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Research Article

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Synthesis, Characterisation and Antimicrobial Activity of Mixed Ligand Complexes of Ni (II) with Furfuralurea as the Primary Ligand

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ABSTRACT

New mixed ligand complexes of the type $[M(Fu)_2A]$, where M is Ni (II), FU is furfural urea and A is either dimethylsulphoxide (DMSO), trimethylamine (TEA) or aniline were synthesized characterized by metal analysis, solubility test, melting/decomposition point, conductivity measurement, IR and UV/VIS spectroscopy. The mixed ligand complexes were also tested for their antimicrobial activity against Escherichia coli, Staphlococcus aureus and Salmonella paratyphi. There was evidence of coordination between the metal and the ligands and the electronic spectra suggested an octahedral geometry. All the complexes recorded appreciable activity against all the test organisms.

Keywords: Nickel, mixed ligand complexes, antimicrobial activity, furfural-urea, spectral data.

INTRODUCTION

Mixed ligand complexes play key roles in biological, environmental systems and also act as active catalyst in reactions of industrial importance including hydrogenation, hydroformation and oxidative hydrolysis of olefins and carboxylation of methanol[6,12,13,14,15]. Furthermore, mixed ligand complexes are found to be more active biologically than the ligand itself and its binary complexes[16], and also from literature, it was widely reported that transition metal mixed ligand complexes is used in fighting microbial infections[1,2,3,4,17]. Furfural-urea used as the primary ligand in this study is a slow release nitrogen fertilizer which releases nitrogen by hydrolysis and microbial activities[18]. The ability of furfural-urea forming a complex with a metal have been investigated[19]. This aim of this paper is to synthesis some new mixed ligand complexes of Ni(II) using furfural-urea as the primary ligand and aniline, trimethylamine and dimethylsulphoxide as the secondary ligand and also study the spectral properties as well as the antimicrobial activity.

EXPERIMENTAL SECTION

All reagents and solvents used were of analytic grade. The metal were analysed by complexometric methods. The electronic spectra of the complexes were obtained using AQUARIUS CE 7500 series uv/vis spectrophotometer in DMSO solution at the range of 190-1100nm. The infrared spectra were recorded on a MATTSON Genesis II FTIR spectrophotometer run in nujol and neat in the range of 4000-500cm^{-1}. Melting/decomposition temperature were determined using electrothermal 9100 melting point equipment. The conductivity measurement were performed at temperature range of 28.5-33.1^oC using JENWAY pH/conductivity meter in DMSO solutions at a concentration of $10^{-3}mol/dm^3$. Polar and non-polar solvents were used to determine the solubility of the complexes. The in vitro

antimicrobial activity of the complexes were performed against *Escherichia coli, Staphlococcus aureus and Salmonella paratyphi* using disc diffusion method.

Synthesis of furfural-urea

In a 250ml flat-bottomed flask fitted with a thermometer, 40ml of furfural, 40g of urea and 10ml of distilled water were added. The mixture was heated on a water bath until the temperature rose to 60^{o}C. Then 1ml of NaOH solution was added and the heating continued for 20 mins. The mixture was cooled in iced water and the precipitate was filtered. The precipitate was then washed with n-hexane and recrystalised from methanol. The crystals were dried at 50^{o}C in the oven[18].

Synthesis of Mixed Ligand Complexes of Ni(II)

To an aqueous solution of furfural urea, 10.4g of $Ni(NO_3)_2.6H_2O$ was added and boiled with stirring on a hot plate for 15mins. The mixture was filtered and the filtrate reflux for 15mins. 20ml of either ammonia, DMSO or trimethylamine was added stirred and reflux further for 1hr 45mins. The mixture was cooled and precipitate filtered out and washed with ethanol. It was dried in the oven at 50^{o}C. The general equation for the formation of the complexes is shown below;

$MX_2.nH_2O + 2FU + A$ ---------- $[M(FU)_2A] + (NO_3)_2 + 6H_2O$

Where,

M = Ni(II), X = NO_3, FU = Furfural-urea, B = ammonia, aniline or trimethylamine.

Antimicrobial Test

Preparation of Turbidity Standard.

A 0.5 McFarland standard was prepared as described by [18]. 1% V/V solution of sulfuric acid was prepared by adding 1 ml of concentrated sulfuric acid to 99 ml of water and mixed well. A 1.175% W/V solution of barium chloride was prepared by dissolving 2.35 g of dehydrated barium chloride ($BaCl_2.H_2O$) in 200 ml of distilled water. To make the turbidity standard, 0.5 ml of the barium chloride solution 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 required for use.

