

Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 59 (2013) 15848-15852



Synthesis, spectroscopic characterisation and structure related antibacterial activities of some metal(II) complexes of substituted triflurobutenol

Aderoju A. Osowole*, Anthony. C. Ekennia, Benedict O. Achugbu and Godwin H. Etuk Inorganic Chemistry Unit, Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

ARTICLE INFO

Article history: Received: 14 April 2013; Received in revised form: 12 June 2013; Accepted: 18 June 2013;

Keywords

Antibacterial activities, Geometry, In-vitro, Schiff base.

ABSTRACT

Synthesis, spectroscopic (IR and electronic) and *in-vitro* antibacterial properties of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of the enolimines derived from condensation of p-nitroaniline and benzoyl trifluoroacetone (HL¹) / theonyltrifluoroacetone (HL²) were reported. The ligands coordinated to the metal ions through the azomethine N and enol O atoms in ratio 1M: 1L, resulting in complexes of the type [ML¹NO₃].xH₂O, [ML²(CH₃COO)].xH₂O and [PdL(Cl)H₂O]. The IR and electronic spectral measurements were consistent with the adoption of a 4-coordinate square planar/ tetrahedral geometry for the metal complexes. The *in-vitro* antibacterial studies of the Schiff bases and their metal(II) complexes against *Bacillus subtilis, Staphylococcus aureus, Proteus mirabilis, Klebsiella oxytoca, Pseudomonas aeruginosa,* and *Escherichia coli* revealed that HL¹ and its metal complexes were generally more active than HL² and its complexes. Interestingly, [Zn(L¹)NO₃].¹/₂H₂O, [Pd(L¹)Cl(H₂O)] and [Ni(L²)₂] had broad-spectrum antibacterial activity against *Staphylococcus aureus, Pseudomonas aeruginosa,* and *Escherichia coli* with inhibitory zones range of 12.5-22.0 mm proving their potential usefulness as broad-spectrum antibacterial agents.

© 2013 Elixir All rights reserved.

1. Introduction

Schiff bases and their metal complexes are used as precursors in metal-organic chemical vapor depositions (MOCVD) [1], anticancer and antimicrobial agents [2-6], catalysts [7-8], in optics and material science [9-10], as MRI contrast agents and biological markers [11-12]. Recently, chloro, methyl and methoxy derivatives of pyrimidinyl Schiff bases inhibited colon and melanoma cancers [13-15]. Extensive literature review shows that little information is available on the Schiff bases derived from p-nitro aniline and 2theonyltrifluoroacetone / benzoyltrifluoroacetone and their metal(II) complexes (M = Mn, Co, Ni, Cu, Zn and Pd). Thus, we present the synthesis and characterisation of these two Schiff bases and their metal complexes with the aims of investigating their structural related antibacterial activities against human pathogens in-vitro, and the effect of the various substituents on their electronic properties and geometries. This study is therefore a continuation of the research activities of our group on synthesis, characterisation and biological activities of various Schiff bases chelates [16-20].

2. Experimental

2.1 Chemicals

Reagent grade p-nitroaniline, benzoyltrifluoroacetone, 2thenoyltrifluoacetone and manganese(II) nitrate-6-H₂O, manganese(II) acetate-4-H₂O, cobalt(II) nitrate-6-H₂O, cobalt(II) acetate-4-H₂O, nickel(II) acetate-4-H₂O, nickel(II) nitrate-6-H₂O, copper(II) acetate-4-H₂O, copper(II) nitrate-6-H₂O, zinc(II) nitrate-6-H₂O, palladium(II) chloride-1- H₂O were purchased from Aldrich and Across chemicals respectively and were used as received. Solvents were purified by distillation.

2.2 Physical measurements

Manganese, cobalt, nickel, copper, zinc and palladium were determined titrimetrically [21].

Infrared spectra were measured in deuterated dimethylsulfoxide solvent on a Shimadzu FTIR-8400 spectrophotometer while electronic spectra were recorded on Unicam Helios $-\gamma$ spectrophotometer, and melting points (uncorrected) were done using a Stuart scientific melting point apparatus smp3.

