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Pt(II) And Ru(III) Complexes Of 5-Substituted-4-Amino-3-Mercapto-1, 2, 4-Triazole Schiff Base: Synthesis, Spectral Characterization And Antimicrobial Studies

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ABSTRACT
Complexes of Pt(II) and Ru(II)[1] ions made from a Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and 4-amino-3-mercepto-5-propyl-1,2,4-triazole were synthesized. Characterization was done on the basis of some physicochemical parameters; infrared and uv-visible spectroscopic studies. The ligand acted as a bidentate molecule coordinating through NS heteroatoms to Pt(II) ion and as a tridentate coordinating through NSO donor atoms to Ru(II) ion. The experimental data obtained were in affirmation with many documented literatures that revealed the complexes to exist as square planar and octahedral geometrical configurations for Pt(II) and Ru(II)ions respectively. The synthesized chelates were screened against some species of bacteria such as *Staphylococcus aureus, Streptococcus pyrogones*, and *fungi such as Candida albican and Aspergillus Niger* using the disc diffusion method and broth agar method. The metal complexes showed better potency as antimicrobial agents than the free ligand and even when compared to the standard, they fair better and therefore, can serve as effective drugs against these pathogens.
KEYWORDS: Ligand, bidentate, tridentates chelate, antimicrobial activities.

INTRODUCTION
The chemistry of 1,2,4-triazoles and their fused heterocyclic derivatives have within the last few decades attracted some considerable attention due to their easy synthetic procedures and effective biological importance. The 1, 2, 4-triazole moiety contain S=C-N-N=C- unit, resembling thiosemicarbazones [1,2] (Hanif and Chohan, 2013,Shneine & Aleaji, 2016) which served as skeletal backbone to a wide range of synthetic intermediates and therapeutic drugs such as antifungal, antibacterial, anti-inflammatory, antiviral, antitumor and others [3,4] (Banerjee et al.,2013,Johnson,et al., 2016). The hybrid molecules made up of the heterocyclic rings and Schiff bases are found to exhibit greater biological activities as well as pharmaceutical and agrochemicals [5,6](Mobinikhaledi et al.,2010, Okon et al.,2016). Triazole derivatives comprise of amine and thione substitutes. The present of exocyclic thione group on the heterocyclic moiety is of considerable importance because the combination of the two groups (amine and thione) generates species with effective and synergistic coordination potential [7, (Dhore *et al.*, 2011, [8] kucukguzel *et al.*, 2001, [9] Rosa *et al.*, 2006[10], zhu *et al.*, 2008). Bonding through amine and thione groups result in the formation of stable metal complexes involving highly favoured five-membered ring systems.[11] (Haddad *et al.*, 2013,[12]Wood et al., 2008,[13]Mavrova et al., 2009). This mercapto-triazole system has a general formula of $R_3N_3SC_2$ and often exist in two tautomeric forms of thiol and thione [14](Abdul, Hameed & Hassan 2014)(Figure 1) .The chemistry of metal complexes with this kind of multidentate ligands with delocalized π –orbitals found in Schiff bases [15](Miyauchi et al.,1995,[16] Nair *et al.*, 1997) and porphyrin provide a model framework for effective

intramolecular electronic exchange which can take place between the drug and living cell thereby resulting in high efficiency of the antimicrobial agent. In continuation of our research on structure-activity relationship modification on chelates, synthesis, characterization and antimicrobial activities of Pt [11] and Ru[11] complexes derived 2-hydroxy-1-naphthaldehyde and 4-amino-3-mercepto-5-propyl-1,2,4-triazole was the core of this investigation

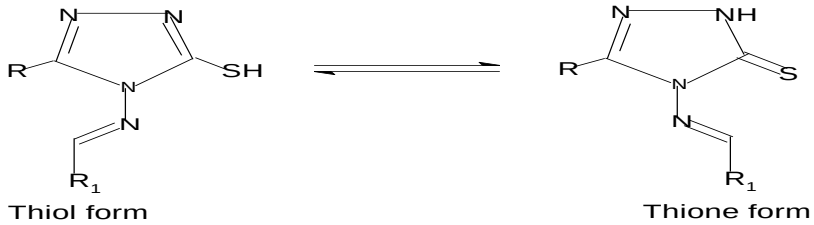

Figure 1

EXPERIMENTAL

The chemicals: thiocarbohydrazide (98.5%), buryric acid (99.9%), 2-hydroxy-naphthaldehyde (98.5%), glacial acetic acid (98.5%) and metal salts- $PdCl_2$, K_2PtCl_4 were of analytical grade and were used without further purification. The solvents used were ethanol, methanol, petroleum ether, n-hexane and distilled water. Instrumental analyses were done with Gallen Kemp Capillary melting point apparatus, Metler P163 conductivity meter in ethanol solution, FTIR– 8400s with KBr disc and UV-2530 Shimadzu spectrophotometer for the electronic absorption. The antimicrobial screening were carried out at the Microbiology Laboratory, Cross River University of Technology (CRUTECH), Calabar-Nigeria with Muller Hinton agar, peptone water and the isolates were *Staphylococcus aureus, Streptococcus pyrogenes (bacteria), Candida albican, Aspergillus niger* (fungi). Amoxicillin were used as control. The susceptibility test, the minimum inhibitory concentration, minimum bactericidal concentration and minimum fungicidal concentration were carried out.