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 te suspension matched the turbidity standard 0.5 McFarland [18].

Disc Preparation

Whatman No.1filter paper discs of (6mm in diameter) were punched out with aid of paper punch and placed in Bijour bottles, which were sterilized by autoclaving at 121^{0}c for 15 minutes and keep in a refrigerator until required for use.

Disc Antimicrobial Activity Testing.

A gar diffusion method as modified and adopted from [19], was employed. The freshly prepared Mueller-Hinton agar plates were dried in a dryer for about 15-minutes to remove surface moisture. The plates were aseptically inoculated uniformly with test organism by streaking methods. With the aid of a sterile forceps, impregnated paper discs (What man No.1filter paper) containing the extract at different concentrations (60, 30 and 15µg/disc) were arranged in three directions and pressed firmly onto the inoculated agar surface to ensure even contact including positive control at the center of the plate and negative control on the other side. Each disc was sufficiently spaced out and kept at least 15 mm from the edge of the plate and 25mm from disc to disc to prevent overlapping of zones. The plates are incubated at 37±2^{0}c for 24hrs. The zone diameters of the semi-confluent growths were measured with the aid of a meter rule to the nearest millimeter.

RESULTS AND DISCUSSIONS

The physical properties of the complexes are shown in Table 1. The various shades of colour exhibited by the complexes was as a result of a charge transfer band or an internal transition in a ligand[4]. The melting/decomposition temperatures indicates that only the $Ni(FU)_2DMSO$ decomposes at 252^{o}C and loses water at 212^{o}C. [$Ni(FU)_2$Aniline] has melting point above 400^{o}C, while $Ni(FU)_2TEA$ melts between 220-222^{o}C. The solubility test carried out also shows that all the complexes are soluble in methanol and DMSO. The conductivity measurement results ranges between 0.138-0.673mS/m. This low conductivity values is an indication that the complexes is non-electrolyte in nature[11].

Table1. Physical properties of the complexes and ligand

Complexes	Colour	Mp/decomposition temp. ^{o}C	Conductivity mS/m	Metal (%)
$Ni(FU)_2DMSO$	Black shiny crystals	252.8*	0.379	17.96
$Ni(FU)_2$Aniline	Black powder	>400	0.138	5.28
Ni(FU)TEA	Grey	220 – 222	0.673	16.78
FU	Light brown	167 – 169	-	-

**= decomposition temperature, FU = Furfural urea, TEA = Trimethylamine, DMSO = Dimethylsulphoxide.*

Electronic Spectra

The electronic spectra of the complexes were done in DMSO and presented in Table 2. The electronic spectra bands in the regions between 34722-37950cm^{-1} of all the complexes is an evidence of charge transfer within the complexes[3]. The bands in the region between 25966-9487cm^{-1} are attributed to $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ which suggest an octahedral environment around Ni(II) ion[3,21,5]. The v_2/v_1 ratio in the range of 1.36-1.55 which is less than 1.8 further suggest an octahedral geometry[3]. The bands in the region of 39292-35587cm^{-1} for furfural-urea can be attributed to $\pi - \pi^*$ and $n - \pi^*$ electronic transitions.

Table 2. Electronic spectra data for the Ni (II) complexes

Complexes	Wave numbers v cm^{-1}	Electronic transitions	V_2/v_1
FU	39292 – 35587	$\pi - \pi^*$ $n - \pi^*$	-
$Ni(FU)_2DMSO$	37523 – 34722 25966 13651(v_2) 9965 (v_1)	CT $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	1.39
$Ni(FU)_2$Aniline	37950 – 34423 22497 15534 (v_2) 9970 (v_1)	CT $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	1.55
$Ni(FU)_2TEA$	37243 – 34662 23223 13661(v_2) 9965 (v_1)	CT $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	1.37