2.3 Synthesis

2.3.1 Preparation of {1-phenyl-3-(p-nitrophenyliminol)-4, 4, 4-trifluorobutenol} (HL^1)

 3.6×10^{-2} mol (5.0 g) of p-nitroaniline was added in bits to a stirring solution of 3.6×10^{-2} mol (7.8 g) of benzoyltrifluooro acetone in 50 mL of absolute ethanol. The resulting yellow-colored solution was then refluxed for 4 h after the addition of 4 drops of acetic acid.

The yellow product formed on cooling to room temperature was filtered, and then recrystallized from ethanol. The ligand $\{1\text{-thiophen-2yl-3-(p-nitrophenylimino)}-4, 4, 4, 4-\text{trifluorobutenol}\}$ (HL²) was prepared usuing similar procedure.

HL¹: Formula mass (238.27); m. p 60 – 64 (°C); color (yellow); yield (5. 15 g, 60%); IR (DMSO cm⁻¹): vOH (3461s), vC=N (1640s 1599s) vC=C(1441s 1437s); UV ($\boldsymbol{\xi}$) λmax (kK):

vC=N (1640s 1599s) vC=C(1441s 1437s); UV (E) λmax (kK): 41.32 (1 × 10⁶), 31.25 (5 × 10⁵), 27.47sh (3 × 10⁵).

HL²: Formula mass (344.27); m. p 60-63 (°C); color (yellow); yield (7.44 g, 60%); IR (DMSO, cm⁻¹): vOH (3480b), vC=N (1650m) vC=C(1490m); UV ($\boldsymbol{\xi}$) λ max (kK): 42.92 (2.2 x 10⁵), 28.99 (6.6 x 10⁴), 27.24 (5.2 x 10⁴).

© 2013 Elixir All rights reserved

2.3.2 Preparation of the Metal(II) Complexes (M = Mn, Co, Ni, Cu, Zn).

A solution of the metal(II) nitrates/acetate/ chloride (0.69 mmol, 0.15-0.30 g) in 20 mL ethanol was added to a stirring solution of the ligands (0.69 mmol, 0.16-0.24 g) in 30 mL ethanol at room temperature (26° C), followed by the gradual addition of triethylamine (0.69 mmol, 0.09 mL). The resulting homogeneous solution was further refluxed for 6 h, during which the products formed. These were later filtered, washed with ethanol and dried in *vacuo* over anhydrous CaCl₂.

[Mn(L¹)NO₃]1¹/₂H₂O: Formula mass (381.27); m. p 330-340 (°C); color (brown); yield (0.16 g, 60%); IR (DMSO, cm⁻¹): vOH (3500s), vC=N (1637s) vC=C (1404s); vM-N (524m 502m), vM-O (458m); UV/Vis(\mathcal{E}) λ max (kK): 23.26 (200), 26.39 (1 × 10⁵), 29.4 (1 × 10⁵), 38.17 (1 × 10⁵); % Mn(Calc.):14.44 (14.43).

[Co(L¹)NO₃]/₂H₂O: Formula mass (367.20); d.t 180(°C); color (green); yield (0.17 g, 65%); IR (DMSO, cm⁻¹): vOH (3427s), vC=N (1634s) vC=C (1476s); vM-N (518m), vM-O (364m); UV/vis(\mathcal{E}) λ max (kK): 15.39(100), 24.39 (200), 26.39 (1 x 10⁵), 29.4 (1 x 10⁵), 40.0(1 x 10⁵); % Co (Calc.):16.04(16.05).

Ni(L¹)₂: Formula mass (533.23); m. p 100-101 (°C); color (green); yield (0.26 g, 70%); IR (DMSO, cm⁻¹): vOH (3421s), vC=N (1616s 1541s) vC=C (1466s); vM-N(587m 527m), vM-O (383m); UV/vis($\mathbf{\hat{E}}$) λ max (kK): 15.39 (100), 22.22 (1000), 26.32 (1 × 10⁵), 30.0 (1 × 10⁵), 40.0 (1 × 10⁵); % Ni(Calc.):11.11 (11.01).

[Cu(L¹)NO₃]2H₂O: Formula mass (398.77); d.t 206(°C); color (green); yield (0.17 g, 60%); IR (DMSO, cm⁻¹): vOH (3457s), vC=N (1604s) vC=C(1424s); vM-N(526m), vM-O(359m); UV/vis(\mathcal{E}) λ max (kK): 18.18sh, 24.39 (2000), 30.4 (1 x10⁶), 40.10 (1 x10⁶); %Cu (Calc.): 15.92(16.05).