3.1 Synthesis of 4-amino-3-mercapto-5-propyl-1, 2, 4-triazole (L_1)

A mixture of thiocarbohydrazide (5g) and n-butyric acid (15 ml) was heated under reflux for 4 hours at 140^{o}C while stirring. At the end of the time, the reaction system was cooled to room temperature and the excess butyric acid distilled under reduced pressure. The residue solid was recrystallized from distilled water (75ml) and dried to obtain colourless shining flakes. The scheme of the synthesis of the ligand is shown in figure 2.

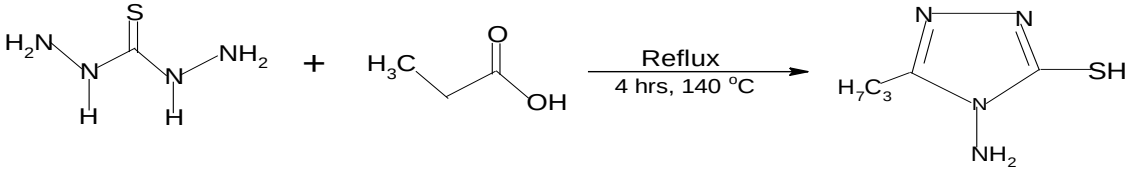

Figure 2: L_1 Synthesis

3.2 Synthesis of 4-(2-hdroxyl-1-naphthyl) methyleneamino-3-mercapto-5-propy1 1, 2, 4-triazole (L_2)

2-hydroxyl-1-naph-thaldehyde (0.005 mol, 1.72 g) was dissolved in glacial acetic acid (10ml), equimolar amount of 4-amino-3-mercapto-5-propyl-1, 2, 4-triazole (L_1) ((0.005 mol, 1.58 g) was added and refluxed for 45 minutes at 100^{o}C. After cooling the solid recrystallized from anhydrous ethanol (75 ml), filtered through suction and dried to obtained yellow shining crystals. The scheme of the synthesis of the ligand (L_2) is shown in Figure 2.

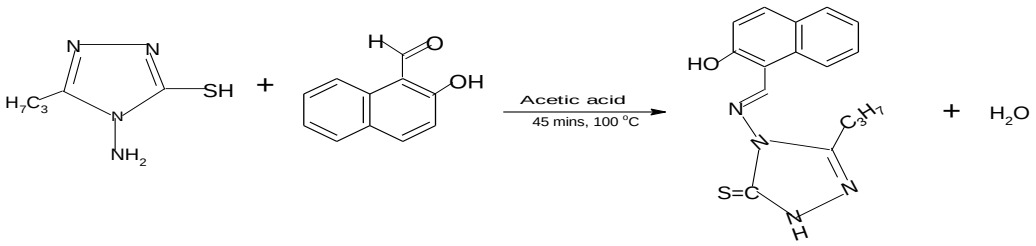

Figure 2: Synthesis of L_2

3.3 Synthesis of Ru(III) complex

Ruthenium trichloride (0.15g) was dissolved in 10ml ethanol, equimolar amount of 4-(2-hydroxy-1-naphthyl) methyleneamino-3-mercapto-5-propyl- 1, 2, 4-triazole (L_2) (0.56 mol, 0.17g) was added and refluxed for 1 hour. After cooling, a black solid was filtered off and dried.

3.4 Synthesis Platinium (II) complexes

Potassium tetra-chloroplatinate(II) (0.20g) was dissolved in 10ml ethanol, equimolar amount of 4-(2-hydroxy-1-naphthyl) methyleneamino-3-mercapto-5-propyl 1, 2, 4-triazole (L_2) (0.56mol, 0.17g) was added and refluxed for 1 hour. After cooling, a black-green solid was filtered off.

