



PRELIMINARY BIOLOGICAL STUDIES OF A BIS(BIDENTATE) SCHIFF BASE LIGANDS,
BIS-[1,1'-(2-NAPHTHYLIMINO)-INDOLE-3-CARBOXALDEHYDE] AND ITS Mn(II), Cr(III),
Pd(II), AND Os(VIII) COMPLEXES

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ABSTRACT

The synthesis, characterization and biological study of a bis(bidentate) schiff-base ligand, bis-1,1'-(2-naphthylimino)-indole-3-carboxaldehyde (Ra) formed by the condensation reaction of (R)-(+)-1,1'-binaphthyl-2,2'-diamine with indole-3-carboxaldehyde is presented. The coordination chemistry of Ra with Mn(II), Cr(III), Pd(II), and Os(VIII) have been investigated. The characterization of this ligand with its complexes was on the basis of melting point, stoichiometry, electronic, and infrared spectroscopic studies. Spectrophotometric analysis gave the stoichiometries to be 1:2 metal to ligand ratio for all its complexes except 2:3 metal to ligand ratio of palladium (II) complex of Ra. Based on the spectral studies, Ra was observed to be bidentate through the participation of its imine nitrogen in bonding with Mn(II), Cr(III), Pd(II) and Os(VIII) ions to yield $[Mn(Ra)_2(H_2O)_2]Cl_2$, $[Cr(Ra)_2(NO_3)_2 \cdot O_3]$, $[Pd_2(Ra)_3]Cl_4$ and $[Os(Ra)_2O_2]^{4+}$ complexes respectively. Therefore, it was proposed that $[Mn(Ra)_2(H_2O)_2]Cl_2$, $[Cr(Ra)_2(NO_3)_2]NO_3$, $[Os(Ra)_2O_2]^{4+}$ are octahedral, $[Pd_2(Ra)_3]Cl_4$ is square-planar in its geometry. This ligand was screened and tested against *Pseudomonas* species (clinical isolate), *Pseudomonas* species (sewage isolate), *Pseudomonas aeruginosa* (typed), *Klebsiella* species (4A), *Klebsiella* species (4B), *Klebsiella pneumoniae*, *Salmonella* species, all with ciprofloxacin as its positive control. Also other micro-organisms employed are vancomycin resistant *Staphylococcus* species with gentamycin as its positive control and *Candida albicans* with nystatin as its positive control. These screenings were performed by the agar-well diffusion method and only Ra was sensitive. Its zone of inhibition and minimum inhibitory concentration was also calculated accordingly.

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INTRODUCTION

Chirality is central to coordination chemistry, and unites fields as diverse as asymmetric catalysis, bioinorganic chemistry and supramolecular chemistry. The stereoselective synthesis of transition metal complexes represents a significant challenge to coordination chemists [1], and one successful approach has been to use chiral ligands derived from building blocks such as amino acids [2], amino alcohols [3], and terpenes [4]. 1,1'-binaphthyl units that are functionalized at the 2- and 2'- positions are often chiral due to restricted rotation about the transannular bond. Though their importance in asymmetric synthesis cannot be overstated, chiral ligands based on binaphthyl frameworks have also found wide application in coordination and metallo-supramolecular chemistry [5]. A diverse range of binaphthyl starting materials are commercially available in an enantiopure form and these can be readily functionalized with a variety of donor groups. It has been reported [1] that a large number of schiff-base ligands can be prepared by using 1,1'-binaphthyl-2,2'-diamine and capping the free amino groups with suitable aldehydes. For

example, salicaldimine derivatives have been prepared and this has found applications in asymmetric catalysis and biomimetic chemistry [6]. Also pyridylimine derivatives [7] have been found to form helicates with high diastereoselectivity that is, the chirality of the ligand controls the handedness of the helicates. While some other literature report featuring pyridylimine derivatives of Ir(I), Rh(I), and Ti(IV) have been shown [8] to be useful catalysts for a range of asymmetric transformations.

Thus, this research focuses on the ligand derived from the synthesis of R-(+)-1,1'-binaphthyl-2,2'-diamine with the carbonyl group from indole-3-carboxaldehyde, its chemistry with Mn(II), Cr(III), Pd(IV), and Os(VIII), and finally how it affects certain micro-organisms of interest in a view to isolating new schiff bases of high antimicrobial potency.