[Zn(L¹)NO₃]/₂H₂O : Formula mass (464.31); d. t 342(°C); color (yellow); yield (0.20 g, 60%); IR (DMSO, cm⁻¹): vOH (3500b), vC=N (1638s 1603s) vC=C(1488s); vM-N(541m), vM-O(367m); UV/vis(\mathcal{E}) λ max (kK): 20.83 (100), 26.0 (1 x10⁵), 30.0 (1 x10⁵), 40.0 (1 x10⁶); % Zn(Calc.):13.85(14.0).

[Pd(L¹)Cl(H₂O)]: Formula mass (396.71), d. t 238(°C); color (brown); yield (0.14g, 50%); IR (DMSO, cm⁻¹): vOH (3438s), vC=N (1655s, 1508s) vC=C (1488s); vM-N (564m), vM-O (350m); UV/Vis(\mathcal{E}) λ max (kK): 23.81 (1000), 26.95 (1 x 10⁵), 40.0(1 x 10⁵); %Pd (Calc.): 26.66(26.82).

[Mn(L²)OAC].¹/₂H₂O: Formula mass (466.18), m. p 110(°C); colour (yellow); yield (0.19 g, 60%); IR (DMSO, cm⁻¹): vOH (3500b), vC=N (1744s 1602m 1561s) vC=C (1413m); vM-N (532m), vM-O (487m); UV/Vis(\mathcal{E}) λ max (kK): 14.81sh, 23.15 (200), 27.25sh, 30.0 (1 x 10⁵), 40.0 (1 x 10⁴); %Mn (Calc.): 11.46 (11.80).

[Co(L²)OAC]: Formula mass (461.20), m. p 196-198(°C); colour (orange); yield (0.17 g, 60%); IR (DMSO, cm⁻¹): vC=N (1732m 1595m 1550m) vC=C (1409m); vM-N (532m), vM-O (487m); UV /Vis($\boldsymbol{\xi}$) λ max (kK): 14. 29 (200), 23.47 (500), 30.0 (1 x 10⁷), 40.0 (1 x 10⁵); %Co (Calc.): 12.30 (12.80).

[Ni(L²)OAC].3H₂O : Formula mass (515.33); m. p 120(°C); colour (Green); yield (0.18 g, 50%); IR (DMSO, cm⁻¹): vOH (3500b), vC=N (1724m 1606m 1541m) vC=C (1404m); vM-N (578m), vM-O (524m); UV/Vis(\mathcal{E}) λ max (kK): 15.40sh, 23.04 (100), 30.0 (1.0 x 10⁷), 40.0 (1.0 x 10⁶); %Ni (Calc.): 11.38 (11.45). [Cu(L²)OAC].4H₂O: Formula mass (537.85); d. t 226(°C); colour (green); yield (0.17 g, 60%); IR (DMSO, cm⁻¹): vOH (3500b), vC=N (1588m 1541s), vC=C (1407m); vM-N (589s 527m), vM-O (393 m); UV/Vis(\mathcal{E}) λ max (kK): 11.77(100), 23.98 (300); 30.0 (1 x 10⁵), 40.0 (1 x 10⁷); %Cu (Calc.): 11.50 (11.81).

[Zn(L²)OAC]: Formula mass (465.82); m. p 102(°C); colour (yellow); yield (0.36 g, 70%); IR (DMSO, cm⁻¹): vC=N (1600m) vC=C (1496s 1409s); vM-N (581s 501m), vM-O (490m 367m); UV/Vis(\mathcal{E}) λ max (kK): 22.88 (200), 30.0 (1 x 10⁷), 40.0 (1.1 x 10⁵); %Zn (Calc.): 13.65(13.64).

[Pd(L²)Cl(H₂O)]: Formula mass (485.19); d. t 212(°C); colour (green); yield (0.17 g, 50%); IR (DMSO, cm⁻¹): vOH (3422b), vC=N (1638m 1573s), vC=C (1404m); vM-N (612m), vM-O (538m); UV/Vis(\mathcal{E}) λ max (kK): 14.82sh, 23.15 (300); 30.0 (1 x 10⁵), 40.0(1 x 10⁴); %Pd (Calc.): 22.22(21.93).

D.t = decomposition temperature, m.p = melting point, 1kK = 1000cm⁻¹.



