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Synthesis, Spectral Characterization and Antibacterial Properties of Isomeric Mixture of Nickel(II) Complexes

Malumi Emmanuel Olusola[*,1], Shoetan Ibrahim Olakunle.[2], Akinyele Folorunsho Olawale[3] and Okoronkwo Elvis Afamefuna[1]

[1]Federal University of Technology, Akure, Nigeria.

[2] Cardiff University, Wales, United Kingdom.

[3]Obafemi Awolowo University, Ile-Ife, Nigeria.

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ABSTRACT

Isomeric Nickel (II) complexes of toluic acid hydrazide-hydrazone, HL have been synthesized through one pot synthesis. The ligand, HL and the complexes were characterized with FTIR, UV-Vis, NMR and Mass Spectroscopies, Melting point, solubility, metal conductance, percentage metal and elemental analyses and magnetic susceptibility. The solubility test revealed that the compounds were generally soluble in DMSO hence the molar conductance of the complexes in DMSO showed that the complexes are electrolytic in nature. The mass spectroscopy, percentage metal and elemental analyses conformed with the formulated masses, while the compounds were stable at room temperature. The FTIR spectra of the ligand proved it to be bidentate and the ligand, HL coordinated to the Ni(II) ions through while the electronic spectra peaks showed that Ni(II) complex isomer I and Ni(II) complex isomer II assumed tetrahedral and square planar geometries respectively. The NMR spectra of Ni(II) complex isomer I gave broad bands due to paramagnetism while Ni(II) complex isomer II revealed the relevant peaks. The antibacterial activities of the compounds showed the complexes are more active against the ligand, with Ni(II) complex isomer 1 showing greater activity against *k.pneumoniea*.

1.1 Introduction

Nickel as a ferromagnetic metal is in the same triad with platinum and palladium in the periodic table[1,2,3]. Researchers have discovered different enzymes with active Nickel centre, for instance urease[4], hydrogenase[5], functioning as an important cofactor. Nickel is vastly used in catalyst development[6], and in bio-transforming the biological use of many heterocyclic compounds[7]. Many isomeric compounds of nickel (II) complexes have reported, a new pair brown and green isomers of nickel (II) complexes of a Schiff base as reported by Akira Takeuchi and Shoichiro Yamada, 1969[8] proved to be a template example of possible isomeric mixture of Nickel complex with Nitrogen atoms active sites ligands[9]

Interestingly, the stereochemistry observed from isomeric Nickel complexes[10] and their various activities against microbes of public health important[[11] have drawn attention of many Biochemists and Coordination chemists.

Hence, our aim is to synthesise, characterise and study the antibacterial properties of Isomeric mixture of Nickel (II) complexes of a toluic acid hydrazide-hydrazone Schiff base.

1.2 Experimental

1.2.1Materials, Reagents and Instrumentation Details

Toluic acid hydrazide, p-nitrobenzaldehyde, nickel (II) tetraoxosulphate(VI) hexahydrate, absolute ethanol, methanol, distilled water, chloroform, dimethylsulfoxide were of analytical grade and were obtained from Aldrich, BDH and Merck chemicals, and were used without further purification. The magnetic susceptibilities were measured at 76-300 K using mercury tetrathiocyanatocobalt (II) as the calibrant on a Cahn RM-2 Electrobalance and the molar conductivity measurements of 1 x 10^{-3} M solutions of the complexes in DMSO were carried out at room temperature using electrochemical analyzer CONSORT C933. The UV-Visible spectra of the ligand and the complexes were recorded as DMSO solution on the Perkin-Elmer 21 spectrophotometer in the range 900-190 cm^{-1}. Melting points were determined with Gallen Kamp melting point apparatus and the C, H and N elemental analysis of the ligand and the complexes was carried out with ThermoScientific Flash2000 elemental analyzer. The percentage of the metals in the complexes was determined via complexometric titration with EDTA using murexide as indicator and, atomic absorption method using Buck Scientific model 210. The ^{1}H and ^{13}C NMR spectra were registered using Bruner DRX (500 MHz). The mass spectra of the ligand and complexes were recorded on a Waters micromass LCT Premier TOF-MS while the stoichiometry of the metal to ligand in the metal complexes was determined via continuous (Job's plot) variation method.