EXPERIMENTAL

Reagents, Micro-organisms/Instruments

All reagents used were of analytical grade, only few were of reagent grade and these were all used

without further purification. The microorganisms were classified before used for analysis. R-(+)-1,1'-binaphthyl-2,2'-diamine and indole-3-carboxaldehyde were products of Fluka, Switzerland. manganese (II) chloride, tetrahydrate and molecular sieves (4Å) were from BDH, chromium (III) nitrate, nonahydrate and palladium (II) chloride from Merck, osmium (VII) oxide/osmic acid and dimethylsulphoxide (DMSO) from Sigma-Aldrich while nutrient agar was from Lab M (United Kingdom). The typed microorganisms used were *Pseudomonas* species- clinical and sewage isolate, *Pseudomonas aeruginosa*, *Klebsiella* species- 4A and 4B, *Klebsiella pneumoniae*- clinical isolate, *Staphylococcus* species- vancomycin resistant, *Salmonella* species- clinical isolate and then *Candida albicans* - clinical isolate. All weighings were carried out using an EO2140 Ohaus Explorer electronic balance having a serial number of E1171119153125. Also a P162N Mettler weighing balance of serial number 425027 was employed during the antimicrobial analysis. 55675 Gallenkamp magnetic stirrer and thermostated hot plate with serial number 1/55675 was utilized during the heating and stirring of the various samples. The melting points of the ligands and complexes were measured using a 4017 model of John-Fisher melting point apparatus. Electronic spectra of the-synthesized ligands and complexes were obtained with a CE 9050 Cecil ultraviolet visible spectrophotometer of serial number 109105 equipped with a printer. The infrared spectra were obtained using a 960M000 model of Maltson Genesis II Fourier Transform infrared spectrophotometer of serial number 9802048 equipped with a computer monitor and a printer. All dryings were carried out using a Memmert oven dryer of TO.30 model and serial number of DIN-40050-IP20. Also a dessicator containing calcium chloride as its dessicant was employed. All incubations carried out during the antimicrobial analysis were performed in a VT5042, EK/N₂ model of Heraeus incubator of serial number 0600341. All sterilizations were performed using a CV II/1000 autoclave machine of serial number A - 4050.

Preparation of Ligand

Synthesis of Bis-[1, 1'-(2-naphthylimino)-indole-3-carboxaldehyde], Ra

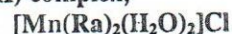
R-(+)-1,1'-binaphthyl-2,2'-diamine (284mg, 1.0mmol) dissolved in 8ml of absolute ethanol was added to a mixture of indole-3-carboxaldehyde (290mg, 2mmol) in 8ml dioxane. Few molecular sieves of 4Å size were added, and the solution was refluxed with continuous stirring for 8hours at 50°C. The sieves were later removed by decantation while the refluxed mixture was still hot,

and the solvent was allowed to evaporate at room temperature. The resulting off-yellow crystals were recrystallized with methanol to get purer crystals. The crystalline product were then dried in air and kept in a desiccator for further use.

Preparation of Complexes

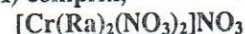
Generally, at this stage, the metal compounds and the various schiff base ligands respectively were reacted together in a 1:2 mole ratio.

Synthesis of Bis-[1,1'-(2-naphthylimino)-indole-3-carboxaldehyde]- Mn(II) complex,



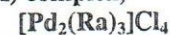
A solution of the schiff base, Ra (11mg, 0.02mmol) in 4ml of dichloromethane was added to manganese(II) chloride tetrahydrate (2mg, 0.01mmol) dissolved in 1ml methanol and this was kept at room temperature for 4 days. The crystals formed were filtered out of the solvent and washed with diethyl ether for recrystallisation. This was later stored in a desiccator for characterization.