Figure 1: The proposed structure for the Schiff bases



Figure 2: The comparative activities of the complexes against bacteria and Streptomycin

2.4 Antibacterial studies

The assay was carried out on the metal-free Schiff bases and their metal(II) complexes using Agar diffusion technique. The surface of the agar in a Petri dish was uniformly inoculated with 0.3 mL of 18 hours old culture of *Bacillus subtilis*, *Staphylococcus aureus*, *Proteus mirabilis*, *Klebsiella oxytoca*, *Pseudomonas aeruginosa*, and *Escherichia coli*. Using a sterile cork borer, 6 mm wells were bored into agar. Then 0.06 mL of 10 mg/mL concentration of each metal complex in DMSO was introduced into the wells and the plates were allowed to stand on bench for 30 min before incubation at 37^oC for 24 h after which inhibitory zones (in mm) were taken as a measure of antimicrobial activity. The experiments were conducted in duplicates and streptomycin was used as the reference drug [22]. **3. Results and discussions**

The reaction of the ligands with the metal(II) nitrates/acetate (Mn, Co, Ni, Cu, and Zn) gave coloured complexes in moderate to good yields (50-70%) according to equations 1 - 3.

 $\dot{M}(NO_3)_2.6H_2O + HL^1 \rightarrow [ML^1(NO_3)]xH_2O + HNO_3 + bH_2O - -$

(when M = Mn, $Zn\{x = 1.5, b = 4.5\}$, $Co\{x = 0.5, b = 5.5\}$, $Cu\{x = 2, b = 4\}$)

 $\begin{array}{l} \text{M}(\text{CH}_{3}\text{CO}_{2})_{2}.4\text{H}_{2}\text{O} + \text{HL}^{2} \rightarrow [\text{ML}^{2}(\text{CH}_{3}\text{CO}_{2})]\text{x}\text{H}_{2}\text{O} + \\ \text{CH}_{3}\text{CO}_{2}\text{H} + \text{b}\text{H}_{2}\text{O} & -----(2) \\ (when M = Co, Zn\{x = 0, b = 4\}, Mn\{x = 0.5, b = 3.5\}, Cu\{x = 4, b = 0\}; Ni\{x = 3, b = 1\}) \\ \text{PdCl}_{2}.\text{H}_{2}\text{O} + \text{HL} \rightarrow [\text{PdLCl}(\text{H}_{2}\text{O})] + \text{HCl} \end{array}$

-----(3)

(where $L = L^1$, L^2).

The formation of the ligands was confirmed by melting points, UV and infrared spectra measurements. The ligands melted at 60-64 $^{\circ}$ C (HL¹) and 60-63 $^{\circ}$ C (HL²) whereas their corresponding metal complexes melted in the range 100-342 $^{\circ}$ C and 102-226 $^{\circ}$ C respectively confirming coordination.

3.1 Infrared spectra

The assignments of the infrared bands were made by comparing the spectra of the compounds with reported literature on similar systems [23-25]. The strong bands at 3461 cm^{-1} in HL^1 and $3457 cm^{-1}$ in HL^2 , which were absent in the spectra of the metal complexes were assigned to vO-H of the enols. Their absence were attributed to coordination through the enol oxygen atom. The broad band at 3500 cm⁻¹ in the hydrated complexes was assigned as vOH water of coordination /hydration. The vC=N bands in HL¹ were observed as two between 1640-1599 cm⁻¹, and were mostly bathochromically shifted to 1634-1541 cm⁻¹ as a single band in the metal complexes with the exception of $[Ni(L^1)_2]$ which had two vC=N bands, indicative of its existence in the trans-isomeric form, a consequence of geometric isomerism [15]. On the contrary, HL^2 had a lone band at 1634 cm^{-1} and the band still remains as one in the metal complexes but were mostly bathochromically shifted to 1606-1588 cm⁻¹. These shifts were attributed to the coordination of the imino nitrogen to metal ions. In the spectra of both ligands, v(M-N)and v(M-O) were expectedly absent but were observed in the range 564-518 cm⁻¹ and 383-350 cm⁻¹ for HL¹ complexes, and in the range 578-528 cm⁻¹ and 538-364 cm⁻¹ respectively for HL^2 complexes, a further evidence of coordination [22-23]. Its interesting to note that HL^1 and its complexes had higher vC=N bands than the HL^2 and its complexes, while with vM-O and vM-N bands the reverse was obsevered. This observation was attributed to the stronger electron withdrwaing ablility of the thienyl group which weakend the vC=N bands and consequently strengthened the vM-O and vM-N bands [24-25].