4.1 Antimicrobial Studies

The isolates used were *Staphylococcus aureus, Streptococcus purogenes (bacteria)* and *Candida albican, Aspergillus Nigers*; fungi. Two solid media namely Potato dextrose Agar (PDA) (for fungi) and Nutrient Agar (NA) (for bacteria) were used for antimicrobial assay. The antibacterial activities were evaluated the nutrient agar by the disc diffusion method. In this method, all the materials used were sterilized in a hot air oven and the colony of each of the test microbes were sub cultured and incubated first for about 6-8hours before being poured into the agar plates. The disc (7.0mm diameter) were soaked in the different test samples (concentration 100ug/ml).Using sterilized forcep they were then placed on the agar plates The plates were then incubated at 37^{o}C temperature for 18-24hours. At the end of incubation, zones of inhibition were measured and recorded in millimeters. Minimum inhibitory concentration of the ligand and complexes were investigated by double serial dilution method where the solutions (synthesized compounds) contained 20, 10, 5 and 2.5 ug/ml. Amoxicillin used as a standard[17]Offiong and Martelli 1994.]

The antifungal activity was also carried out. Eight clean test-tubes for each isolate were place on the tube rack and were clearly labeled (each representing its concentration). Next, 1ml of diluent (ethanol in this case) was placed on each of the test tubes labeled 2-7 excluding the 1st tube which contained 2ml of stock solution of the drug. Thereafter, 1ml of the stock solution of the drug was transferred from tube 1 to tube 2 using a sterile pipette, and then to subsequent tubes from 2-3, 3-4, 4-5, 5-6 and 6-7. This was accompanied by thorough shaking to enhance efficient mixing. Later, 4ml of peptone water (Mueller Hinton agar, nutrient broth, MacConkey broth) was placed in each of the test tubes and was further shaken for their contents to mix well. Finally, with the aid of a clean pipette, 0.4ml of 24hours broth culture of the standard cultures to be used viz, *staphylococcus aureus, streptococcus pyogenes, pseudomonas aeruginosa* and *candida albicans* was inoculated into each test tube and the test tube was gently shaken. The test tubes were then sealed with sterile corks and incubated at 37^{o}C for 24 – 48 hours. At the end, the test tubes were observed for turbidity. The tube with the highest degree of turbidity or clearance was taken as the minimum inhibitory concentration (MIC) tube, while tubes with no clearance were taken as negative tubes (this imply that those dilutions or concentration of the drug cannot inhibit the growth of micro-organism. However, the tube preceding the MIC tube is regarded as the MBC (minimum Bacterial Concentration)

tube or MFC (minimum Fungicidal concentration) tube. BothMIC, MBC and MFC results are expressed in microgram per ml (Ng/ml). For instance, if the tube with the highest degree of clearance is tube number 5, the MIC of that particular drug will be given as 6.25Ng/ml.

RESULTS

Table 1: Physical data of the compounds

Ligands and complexes	Colour	Melting point	% yield	Molar conductivity Ωcm^2mol^{-1}
L1	Colourless	-	73.5	-
L2	Yellow	230.231	72.8	-
Pd(II) complex	Dark green	230	55.6	11.5
Pt(II) complex	Dark green	234	66.7	10.9

Table 2: Selected IR SPECTRA BANDS (KBr-disc) / Electronic Spectra Bands (cm^{-1})

Compound	ν(O-H)	ν(N-H)	ν(C=S)	ν(C=N)	ν(N-N)	ν(C-O)	λ_{max} Assignment
L2	3500	3109	1170	1606	970	-	
Pt(II) complex	3500	-	1197	1581	980		16200 $^1A_{1g}\rightarrow{}^1A_{2g}$ 24500 $^1A_{1g}\rightarrow{}^1B_{1g}$ 27300 $^1A_{1g}\rightarrow{}^1Eg$
Ru(II) Complex	3480	3090	1189	1505	960	1030	17700 $^2T_{2g}\rightarrow{}^2E_g$ 20500 $^2T_{2g}\rightarrow{}^2A_{2g}$ 24600 $^2T_{1g}\rightarrow{}^2A_1g$

Table 3: Antimicrobial results

Compound	Zone of Inhibition(mm) Sa.	Sp.	Ca.	An.	MIC (µg/ml)	MBC MFC (µg/ml)
L2	8.0	10.0	7.0	11.0	-	-
Ru(III) complex	23.5	19.0	10.0	12.0	5.0	5.0 2.5
Pt(II)complex	25.0	28.5	23.0	22.0	2.5	2.5 5.0
Control	20.0	22.5	20.0	22.0		-

**Sa=Staphylococcus aureus, Sp= Streptococcus pyrogenes (bacteria)* and *Ca=Candida albican, An= Aspergillus niger*

5.0 DISCUSSION

The synthesized ligands and complexes were variedly colouυ solids (data in Table 1). They were generally insoluble in common organic solvents but soluble in coordinating solvents such as methanol, ethanol, and acetone. They were stable in air and exist in crystalline form. The molar conductance values are quite low inferring the non electrolytic nature and they have high melting points indicating strong bonding network within the compound.