Synthesis of Bis-[1,1'-(2-naphthylimino)-indole-3-carboxaldehyde]-Cr(III) complex,



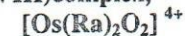
Chromium (III) nitrate, nonahydrate, (4mg, 0.01mmol) was dissolved in methanol (1ml) and added to a stirred solution of the schiff base, Ra (11mg, 0.02mmol) in dichloromethane (4ml). The solution developed a lemon green colour and after 2 days at room temperature some solvent evaporated and the crystals formed was filtered out. The product was recrystallized in diethylether and it was stored in a desiccator for further analysis.

Synthesis of Bis-[1, 1'-(2-naphthylimino)-indole-3-carboxaldehyde]- Pd(II) complex,



The schiff base, Ra(11mg, 0.02mmol) dissolved in 4.4ml dichloromethane was added to a solution of palladium (II) chloride (2mg, 0.01mmol) in 3.3ml, 0.1M HCl. The light brown solution formed after a while was noticed to have a yellowish brown colour on standing. After about 30 minutes, the solution changed to light orange with the formation of crystals, which was filtered out. Recrystallisation was done on the crystals with dichloromethane as the solvent.

Synthesis of Bis-[1, 1'-(2-naphthylimino)-indole-3-carboxaldehyde]- Os(VIII)complex,



Osmium tetroxide (3mg, 0.01mmol) diluted further with 1ml methanol was added to a

solution of the schiff base, Ra(11mg, 0.02mmol) dissolved in 4ml dichloromethane. The light milk solution formed was allowed to stand for 3days and the crystals was filtered out and recrystallised with diethylether. It was later dried in open air and stored in a desiccator.

Stoichiometry of the Complexes

The stoichiometries of these complexes were determined by employing the Job's continuous variation method of analysis [9]. This was done by the preparation of $10^{-3}M$ solutions of the synthesized ligands and the various metal salts used for complexing individually. For each reaction performed, a total of nine (9) different mixtures were made. This involved varying the volumes of each metal and ligand to total 1.0ml. 4ml of absolute ethanol was then added into each mixture making a total volume of 5.0ml each. These mixtures were corked, shaken and then allowed to stand and react for 20minutes. Their absorbances were later read from the ultraviolet- visible spectrophotometer. The values obtained were plotted against the mole ratio of each mixture and then each complex's stoichiometry was extrapolated.

Antimicrobial Test

Due to insufficient quantity of the synthesized complexes, only the ligand (Ra) was screened against *Pseudomonas species* (clinical isolate), *Pseudomonas species* (sewage isolate), *Pseudomonas aeruginosa* (typed), *Klebisella species* (4A), *Klebisella species* (4B), *Klebisella pneumoniae*, *Salmonella species*, all with ciprofloxacin as its positive control. Also other micro-organisms employed are vancomycin resistant *Staphylococcus species* with gentamycin as its positive control and *Candida albicans* with nystatin as its positive control. These screenings were performed by the agar-well diffusion method [10]. Briefly, each Mueller-Hinto agar (and Sabouraud dextrose agar for *Candida albicans*) plate was inoculated with 0.1 ml of 3 hours broth culture of each test organism. Wells (7 mm in

diameter and 2.5 mm deep) were cut into the inoculated agar and labelled from one to seven. 50 μ l of 20mg/ml of Ra were placed in wells labelled 1 to 6; and 20% v/v dimethylsulfoxide (DMSO) was delivered into the 7th well. The set up was left on the laboratory bench for one hour for the solutions and DMSO to diffuse into the media. The plates were then incubated at 37°C for 24 hours. Assessment of antibacterial activity was based on the measurement of the diameter of inhibition zone around the wells. The experiment was replicated three times and the mean inhibition zone was recorded to the nearest whole millimetre. Growth inhibition was also calculated with reference to positive control. Also the percentage zone of inhibition was calculated using the formula:

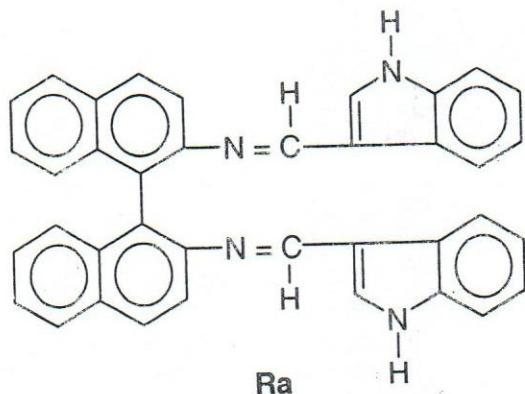
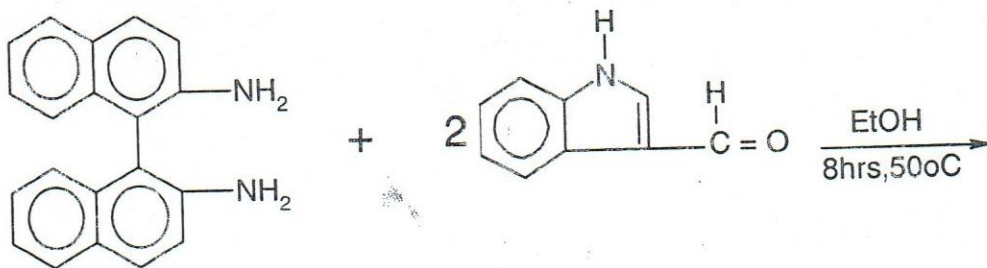
$$\% \text{ Inhibition} = \frac{(a - b)}{a} \times 100$$

Where a is zone of inhibition of control and b is the zone of inhibition of ligands or complexes.

Since Ra contains high anti-microbial activities (over 60%) it was then selected for minimum inhibitory concentration (MIC) study. The minimum inhibitory concentration was determined using the agar-well diffusion technique discussed previously by preparing dilutions containing concentrations of 12.5, 25, 50 and 100 μ g/ml respectively. After the procedure was completed entirely, the zones of inhibition was measured and recorded after incubation for 24hours.

RESULTS AND DISCUSSION

The synthesis of this ligand was based on the well-known condensation reactions of 1,1'-binaphthyl-2,2'-diamine and the free amino groups from suitable aldehydes. The reaction of R-(+)-1,1'-binaphthyl-2,2'-diamine with indole-3-carboxaldehyde afforded Bis-[1, 1'-(2-naphthylimino)-indole-3-carboxaldehyde] herein denoted as Ra according to Scheme (1). The reactions of $Mn(Cl)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $PdCl_2$, and OsO_4 with Ra afforded the complexes.



Physical Properties

The physical properties of this ligand with its complexes are presented in Table 1. Table 1: Colour, texture, melting point and yield of the ligand with its complexes

Compound	Colour	Texture	Melting point(°C)	Yield	
				(g)	(%)
Ra	Light-yellow	Crystalline	205-212	0.23	43
[Mn(Ra) ₂ (H ₂ O) ₂]Cl ₂	Yellow	Crystalline	185-187	0.005	85
[Cr(Ra) ₂ (NO ₃) ₂]NO ₃	Lemon-green	Crystalline	150 dec	0.0057	97
[Pd ₂ (Ra) ₃]Cl ₄	Light-orange	Powdery	220 dec	0.0021	33
[Os(Ra) ₂ O ₂] ⁴⁺	Yellow	Crystalline	270 dec	0.0053	73

* dec = Decompose

Bis-[1,1'-(2-naphthylimino)-indole-3-carboxaldehyde] i.e. Ra was observed to be a crystalline, light yellow compound with melting point of 205-212°C. Its Mn(II) complex ie [Mn(Ra)₂(H₂O)₂]Cl₂, is yellow and crystalline in texture having a melting point of 185-187°C. [Cr(Ra)₂(NO₃)₂]NO₃, a lemon green crystalline complex was found to decompose at 150°C. [Pd₂(Ra)₃]Cl₄ is a light orange powdery compound that decomposes at a temperature of 220°C. [Os(Ra)₂O₂]⁴⁺ a yellow crystalline complex, was observed to decompose at 270°C

Stoichiometry of the Complexes

The stoichiometric results for these complexes showing metal to ligand mole ratio are presented in Table 2.