3.2 Electronic spectra

The Mn(II) complexes showed lone band each around 23.21 kK and a shoulder in [Mn(L²)OAC] at 14.18 kK respectively, typical of 4-coordinate tetrahedral geometry and were assigned as ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$ and ${}^{6}A_{1} \rightarrow {}^{4}T_{2}$ transitions [26]. On the contrary, the Co(II) complexes displayed two bands around 14.84 and 23.93 kK assigned to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$, (v₂), and ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$, (v₃) transitions of a tetrahedral geometry [17]. The spectra of the Ni(II) complexes showed two absorption bands around 15.22 and 22.63 kK indicative of a 4-coordinate square-planar geometry and were assigned to ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and

 ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transitions of a four-coordinate, square-planar geometry [24].

The observance of two bands around 14.98 and 24.19 kK in the Cu(II) complexes indicated square planar geometry with the assignment of the bands as ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{1g}$ transitions, because tetrahedral Cu(II) complexes usually have a single absorption band below 10.0 kK [3].

The Zn(II) complexes showed M \rightarrow L CT transitions around 21.86 kK since no d-d transition is expected [13]. Similarly, the spectra of the Pd(II) complexes showed lone absorption bands around 23.48 kK, typical of square planar geometry which were assigned to ${}^{1}A_{1g} \rightarrow {}^{1}E_{2g}$ transitions [23].

The ligand bands were bathochromic/ hypsochromic shifted in the complexes, indicative of coordination, with two band maxima between 27.00-30.00 and 31.0- 40.00 kK assigned to π - π^* and charge transfer transitions respectively [24]. In this study, the replacement of phenyl ring in HL¹ complexes with thienyl ring in HL² does not have any significant effect on geometry and electronic properties.

3.3 Antibacterial activities

The antibacterial activities of the ligands and their metal(II) complexes against *Bacillus subtilis, Staphylococcus aureus, Proteus mirabilis, Klebsiella oxytoca, Pseudomonas aeruginosa,* and *Escherichia coli* are presented in Table 1 and shown in Figure 2. The ligand (HL¹) had activity against all the bacteria with the exception of *Pseudomonas sp* with inhibitory zones range of 13.0-26.0 mm, while its thienyl analog (HL²) had activity against two bacteria namely *E. coli* and *S. aureus* with inhibitory zones of 11.5 mm and 17.0 mm respectively. Similarly, the metal complexes of HL² were less effective against the bacteria used than the metal complexes of HL¹. The better antibacterial activities of the phenyl trifluroacetone Schiff base complexes were attributed to mild electronwithdrawing ability of the phenyl ring and the toxic effect of the coordinated nitrate group [18, 27].

All the complexes were inactive against *K. oxytoca* with the exceptions of HL^1 , [MnL¹(NO₃)], [ZnL¹(NO₃)] and [PdL¹(Cl)H₂O] with inhibitory zones of 17.0, 14.0, 15.0 and 13.0 mm respectively.

The insensitivity of *K. oxytoca* to most of the compexes was attributed to the production of extended-spectrum betalactamase, which inactivates the compounds [28]. Similarly, *P. aeruginosa* and *B. subtilis* were not sensitive to most of the complexes with the exceptions of $[ZnL^1(NO_3)]$, $[PdL^1(Cl)H_2O]$, $[NiL^2]$, $[ZnL^2(OAc)]$; HL^1 , $[Ni(L^1)_2]$, $[CoL^2(OAc)]$.¹/₂ H₂O, $[NiL^2(OAc)]$.³H₂O and $[NiL^2(OAc)]$.³H₂O respectively, with inhibitory zones range of 13.0-15.0 and 13.0-16.5 mm.

Interestingly, HL^2 and its complexes were not active against *P. mirabilis* while HL^1 and its metal complexes had activity with inhibitory zones range of 17.0-24.0 mm.

This we could not explain. On the contrary, all the complexes and their ligands were active against *E. coli* with the exception of $[Cu(L^1)NO_3].2H_2O$ and inhibitory zones range of 11.0-16.0 mm. Similarly, *S. aureus* was sensitive to all the ligands and their complexes with inhibitory zones range of 13.0-26.0 mm with the exceptions of $[Mn(L^1)NO_3].\frac{1}{2}H_2O$ and $[Pd(L^2)Cl(H_2O)]$. Furthermore, it was observed that the ligands were mostly more active than their corresponding metal complexes due to their propable lipophobic nature.