5.1 Infrared spectra

The IR spectra (Table 2) υthe ligand (L_2) gave a characteristic band at $3500cm^3$ assignable to υ(O-H) of naphthylic rings. A strong band observed at $1581cm^3$, this lowering from the normal $1630cm^{-1}$ of υ(C=N) absorption may be due to conjugation effect of heterocyclic naphthylic system. The absorption at 3109 and $1197cm^{-1}$ were attributed to υ(N-H) and

(C=S) stretching vibration, and absorption of S-H stretching vibration at 2550cm^{-1} disappeared, reflecting that the compound existed mainly as the thione form in the solid state [18, 19, 20). The 1R spectra of Pt(II) and Ru(III) complexes possessed characteristic absorption bands at 1197cm^{-1} and 1505cm^{-1} attributed to υ(C=S) and (C=N) coordination to the metal ions. The lowering in shift when compared to that of the free ligand also confirmed the coordination of the metals to thionyl sulphur and azomethine nitrogen. The υ(OH) band is absent in the spectrum of the Ru(III) complex, indicating the deprotonation of the naphthylic OH followed by coordination of the oxygen to the metal ion[21,28]Sharma&srivastava,2007]. The band (2550cm^{-1}) in the spectrum of free ligand disappeared in those of the metal complexes.

5.2 Electronic absorption spectra

The absorption bands of the complexes are given in Table 2. The electronic absorption bands of the ligand were in the region of 28,600-32,000cm^{-1} mainly due to unsaturation, delocalization of electrons within the molecule and intraligand charge transfer causing n-σ*, π-π* and n-π* transitions[. The diamagnetic nature of Pt(II) complex, displayed intense bands in the region 16,200, 23500, 27300cm^{-1} and were elucidated to be $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1Eg$ spin allowed transitions from the three low-lying *d* levels to the empty dx^2-y^2 orbital [24,25](Abdullah et al.,2007,). This is concomitance with the square planar stereochemical arrangement around a d^8, Pt(II) ion[22]Afrasiabi et al., 2004] . The electronic spectrum of Ru(III) complex also displayed three bands at 17700, 20500,24600cm^{-1} assignable to $^2T_{2g}\rightarrow{}^2Eg$; $^2T_{2g}\rightarrow{}^2A_{2g}$ and $^2T_{1g}\rightarrow{}^2A_{1g}$ due to spin allowed transitions from the three low lying d levels to the empty dz^2, dx^2-dy^2 orbitals. This again is conformity with an octahedral geometrical configuration reported in many literature [23, 26] Reddy et al 2008,(Fig. 3 a & b).

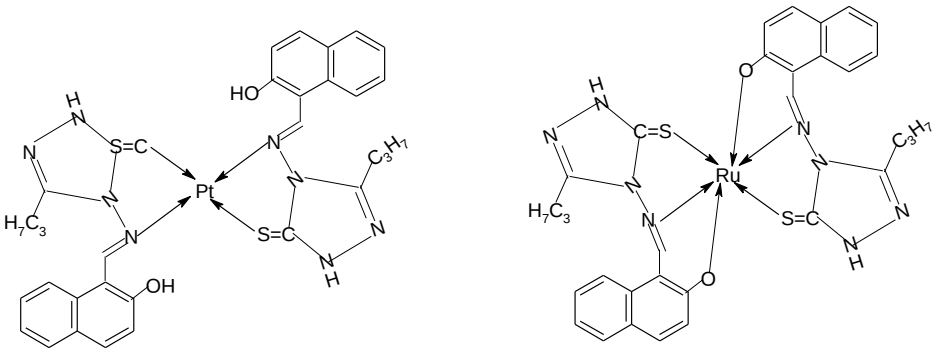

Figure 3a & b

5.3 Antimicrobial analysis

The antimicrobial studies were carried out by the disc diffusion method and broth method, the results compared to that of amoxicillin. The results indicated that the complexes have better antimicrobial properties than the free ligand. The increased activity of the metal chelates can be explained based on the chelation theory [14, 27]. The anti microbial data are shown in Table 4.

Conclusion

On the basis of IR and UV-visible spectra, Pt(II) and Ru(III) complexes were found to adopt the square planar and octahedral geometry in a 1:2 metal to ligand molar ratio. The synthesized ligand exhibited both bidentate and tridentate nature, coordinating through the nitrogen atom of the azomethine group and sulphur of thionyl group to both Pt(II) and Ru(III) ions while also making up the sixth coordinate in the ruthenium complex by bonding with the deprotonated oxygen atom of the naphthylic system. The antimicrobial screening of the compounds indicated that the metal complexes show higher inhibitory activities than the free ligand and also better than the standard.

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