Table 2: Stoichiometric Results

Complex	Metal to Ligand Mole Ratio
[Mn(Ra) ₂ (H ₂ O) ₂]Cl ₂	1:2 (ML ₂)
[Cr(Ra) ₂ (NO ₃) ₂]NO ₃	Not determined
[Pd ₂ (Ra) ₃]Cl ₄	2:3 (M ₂ L ₃)
[Os(Ra) ₂ O ₂] ⁴⁺	1:2 (ML ₂)

* M – metal, L = ligand

Ra's complexes especially $[\text{Mn}(\text{Ra})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ and $[\text{Os}(\text{Ra})_2\text{O}_2]^{4+}$ were found to have the same metal to ligand mole ratio of 1:2 while $[\text{Pd}_2(\text{Ra})_3]\text{Cl}_4$ exhibited a rare kind of stoichiometry that is 2:3 (binuclear triplestranded) metal to ligand mole ratio. This type of mole ratio (ie, 2:3) has been reported [1] to be possible for certain binaphthyl-2, 2-diamine complexes. For $[\text{Cr}(\text{Ra})_2(\text{NO}_3)_2]\text{NO}_3$, no stoichiometric result was obtained using this method.

Electronic Spectral Properties

The electronic spectral data of this ligand with its complexes as obtained from ethanolic solution are presented in Table 3. The various absorption bands for this ligand with its complexes are grouped for better clarity.

Table 3: Electronic Spectral Data showing wavelength (nm) and Wave-number (cm^{-1})

Compound	nm (cm^{-1})	nm (cm^{-1})	nm (cm^{-1})	nm (cm^{-1})	nm (cm^{-1})	nm (cm^{-1})
Ra			294.0s (34013.61)	249.2s (40128.41)	230sh (44478.26)	202.8m (49309.66)
$[\text{Mn}(\text{Ra})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	766.8w (13041.21)	370w (27027.03)	294.4s (33967.39)	250s (40000)		203.6m (49115.91)
$[\text{Cr}(\text{Ra})_2(\text{NO}_3)_2]\text{NO}_3$			294.0s (34013.61)		239.5sh (41834.06)	191.2m (52301.26)
$[\text{Pd}_2(\text{Ra})_3]\text{Cl}_4$		482.4br (20729.68)	276.8br (36127.17)			211.2s (47348.48)
$[\text{Os}(\text{Ra})_2\text{O}_2]^{4+}$			294.8s (33921.30)	248.8s (40192.92)		198.8s (50301.81)

* Intensities: s-strong, m-moderate, br-broad, w-weak, sh-shoulder

The spectra of Ra showed strong bands at 294nm and 249.2nm, a shoulder and moderate band at 230nm and 202.8nm. These absorption bands observed is attributed to be mainly due to $\pi \rightarrow \pi^*$ transitions and $n \rightarrow \pi^*$ transitions of the non-bonding in the ligand.

In the spectrum of $[\text{Mn}(\text{Ra})_2(\text{H}_2\text{O})_2]\text{Cl}_2$, five absorption bands ranging from strong to weak intensities were observed and this agrees favorably to what has been reported [11,12] that most octahedral or tetrahedral d^5 configuration reveals prominently five absorption bands. The colour of this complex (which is yellow) can give an insight into the geometry of $[\text{Mn}(\text{Ra})_2(\text{H}_2\text{O})_2]\text{Cl}_2$. It has been reported that [13] this complex, which is a d^5 complex would have most of its transitions to be spin-forbidden. Based on the Job's continuous variation results, the transitions of this complex can be completed as an octahedral complex because its absorptions is centered around absorption bands of other octahedral Mn(II) complexes reported [11,13]. The terms of these transitions are ${}^6A_{1g}$ to ${}^4T_{1g}$, ${}^4T_{2g}$ (G), 4E_g and ${}^4A_{1g}$ (G), ${}^4T_{2g}$ (D) and finally 4E_g (D) transitions respectively. The 13041.21cm^{-1} and 27027.03cm^{-1} weak absorption bands are known to correspond to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and

${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) transitions respectively. These absorptions can be attributed to be due to charge transfer and not only d-d transitions and this is with respect to their weakness in intensity. The stronger bands at 33967.39cm^{-1} and 40000cm^{-1} corresponding to ${}^6A_{1g} \rightarrow {}^4E_g$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (D) reveal bands present in the ligand. At 49115.91cm^{-1} , a band corresponding to ${}^6A_{1g} \rightarrow {}^4E_g$ (D) transition was observed. All these transitions have been interpreted in agreement with other Mn(II) octahedral complexes reported [11,14]. An evidence of complexation is seen from the band in the ligand at 40128.41cm^{-1} shifting to 40000cm^{-1} in the complex and another band at 49309.66cm^{-1} of the ligand shifting to 49115.91cm^{-1} reveals the interaction of the metal ion with the bonding electrons on the nitrogen atom and this is in agreement with earlier works on schiff base complexes [11,16].