1.2.2Synthesis of Toluic Acid Hydrazide-Hydrazone Schiff Base, HL

The toluic acid hydrazide-hydrazone Schiff base, HL was synthesised by mixing toluic acid hydrazide (2.9 mmol, 4.0 g in 50 ml in methanol) and p-nitrobenzaldehyde (2.9 mmol, 4.03 g in 50 ml solution) for 4 hours at 50 ^{0}C. The mixture was refluxed on a magnetic stirrer hotplate. The formed solid product was filtered off, washed with methanol several times

Tele:+2347032482480

E-mail address:qcvpacad@gmail.com

followed by re-crystallization from warm methanol and then dried under vacuum[12].

Colour: Cream yellow; Yield: 93.08 %; M.pt.: 242-244 ^{0}C; FT-IR (KBr, *v*, cm^{-1}): 3189 (N-H)(sec. amine), 1780 (C=O)(amine), 1609 (C=N)(azomethine); ^{1}H NMR (500, MHz, DMSO-d_6, ppm): 12.06. (s, 1H, =N-NH-CO), 8.55 (s, 1H, CH=N-N, 8.31 (d, 2H, Ar-H), 8.29 (d, 2H, Ar-H), 7.99 (d, 2H, Ar-H), 7.97 (2H, Ar-H), 2.39 (s, 3H, Ar-Me). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): 163.20 (1C, C=N), 147.77 (1C, C=O), 147.71-127.73 (12C, Ar-C), 124.02 (3C, Ar-Me); MS (EI, m/z(%)): 218 (M^+, 100); UV/Vis (DMSO, nm): 294, 357.

1.2.3Synthesis of Isomeric Mixture of Nickel(II) Complexes of the Synthesized Hydrazone

The procedure used for the preparation of the isomeric mixture of nickel (II) complexes of toluic acid hydrazide-hydrazone was carried out in line with Osowole et al.,2015[13] with slight modifications. A solid powered nickel salt ($NiSO_4.6H_2O$) (0.47 g, 1.8 mmol in 40 ml methanol) was added to a stirring solution of toluic acid hydrazide-hydrazone, HL (1.02 g, 3.6 mmol in 40 ml methanol) on a magnetic stirrer hotplate at 50 ^{0}C for 3 hours. A yellow precipitate was filtered and dried over silica gel in a desiccator. The filtrate was left to settle down and after 40 minutes another orange precipitate was obtained and filtered and dried over silica gel in a desiccator.

1.3 Antibacterial Assay

Antibacterial properties of the ligand and isomeric mixture of nickel complexes were carried out via the Agar-well diffusion method with slight modifications following the procedure previously reported by Osowole et al., 2015[13] and NCCLS, 1997[14]. Muller Agar plates were prepared, and test bacteria isolates were inoculated by streak plate method. Five wells of 4 mm in diameter each were bored evenly so that they are no closer than 20 mm from each other, center to center. 50 μl of the sample containing the ligand and the complexes of various concentrations of 200 to 50 mg/ml and commercial antibiotic (Tetracycline 20 mg/ml) as control were introduced into the wells of 4 mm in diameter. Each well was allowed dried to ensure complete diffusion with the agar surface and the agar plates were then incubated at 37 ^{0}C. After 18 hours of incubation, each plate was examined. The resulting zones of inhibition were uniformly circular with a confluent lawn of growth. The diameter of the zones of complete inhibition was measured using Vernier caliper, including the diameter of the tetracycline used as control.

2.0 Results and Discussion

2.1 Analytical Data

The ligand and its isomeric mixture complexes were stable at room temperature, and of different colours due to d-d transitions[15, 16] . The ligand decomposed at 242-244 ^{0}C, and the complexes decomposed in the range of 286-290 ^{0}C and 260-264 ^{0}C confirming coordination[17]. The elemental analysis and the quantitative analysis showed good agreement with the calculated percentage of the constituent's elements corroborating the formulation of the complexes and the stoichiometric ratio of the metal salts and the ligand was 1:2[18] as presented in Table 1.

2.2 Solubility and Molar Conductance Measurements

The ligand, HL and the complexes were generally soluble in DMSO and chloroform while the metal conductance measurement of the complexes in DMSO showed they are electrolytes[19, 20] as presented in table 2.

2.3 Electronic Spectra

The electronic spectrum of the ligand, HL showed two bands at 294 nm and 357 nm assignable to $\pi \rightarrow \pi*$ and n→$\pi*$ transitions respectively[21]. The Ni(II) complex isomer 1 spectrum exhibited three bands at 482 nm, 560 nm and 683 nm assigned to $^3T_{1(F)} \rightarrow {}^3T_{1(P)(v3)}$, $^3T_{1(F)} \rightarrow {}^3A_{2(v2)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(v1)}$ respectively. These bands are consistent with a 4-coordinate tetrahedral geometry [22]. The Ni(II) complex isomer II spectrum also revealed three distinct bands at 678 nm, 506 nm and 480 nm assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ respectively. These bands corroborate a 4-coordinate square planar geometry[23].

