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

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Abstract

Some new mixed ligand complexes of the type $[M(\text{Fu})_2\text{B}]$, where M is Ni (II) or Co(II), FU is furfural urea and B is ammonia 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*, *Staphylococcus aureus* and *Salmonella paratyphi*. There was evidence of coordination between the metals and the ligands and the electronic spectra suggested an octahedral and tetrahedral geometry for the Ni(II) and Co(II) complexes respectively. All the complexes recorded appreciable activity against all the test organisms.

Keywords: Transition metals, 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.

Materials and Methods

All reagents and solvents used were of analytic grade. 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 4000-500 cm^{-1} . Melting/decomposition temperature were determined using electrothermal 9100 melting point equipment. The conductivity measurement was performed at temperature range of 28.5-33.1 $^{\circ}\text{C}$ 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 activities of the complexes were performed against *Escherichia coli*, *Staphylococcus 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 $^{\circ}\text{C}$. 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 recrystallised from methanol. The crystals were dried at 50 $^{\circ}\text{C}$ in the oven[18].

Synthesis of Mixed Ligand Complex of Ni(II)

To an aqueous solution of furfural urea, 10.4g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and boiled with stirring on a hot plate for 15mins. The mixture was filtered and the filtrate reflux for 15mins. 20ml ammonia, 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°C.

Synthesis of Mixed Ligand Complex of Co(II)

To an aqueous solution of furfural urea, 8.5g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added and boiled with stirring on a hot plate for 15mins. The mixture was filtered and the filtrate reflux for 15mins. Then 20ml of ammonia was added, stirred and reflux further for 1hr 45 mins. The mixture was cooled and precipitate filtered out and washed with 50% ethanol. It was then dried in the oven at 50°C.

The general equation for the formation of the complexes is shown below;



Where,

M = Ni(II) or Co(II), X = Cl₂, FU = Furfural-urea, B = ammonia.

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 ($\text{BaCl}_2 \cdot \text{H}_2\text{O}$) 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 the suspension matched the turbidity standard 0.5 McFarland [18].

Disc Preparation

Whatman No.1 filter 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°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.1 filter 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°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 different colours 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 shows that only the $[\text{Co}(\text{FU})_2\text{Ammonia}]$ decomposes at 72°C, while that of $[\text{Ni}(\text{FU})_2\text{Ammonia}]$ has melting point of 85.5°C. The solubility test carried out also shows that all the complexes are soluble in methanol and DMSO. The conductivity measurement results indicate 0.0477 and 0.998 for the Co and Ni complexes respectively. 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. °C	Conductivity mS/m
Ni(FU) ₂ Ammonia	brown	72.8*	0.0477
Co(FU) ₂ Ammonia	Dark brown	85.5	0.998
FU	Light brown	167 – 169	-

*Decomposition temperature, FU = Furfural urea.

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 37807-34722cm⁻¹ of all the complexes is an evidence of charge transfer within the complexes [3]. The bands in the region between 19028-9487cm⁻¹ of the Co(II) complex are attributed to ⁴T_{1g}(F) → ⁴T_{1g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) electronic transitions, while the bands in the region of 20224-9487cm⁻¹ of the Ni(II) complex are attributed to ³A_{2g}(F) → ³T_{1g}(P), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{2g}(F) [3,21,5]. The v₂/v₁ ratio for the Ni complex is 1.45 suggesting an octahedral geometry and that of Co complex is 1.28 suggesting a tetrahedral geometry [3,4]. The bands in the region of 39292-35587cm⁻¹ for furfural-urea can be attributed to π - π* and n - π* 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	π - π* n - π*	-
Ni(FU) ₂ Ammonia	37878-35149 20224 13815(v ₂) 9487(v ₁)	CT ³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F) ³ A _{2g} (F) → ³ T _{2g} (F)	1.45
Co(FU) ₂ Ammonia	37950 – 34423 22497 15534 (v ₂) 9970 (v ₁)	CT ⁴ T _{1g} (F) → ⁴ T _{1g} (F) ⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P)	1.28