Three absorption bands ranging between moderate and shoulder intensities were observed in $[\text{Cr}(\text{Ra})_2(\text{NO}_3)_2]\text{NO}_3$'s spectrum and this agrees with what octahedral and tetrahedral Cr^{3+} complexes display. Its absorption bands at 34013.61cm^{-1} , 41834.06cm^{-1} and 52301.26cm^{-1} agree to octahedral cases of Cr^{3+} complexes [11]

and therefore correspond to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions in the order of increasing energy. This conclusion was made based on the calculations involving the Racah parameter for Cr^{3+} ion where the experimentally measured spectra was compared with those expected from theory as given by Reedijk et al [15]. Here the energy of ν_1 corresponds to $10\Delta_0$ and the value of Δ_0 is obtained from it. It was observed that the absorption bands measured at $34013.61cm^{-1}$ and $52301.26cm^{-1}$ is comparable with the theoretical band at $34013.61cm^{-1}$ and $54586.33cm^{-1}$ and these corresponds to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. The third band experimentally measured at $41834.06cm^{-1}$ was found not to compare favourably with that expected from theory i.e. $61224.498cm^{-1}$ and this very absorption corresponds to ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition. All these transition are established to be spin-allowed as their frequencies is high and these are in agreement with Aquo Cr^{3+} complexes [13].

Three absorption bands were observed for $[Pd_2(Ra)_3]Cl_4$ complex and these absorption bands have been known to be exhibited by other Pd(II) complexes [11,13]. A very prominent and broad band categorized as a d-d transition band and a metal to ligand charge transfer band tailing the visible region was observed at $20729.68cm^{-1}$. A $\pi \rightarrow \pi^*$ transition band attributed to be due to the ligand was observed at $36127.17cm^{-1}$. This very band at $36127.17cm^{-1}$ was observed to have shifted from $34013.61cm^{-1}$ of the ligand revealing an evidence of complexation and this shifting is as a result of some dislocation of the π electrons in the ligand. Another band at $47348.48cm^{-1}$ of the

complex was noticed to have shifted from $49309.66cm^{-1}$ of the ligand, also revealing the occurrence of coordination is attributed to be due to $\pi \rightarrow \pi^*$ transition. In line with the Job's continuous variation result and the absorption bands of other Pd(II) complexes reported [11,13], the absorption bands of $[Pd_2(Ra)_3]Cl_4$ at $20729.68cm^{-1}$, $36127.17cm^{-1}$, $47348.48cm^{-1}$ are interpreted in terms of ${}^3A_2 \rightarrow {}^3T_1(P)$, ${}^3A_2 \rightarrow {}^3T_1(F)$ and ${}^3A_2 \rightarrow {}^3T_2$ square planar transitions respectively. Due to its square planar environment as seen from other Pd(II) complexes [11,13] this complex is spin-paired in its dx^2-y^2 , dz^2 , and dxy orbitals and therefore assumes a diamagnetic state.

No band was observed in $[Os(Ra)_2O_2]^{4+}$'s visible region and this agrees strongly with suggestions on d^0 complexes [11,13] since Os(VIII) is a d^0 complex. Due to its heaviness, its d-orbitals are large and can't overlap that is why no d-d transition can exist in this complex [17]. Also, the colour of this complex (yellow) can give an insight that transition is largely due to metal to ligand charge transfer or vice versa and this is in agreement with other d^0 complexes reported [11]. Its spectrum shows three strong absorption bands in the ultraviolet region, and they are $33921.30cm^{-1}$, $40192.92cm^{-1}$ and $50301.81cm^{-1}$. An evidence of complexation as reported for other complexes [18,19] was noticed when $40128.41cm^{-1}$ and $49309.66cm^{-1}$ of the ligand shifted to $40192.92cm^{-1}$ and $50301.81cm^{-1}$ in the complex respectively.

