoindoline-1, 3-dione. International Journal of Chemtech Research, 4 (2): 805-815.

[4] Neeraj S, Ravi P, Chaturvedi K (2012) Spectroscopic and antimicrobial studies of mixed ligand complexes of transition metal (II) ions with nitro quinoline and dibenzoyl methane. Sci. Revs. Chem. Commun., 2 (2): 108-114.

[5] Sanap SV, Patil RM (2013) Synthesis, characterization and biological activity of chiral mixed ligand Ni (II) complexes. Research Journal of Pharmaceutical Sci. 2 (1): 1-10.

[6] Ajay RP, Kamini JD, Sambhaji SR, Vishwanath RP, Rama SL (2012) Synthesis characterization and biological activity of mixed ligand Co(II) complexes of Schiff base 2-amino-4-nitrophenol-n-salicylidene with some amino acids. J. Chem. Pharm. Res. 4 (2): 1413-1425.

[7] Geary WJ, (1997) Use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord. Chem. Rev. 7: 81-122.

[8] Khanol K, Jahagirdar DV, Khanolkar DD (1973) Mixed ligand chelates of uranyl ion. J. Inorg. Nucl. Chem. 35 (3): 931-940.

[9] Bruce MR, Ronaldo P (1974) Some factors influencing mixed ligand complex formation. J. Inorg. Nucl. Chem. 36: 1665-1670.

[10] Malik GS, Singh SP, Tandon JP (1977) Studies on the mixed ligand complexes involving ligands of biological importance [Ni (II), Zn (II), or Cd (II) 1-10 phenanthroline-amino acids]. J. Inorg. Nucl. Chem. 39 (7): 1279-1982.

[11] Agwara MO, Ndifon MT, Ndosori NB, Paboudam AG, Yufanyi DM et al. (2010) Synthesis, characterization and antimicrobial activity of Co (II), Cu (II), and Zn (II) mixed ligand complexes containing 1,10-phenanthroline and 2, 2-bipyridin. Chem. Soc. Of Ethiopia. 24 (3): 383-389.

[12] Omojola MO (1993) Modification of urea with maize cob waste for use as slow release nitrogen fertilizer. Ph. D. Thesis; Ahmadu Bello University, Zaria, Nigeria.

[13] Idoko O, Thomas SA (2007) Preparation and characterization of furfural-urea metal complexes of Ni(II) and Co (II). B. Sc. Thesis; university of Abuja, Nigeria.

[14] Hamrit H, Ojebba-sid S, Benli-Baitich O, Khan MA, Bouet GM (2000). Potentiometric studies, synthesis and characterization of mixed ligand complexes of Cu (II), Ni (II), Co (II) and Mn (II) with N-acetomidioiminodiacetic acid as the primary ligand and histidine as the secondary one. Synth. React. Inorg. Met-Org. Chem. 30 (10): 1835-1848.

[15] Iniama GE, Offiong OE, Nfor E, Ayi AA (2007) Mixed ligand complexes of Nickel (II) with 2-acetylpyridine thiosemicarbonzone and some N/S monodentate ligands: synthesis, structural characterization and biological activity. Proceedings of the 30th annual international conference of chemical society of Nigeria (CSN) Abuja, Nigeria.

[16] Clinical Laboratory Standard institute/national committee for clinical laboratory standard 2006.

[17] European committee on antimicrobial susceptibility testing, version 2.1, 2012.

[18] Alimarin IP, and Shlenskaya VI. (1996). The analytical chemistry of mixed ligand complexes. Institute of Analytical Chemistry, M. V. Lomonosov Mosco State.

[19] Osunlaya AA, Ndahi NP and Ameh JA. (2007). Physico-chemical and antimicrobial properties of CoII, NiII and CuII mixed ligand complexes of dimethylglyoxime. Proceedings of the 30th annual international conference of chemical society of Nigeria. 89 – 98.

[20] Faridul I, Amran H, Nur MS, Hridika TB, Alagir K, Mohammad JK and Romel M. (2015). Synthesis, characterization, and antimicrobial activity studies of Ni (II) complex with pyridine as a ligand. Journal of Chemistry. 2015 (2015).

[21] Jegede CA. (2005). Synthesis, characterization, and biological studies of some metal fluoroquinolone complexes, PhD thesis, University of Ilorin, Kwara State, Nigeria.