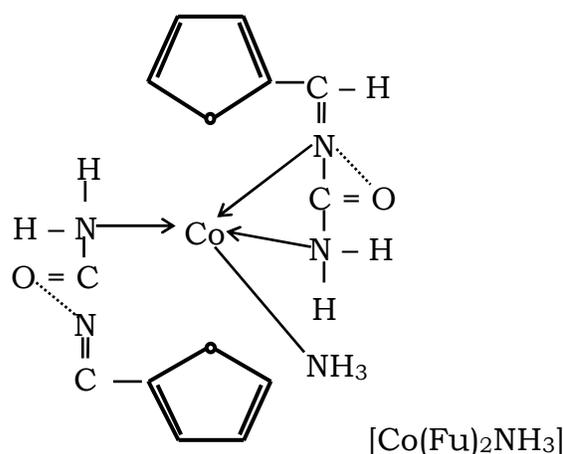
Infrared Spectra

The IR band of furfural-urea for v_a(NH₂) and v_s(NH₂) was at 3444.40cm⁻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. Upon coordination with the metal ion the two bands shift to a higher wave numbers as shown in Table 3. The vC-N band was seen at 2188.82cm⁻¹ in the spectra of [Ni(FU)₂Amonia] but absent in the spectra of the Co complex. The bands around 775 and 827cm⁻¹ of the complexes are evidence of ligand coordination around the metal ions through the nitrogen atoms[23].

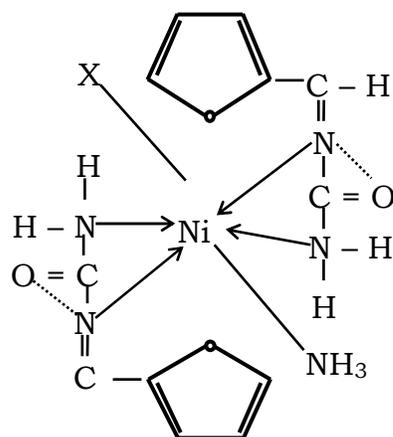
Table.3 Infrared spectra data of the Ni(II) complexes and furfural urea

Complexes	v _a NH ₂	v _s NH ₂	vC=N	vC=O	vCN	vM-N
FU	3444.40	3299.62	1592.92	1666.20	-	-
Ni(FU) ₂ NH ₃	3364.19	3170.57	1357.64	1629.56	2188.82	827.31
Co(FU) ₂ NH ₃	3380.62	-	1465.64	1589.06	-	775.24

a. Proposed Structure for Co(II) mixed Ligand Complex



b. Proposed Structure for Ni(II) mixed Ligand Complex



X = Cl



Antimicrobial Activity

The antimicrobial testing of the complexes was carried out by a previous method described by [18,19], where the complexes were dissolve separately in DMSO at different concentrations of 15, 30 and 60µg/ml/disc and tested against *Escherichia coli* (E.coli), *Staphylococcus aureus* (Staph. aureus) and *Salmonella paratyphi* (Sal. Typhi). The results in Table 4 shows that all the complexes show high inhibitory activities against the test organisms at the concentration of 60µg/ml. The Co complex is more effective against E. coli with zone of inhibition of 20mm at 60µg/ml, while the Ni complex is more effective against Sal. Typhi with zone of inhibition of 23mm at 60µg/ml.

Table 4: Antimicrobial activities of the mixed ligand complexes

Complex	Test organisms	Concentrations µg/ml		
		15	30	60
Ni(FU) ₂ NH ₃	E.C	10	12	16
	S.P	15	19	23
	S.A	14	18	22
Co(FU) ₂ NH ₃	E.C	10	16	20
	S.P	10	12	18
	S.A	10	12	19

E.C–*Escherichia Coli*; S.P- *Salmonella paratyphi*; S.A - *Staphylococcus aureus*; FU- furfural-urea

Conclusion

As seen in this work, mixed ligand complexes of Co(II) and Ni(II) and furfural-urea as the primary ligand were synthesized. The infrared spectra indicate that there is coordination between the metal ion and ligands. The electronic spectra data suggest an octahedral and a tetrahedral geometry for the Ni and Co complexes respectively.

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