Infrared Spectral Properties

The characteristic frequencies of Ra with its complexes and their assignments are listed in Table 4 for better clarity.

Table 4: Infrared absorption frequencies (cm^{-1}) in Nujol Mulls of Ra and complexes

Ra	$[Mn(Ra)_2(H_2O)_2]Cl$	$[Cr(Ra)_2(NO_3)_2]NO_3$	$[Pd_2(Ra)_3]Cl_4$	$[Os(Ra)_2O_2]^{4+}$	Assignment
	3420.10br				$\nu(H_2O)$
2750w	2750w	2730w	2730w	2740w	$\nu(C-H)$ aromatic
1618w	1600w	1605w	1590w	1614.75w	$\nu(C=N)$
1560w	1560w	1560w	1562.14w	1520w	$\delta(N-H)$
1461.36s	1461s	1469s	1461.73s	1460.92s	$\nu(C=C)$ aromatic
1377.76s	1385m	1390w	1376.88s	1376.80m	$\delta(C-H)$, α and β - naphthalenes
	1243.04s				$\delta(H_2O)$

101
880
722.15
590w
493w

were rev
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2750 cm^{-1} ,
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similar.
3420.10 cm^{-1}
presence of
at 1243.04
also observ
At 1600 cm^{-1}

1110w	1124.40w	1123.29w	1153.62w	1123.43m	δ (ring)
1019.79w	1090w	1090w	1090w	1100w	ν (C-C)
880w	880w	880w	870w	890w	ρ (N-H)
722.15m	722.31s	722.27m	722.16m	722.14m	ρ (C-H)
590w	580w	580w	560w	573.62w	Ring breathing
493w	495.0w	480w	490.3w	476.65w	γ (C-C) ring
		1390w			ν (NO ₃ ⁻)
		820w			ν (NO ₃ ⁻)

s - strong, m - medium, w - weak, br - broad [Intensities]

In the spectrum of Ra, bond formations were revealed by the absence of absorption bands in the 3500-3300cm⁻¹ and 1740-1695cm⁻¹ region of the spectrum which is assigned to -NH₂ of the amines and C=O of the carboxaldehyde from the reactants respectively. The absence of these bands indicates the formation of an imine linkage (C=N) centered at 1618cm⁻¹ and the formation of a naphthylimino moiety. A stretching vibration at 1618cm⁻¹ assigned to (C=N) of the imine linkage was observed and this same observations have been made for other schiff bases studied [1,21,22,23]. It was observed that the absorption band of this imine linkage upon complexation shifted towards lower frequencies of 1590-1614.75cm⁻¹ range as seen from the spectra of its complexes. Similar observations have been documented involving the use of the imine nitrogen for bonding [20]. Weak absorption bands at 1560cm⁻¹ and 880cm⁻¹ indicate the presence of indole (N-H) in-plane bending and rocking frequencies respectively. At 1377.76cm⁻¹, a sharp band assignable to α , β -naphthalene vibration was observed. Bands assignable to (C-H) aromatic stretchings, bendings and rockings were observed at 2750cm⁻¹, 1377.76cm⁻¹ and 722.15cm⁻¹ as weak, strong and moderate bands respectively. Also observed were (C-C) ring stretching and rocking vibrations and even ring breathing and bending vibrations. Far-infrared analysis was not recorded for this ligand.

In the spectrum of [Mn(Ra)₂(H₂O)₂]Cl₂, sharper bands than those obtained from the ligand were observed such that their spectra were almost similar. A broad absorption band centered at 3420.10cm⁻¹ from its spectrum suggests the presence of coordinated water molecule. Precisely at 1243.04cm⁻¹, an in-plane bending vibration was also observed for this coordinated water molecule. At 1600cm⁻¹, a moderate band assigned to imine

stretching was observed. This frequency reveals a decrease from that of its ligand suggesting the participation of the imine nitrogen in the coordination with the metal ion. Coordination of the imine nitrogen with the metal ion results to a reduction of bond order and an increment in the vibrational constant existing between the double bond carbon-nitrogen end as have been documented for complexation reactions [1,24,25]. The bending and rocking frequencies of the indole (N-H) end were unaltered even after complexation from that obtained from the ligand's spectrum. This greatly suggests that its nitrogen was not involved in bonding. Other vibrations observed in the ligand, all remained unaltered. Far-infrared analysis was also not recorded for this complex.