Complexes	S. aureus	B. subrilis	K. oxytoca	P. aeruginosa	E. coli	P. mirabilis
HL^1	26.0 ± 1.41	13.0 ± 0	17.0 ± 0	R	16.0 ± 1.41	24.0 ± 1.41
$[Mn(L^1)NO_3] .^{1/2}H_2O$	R	R	14.0 ± 1.41	R	13.0 ± 0	19.0 ± 0
$[Co(L^1)NO_3]$. $\frac{1}{2}H_2O$	20.0 ± 1.41	R	R	R	13.0 ± 0	19.0 ± 0
$[Ni(L^1)_2]$	16.0 ± 1.41	14.0 ± 1.41	R	R	13.0 ± 0	17.0 ± 0
$[Cu(L1)NO_3].2H_2O$	21.0 ± 0	R	R	R	R	20.0±1.41
$[Zn(L^1)NO_3]$. $\frac{1}{2}H_2O$	27.0 ± 0	R	15.0 ± 0	13.0 ± 0	13.0 ± 0	20.0±1.41
$[Pd(L^1)Cl(H_2O)]$	22.0 ± 1.41	R	13.0 ± 0	15.0 ± 0	15.0 ± 0	21.0 ± 0
HL^2	17.0±1.4	R	R	R	11.5±0.7	R
$[Mn(L^2)OAC].\frac{1}{2}H_2O$	14.5±0.7	R	R	R	13.0±0	R
$[Co(L^2)OAC].\frac{1}{2}H_2O$	18.0±2.8	16.5±2.1	R	R	11.0±0.	R
$[Ni(L^2)OAC].3H_2O$	14.5±2.1	16.0±1.4	R	17.0±2.8	12.5±0.7	R
$[Cu(L^2)OAC].4H_2O$	13.0±2.8	R	R	R	13.5±0.7	R
$[Zn(L^2)OAC]$	14.0 ± 1.4	R	R	19.0±1.4	12.0±0	R
$[Pd(L^2)Cl(H_2O)]$	R	R	R	R	13.0±0	R
Streptomycin (+)	36.0 ± 1.41	44.0 ± 1.41	38.0 ±4.24	35.0 ± 1.41	34.0 ± 4.24	31.0 ± 0

Table 1. Zones of inhibition (in mm) of the compounds against various bacteria

R = Resistance, + = positive standard

Since chelation theory states that chelation increases the lipophilic character of the chelate, favouring its permeation into the bacterial membrane, thus causing the death of the organism [3-4, 22].

In addition, $[Zn(L^1)NO_3].\frac{1}{2}H_2O$ and $[Pd(L^1)Cl(H_2O)]$ had broad-spectrum antibacterial activity against *Staphylococcus aureus, Proteus mirabilis, Klebsiella oxytoca, Pseudomonas aeruginosa,* and *Escherichia coli* with inhibitory zones range of 13.0-22.0 mm while $[Ni(L^2)_2]$ had broad-spectrum against *Staphylococcus aureus, Bacillus subtilis, Pseudomonas aeruginosa,* and *Escherichia coli* with inhibitory zones range of 12.5-17.0 mm respectively, proving their potential usefulness as broad-spectrum antibacterial agents. In all cases, the antibiotic Streptomycin was more active than the ligands and their complexes expectedly with optinum activity being that of HL¹ against *P. mirabilis* and $[Zn(L^1)NO_3]$. $\frac{1}{2}H_2O$ against *S. aureus* with about 80% of Streptomycin's activity.