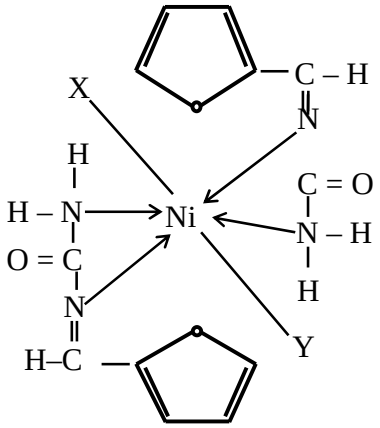
Infrared Spectra

The IR band of furfural-urea for $v_a(NH_2)$ and $v_s(NH_2)$ was at 3440.40cm^{-1} and 3299.62cm^{-1} while the bands at 1592.92cm^{-1} and 1666.20cm^{-1} corresponds to v(C=N) and v(C=O) respectively and upon coordination with the metal ion the two bands shift to a higher wave numbers as shown in Table 3. The absence of v(CN) in [$Ni(FU)_2$Aniline] was probably due to the interference of the vibrational bands of nujol or bond formation involving this. The bands around 2200-2100cm^{-1} corresponding to v(C-N) was seen in the $Ni(FU)_2DMSO$ and $Ni(FU)_2TEA$ but absent in the $Ni(FU)_2$Aniline. The presence of v(NH) in all the complexes provides good evidence for the ligand coordination around the Ni(II) ion through the thione sulphur atom of the aniline and DMSO, azomethine nitrogen and the nitrogen atom of trimethylamine[20]. The v(N-O) was seen in the region of 1035.59cm^{-1} and 1027.87cm^{-1} for all the complexes except in the spectra of $Ni(FU)_2TEA$.

Table 3. Infrared spectra data of the Ni(II) complexes and furfural urea

Complexes	vaNH2	v_sNH_2	vC=N	vC=O	vCN	v N-O
FU	3444.40	3299.62	1592.92	1666.20	-	-
$Ni(FU)_2DMSO$	3338.19	2921.64	1380.79	1644.99	2200.39	1016.30
$Ni(FU)_2Aniline$	3363.26	-	1450.00	1600.63		1027.87
$Ni(FU)_2TEA$	3386.40	-	1376.93	1627.63	2186.89	-

Proposed Structure for the Ni (II) Mixed Ligand Complexes



X = S(Aniline or DMSO) or N(TEA)
Y = NO_3

Antimicrobial Activity

The antimicrobial testing of the complexes was carried out by a previous method described by EUCAST 2012, where the complexes were dissolve separately in DMSO at different concentrations of 15, 30 and 60µg/ml/disc and tested against *Escherichia coli, Staphlococcus aureus* and *Salmonella paratyphi*. The results in Table 4 shows that all the complexes show high inhibitory activities against the organisms at the concentration of 60µg/ml. The nickel complexes of TEA and DMSO is more effective against *Staphlococcus aureus* with a zone of inhibition of 14mm and 22mm respectively, while that of aniline is more effective against *Salmonella paratyphi* as shown in Table 4. At a lower concentration of 15µg/ml the mixed ligand complex of DMSO is more effective against *Salmonella paratyphi* with a zone of inhibition of 12mm compared to an antimicrobial drug Kanamycin with inhibition zone of 9mm at the concentration of 25µg/ml reported by[3], and also at 15µg/ml, $Ni(FU)_2DMSO$ was more effective against *Escherichia coli* with zone of inhibition of 12mm compared to tetracycline with a zone of 10mm at a 25µg/ml as reported by[3].

Table 4: Antimicrobial activities of the mixed ligand complexes

Complex	Test organisms	Concentrations µg/ml		
		15	30	60
		Zone of inhibition (mm)		
$Ni(FU)_2DMSO$	E.C	12	14	16
	S.P	12	15	18
	S.A	14	18	22
$Ni(FU)_2TEA$	E.C	9	10	12
	S.P	9	10	12
	S.A	10	11	14
Ni(FU)Aniline	E.C	9	12	12
	S.P	10	14	15
	S.A	9	10	11

E.C–Escherichia Coli; S.P- Salmonella paratyphi; S.A - Staphlococcus aureus; DMSO- dimethylsulphoxide; TEA- trimethylamine; FU- furfural-urea.

CONCLUSION

As seen in this work, mixed ligand complexes of Ni(II) and furfural-urea as the primary ligand were synthesized. The infrared spectra indicates that there is coordination between the metal ion and ligands. The electronic spectra also suggest an octahedral geometry for all the complexes. The antimicrobial activities of the complexes shows that

there is greater activity against the gram –ve organisms compared to the gram +ve. The [Ni(FU)$_2$DMSO] show more activity against *Escherichia coli* and *Staphlococcus aureus* compared to drugs like tetracycline and kanamycin respectively.

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