The spectrum [Cr(Ra)₂(NO₃)₂]NO₃ revealed no alteration in the bending and rocking frequencies of the indole (N-H) band therefore; suggesting that its nitrogen end was not involved in bonding. A weak shift of the absorption frequency of the ligand from 1618cm⁻¹ to a lower frequency of 1605cm⁻¹ as observed in the complex suggests that complexation has occurred by involving the imine nitrogen as has been observed for some other schiff base complexes [21,22,23] reported. Stretching frequencies assignable to (NO₃⁻) was observed at 1390cm⁻¹ and 820cm⁻¹ and this tallies with reports [19,26,27] involving coordination with (NO₃⁻). Bands assignable to (C-H) aromatics, ring breathings and others were unaltered even after complexation.

The spectra of [Pd₂(Ra)₃]Cl₄ and [Os(Ra)₂O₂]⁴⁺ were observed to be similar. No alteration in both was observed for the absorption bands of indole (N-H), aromatic (C-H), (C-C) ring stretching, bendings and rockings as compared with their energies from the ligands spectrum. A weak and moderate shift of [Pd₂(Ra)₃]Cl₄ and

[Os(Ra)₂O₂]⁴⁺'s absorption bands to 1590cm⁻¹ and 1614.75cm⁻¹ from 1618cm⁻¹ of Ra strongly suggests that coordination/complexation has occurred by involving their imine nitrogens in bonding with Pd(II) and Os(VIII) ions respectively. No far-

infrared analysis was recorded also for these complexes.

Antimicrobial Properties

An overview of the antimicrobial properties exerted by the ligand is given in Tables 5, 6 and 7 respectively;

Table 5: Antimicrobial Activity of the Ligand

	Zones of Inhibition (mm)	
	Controls	Ra
	Ciprofloxacin	
<i>Pseudomonas</i> species (clinical)	30	Nil
<i>Pseudomonas</i> species (sewage)	30	Nil
<i>Pseudomonas aeruginosa</i> (typed)	28	Nil
<i>Klebisella</i> species (4A)	25	Nil
<i>Klebisella</i> species (4B)	32	Nil
<i>Klebisella pneumonia</i>	30	12
<i>Salmonella</i> species	45	Nil
	Gentamicin	
<i>Staphylococcus</i> species (Vancomycin resistant)	23	Nil
	Nystatin	
<i>Candida albicans</i>	16.9	Nil

Table 6: Growth Inhibition of the Ligand

Organism	Percentage (%) Zone of Inhibition of Ra
<i>Pseudomonas</i> species (Clinical)	-
<i>Pseudomonas</i> species (Sewage)	-
<i>Pseudomonas aeruginosa</i>	-
<i>Klebisella</i> species (4A)	-
<i>Klebisella</i> species (4B)	60
<i>Klebisella pneumoniae</i>	-
<i>Salmonella</i> species	-
<i>Staphylococcus</i> species (Vancomycin Resistant)	-
<i>Candida albicans</i>	-

Table 7: Minimum Inhibitory Concentration (MIC)

Organisms	Ligand	Concentrations in µg/ml [Zones of Inhibition (mm)]			
		100	50	25	12.5
<i>Klebisella pneumoniae</i>	Ra	7mm	nil	nil	nil

From the tables above, Ra (ie Bis-[1,1'-(2-naphthylimino)-indole-3-carboxaldehyde]), revealed antibacterial activity only against *Klebsiella pneumoniae* with zone of inhibition (ZIB) of 12mm and a minimum inhibitory concentration (MIC) of 100 µg/ml. Also, since Ra did not yield an MIC but remained active at the initial concentration of 100µg/ml then, it would pose a disadvantage to therapy assuming it has high toxicity.

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CONCLUSION

The results of this work revealed that in considering the Job's continuous variation method of stoichiometric analysis, electronic, and infrared spectra, Ra is concluded to be bidentate through its two imine nitrogens.

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