4. Conclusion

The Schiff bases, {1-phenyl-3-(p-nitrophenyliminol)-4, 4, 4-(HL^I) and1-thiophen-2yl-3-(ptrifluorobutenol} nitrophenylimino)- 4, 4, 4-trifluorobutenol} (HL²) coordinated to the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) ions using the azomethine N and enol O atoms. The assignment of a 4coordinate square planar/ tetrahedral geometry for the metal(II) was corroborated by % metal, infrared and complexes electronic spectral measurements. The in-vitro antibacterial studies showed that HL¹ and its metal(II) complexes had very good antibacterial activities while HL^2 and its metal(II) complexes exhibited weak antibacterial activities. In addition, $[Zn(L^1)NO_3]$.¹/₂H₂O, $[Pd(L^1)Cl(H_2O)]$ and $[Ni(L^2)_2]$ had broadspectrum antibacterial activity against Staphylococcus aureus, Pseudomonas aeruginosa, and Escherichia coli with inhibitory zones range of 12.5-22.0 mm proving their potential usefulness as broad-spectrum antibacterial agents

References

1. Franceschini, P.L., Morstein, M., Berke, H., Schmalle, H.W. Volatile β -ketoiminato- and β -diketiminato-based zirconium complexes as potential MOCVD precursors. Inorg. Chem., 42, 7273-7282, 2003.

2. Raman, N., Selvan, A., Pothiraj, A., Jeyamurugan, R. New insights into the antibacterial and antifungal activity study of mixed-ligand metal complexes containing tridentate Schiff base. Journal for Bloomers of Research, 3(1), 6-12, 2010.

3. Ceyhan, G., Çelik, C., Uruş, S., Demirtaş, İ., Elmastaş, M., Tümer, M. Antioxidant, electro chemical, thermal, antimicrobial and alkane oxidation properties of tridentate Schiff base ligands and their metal complexes. Spectrochim. Acta A Mol. Biomol. Spectr., 81, 184-198, 2011

4. da Silva, C.M., da Silva, D.L., Modolo, L.V., Alves, R. B., de Resende, M.A., Martins, C.V.B., de Fatima, A. A. Schiff bases: A short review of their antimicrobial activities. J. Adv. Res., 2, 1-8, 2011.

5. Jin, C., Liang ,Y.J., He, H., Fu, L. Synthesis and antitumor activity of ureas containing pyrimidinyl group. Eur. J. Med .Chem., 46(1), 429-432., 2011.

6. Osowole, A. A., Ott, I.,Ogunlana, O. M. Synthesis, spectroscopic, anticancer and antimicrobial properties of some Metal(II) complexes of 2-[(2,3- dihydrom1*H*-inden-4-ylimino) methyl]-5-nitrophenol. International Journal of Inorganic Chemistry, Vol. 2012, Article ID 206417, 6 pages, 2012.

7. Li, Z., Fernandez, M., Jacobsen, E. N. Enantioselective ring opening of meso aziridines catalyzed by Tridentate Schiff base chromium(III) complexes. Organic letters, 1(10), 1611-1613, 1999.

8. Bryliakov, K.P., Talsi, E., Boreskov, P. Asymmetric oxidation of sulfides with H_2O_2 catalyzed by titanium complexes with amino alcohol derived Schiff bases. Journal of Molecular Catalysis A: Chemical, 264(1-2), 280-287, 2007.

9. Fleischhaker, F., Arsenault, A. C., Kitaev, V., Peiris, F. C., Freymann, G., Manners, I., Zentel, R., Ozin, G. A. Photochemically and thermally tunable planar defects in colloidal photonic crystals. J. Am. Chem. Soc., 127, 9318–9319, 2005.

10. Sun, S., Murray, C. B., Weller, D., Folks, L., Moser, A. Monodisperse FePt nano particles and ferromagnetic FePt nanocrystal superlattices. Science, 287, 1989–1992, 2000.

11. Yang Z., Li, F., Yang, L., and Yang, R. Synthesis and relaxivity of polycarboxylic hydrazone rare earth complexes-

Relaxivity of *a*-oxo-pentanedioic acid benzoyl hydrazone Gd-complexes. Chinese Science Bull., 45(20), 1844–1850, 2000.

12. Briggs, M.S.J., Fossey, J.S., Richards, C.J., Scott, B., Whateleym, J. Towards novel biolabels: synthesis of a tagged highly fluorescent Schiffbase aluminium complex. Tetrahedron Lett., 43(29), 5169–5171, 2002

13. Osowole A.A., Kempe R., Schobert, R., Effenberger, K. Synthesis, spectroscopic, thermal and in-vitro anticancer properties of some metal(II) complexes of 3-(-1-(4,6-dimethyl-2-pyrimidinylimino)methyl-2-napthol. Synth. React. Inorg. Met. Org. Chem & Nano-Met.Chem., 41(7), 825-833, 2011.

14. Osowole, A. A.Synthesis, characterization, in-vitro antibacterial and anticancer studies on some metal(II) complexes of (methylsulfanyl) chromenol Schiff base. Elixir Applied Chemistry, 39, 4827-4831, 2011.

15. Osowole, A. A. Synthesis, characterization, magnetic and thermal studies on some metal(II) thiophenyl Schiff base complexes. International Journal of Inorganic Chemistry, Vol. 2011, Article ID 650186, 1-7, 2011.

16. Osowole, A. A., Kempe, R., Schobert, R. Synthesis, spectral, thermal, *in-vitro* anti-bacterial and anticancer activities of some metal(II) complexes of 3-(-1-(4-methoxy-6-methyl)-2-pyrimidinylimino)methyl-2-napthol. International Research Journal of Pure and Applied Chemistry, 2(2), 105-129, 2012.

17. Osowole, A. A., Akpan, E. J. Synthesis, spectroscopic characterisation, *in-vitro* anticancer and antimicrobial and properties of some metal(II) complexes of 3-{4,6-dimethoxy pyrimidinyl) imino methyl} naphthalen-2-ol. European Journal of Applied Sciences, 4(1), 14-20, 2012.

18. Osowole, A. A., Oni, A. A., Onyegbula, K., Hassan, A. T. Synthesis, spectral, magnetic and *in-vitro* anticancer properties of some Metal(II) complexes of 3-[2,4-

dihydro-1H-inden-4-ylimino) methyl] napthalen-2-ol. International Research Journal of Pure and Applied Chemistry, 2(3), 211-220, 2012.

19. Osowole, A. A., Balogun S.A. Spectral, magnetic, thermal and antibacterial studies on some metal(II) complexes of aminoindanyl Schiff base. European Journal of Applied Sciences, 4(1), 6-13, 2012.

20. Osowole, A. A., Kempe, R., Schobert, R.Synthesis, spectral, thermal, *in-vitro* antibacterial and anticancer activities of some metal(II) complexes of 3-(-1-(4-methoxy-6-methyl)-2-pyrimidinylimino)methyl-2-napthol. International Research Journal of Pure and Applied Chemistry, 2(2), 105-129, 2012.

21. Bassett, J., Denney, R.C., Jeffery, G.H., Mendham, J. Vogel's Textbook of Quantitative Inorganic Analysis. 4^{th} ed, ELBS, London, 1978.

22. Obaleye, J. A., Adediji, J. F., Adebayo, M. A. Synthesis and biological activities on metal complexes of 2,5-Diamino-1,3,4-thiadiazole derived from semicarbazide hydrochloride. Molecules, 16, 5861-5874, 2011.

23. Cherayath, S., Alice, J., Prabhakaran, C. P. Palladium(II) complexes of Schiff bases derived from 5-amino-2,4-(1H, 3H)pyrimidinedione (5-aminouracil) and 1,2-dihydro-1,5-dimethyl-2-phenyl-4-amino-3H-pyrazol-3-one. Transition Metal Chem., 15(6), 449–453, 1990.

24. Khalil, S. M. E., Seleem, H.S., El-Shetary, B.A., Shebl, M. Mono- and bi-nuclear metal complexes of Schiff base hydrazone (ONN) derived from o-hydroxy acetophenone and 2-amino-4-hydrazino-6-methyl pyrimidine. J. Coord. Chem., 55(8), 883-899, 2002.

25. Nejo, A. A., Kolawole, G. A., Opoku, A. R., Muller, C., Wolowska, J. Synthesis, characterization and insulin-enhancing studies of unsymmetrical tetradentate Schiff base complexes of oxovanadium(IV). Journal of Coordination Chemistry, 62(21), 3411-3424, 2009.

26. Lever, A. B.P. Inorganic Electronic Spectroscopy, 2nd ed, Elsevier, Amsterdam, Netherlands, 1980

27. Sondhi, S. M., Verma, R. P., Singhal, N., Sharma, V. K., Husiu, C., Vargiu, L., Longu, S., La Colla, P. Anti HIV, antibacterial and antifungal potential of a variety of heterocyclic compounds containing nitrogen and/or sulphur. Indian J. Pharm. Sci., 62(1), 71-76, 2000.

28. Pelczar, M. J Jr., Chan, E. C. S., Krieg, N. R. Microbiology. McGraw-Hill. New York, USA, 1996.