Table 1. Analytical data of ligand, HL and its isomeric Ni(II) complexes.

Compound	F. mass	Colour	M.pt.(^{0}C)	Elemental Analysis/% Metal Analysis Exp. (Calc.)				% Yield
				C	**H**	**N**	**M**	
HL ($C_{15}H_{13}N_3O_3$)	283.3	Cream Yellow	242-244	62.11 (63.59)	5.21 (4.63)	15.10 (14.83)	-	93.08
$[Ni(HL)_2]SO_4$ isomer I	721.3	Yellow	286-290	50.14 (49.91)	4.19 (3.63)	11.55 (11.65)	8.14(8.20)	67.32
$[Ni(HL)_2]SO_4$ isomer II	721.3	Orange	260-264	38.06 (49.91)	4.40 (3.63)	8.75 (11.65)	8.14(8.20)	32.26

M.pt. = Melting point

Table 2. Solubility tests and molar conductance Measurements.

Compound	*MeOH*	*EtOH*	*$CHCl_3$*	*DMSO*	*DMF*	*H_2O*	*^M*
HL	I	I	SS	S	SS	SS	-
$[Ni(HL)_2]SO_4$ isomer I	I	SS	S	S	SS	I	58
$[Ni(HL)_2]SO_4$ isomer II	I	SS	S	S	SS	I	51

Footnote: S= soluble, SS= slightly soluble, I= insoluble

Table 3. Magnetic Susceptibility Data of $[Ni(HL)_2]SO_4$ ISOMER 1

T/K	□ X_m x 10^6 cm^3mol^{-1}	μ_{eff} (B .M)	□ X_m.T x 10^6 $cm^3mol^{-1}K$
76	14830	3.52	1127080
100	12071	3.50	1207100
125	10713	3.41	1339125
150	10160	3.38	1524000
175	9430	3.40	1650250
200	8230	3.38	1646000
225	6680	3.37	1503000
250	5541	3.38	1385250
275	4125	3.35	1134375
300	3820	3.35	1146000

2.4 Magnetic Moment Susceptibility

The variable temperatures measurement of the magnetic susceptibilities of the isomeric mixture of the Ni (II) complexes are presented in Table 3. The results of the measurement showed that the isomer I is paramagnetic in nature[1] while isomer II is diamagnetic[24]. In Table 3, it was observed that the decrease in μ_{eff} with the temperature suggested a paramagnetic shift from high spin to low spin were observed[25] culminating into ferromagnetic exchange interaction and as also observed from Curie's and Curie-Weiss's curves[26] in figures 1 and 2.

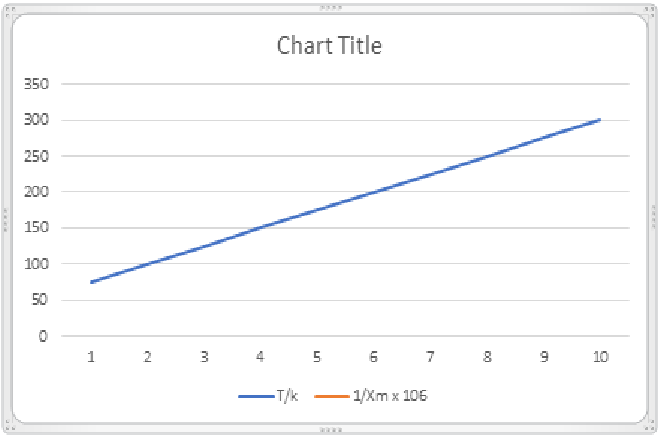

Fig 1. Curie's curve for $[Ni(HL)_2]SO_4$ ISOMER 1

Fig 2. Curve-Weiss's curve for $[Ni(HL)_2]SO_4$ ISOMER 1

2.5 Infrared Spectroscopy

The important infrared spectral bands of the ligand, HL and its isomeric mixture nickel (II) complexes are present in Table 4. The notable IR bands of the ligand, HL at 3189, 1780, 1609 and 1588 cm^{-1} were attributed to *v*(N-H), *v*(C=O)[27], and *v*(C=N) in azomethine group respectively. On coordination to Ni(II) complex isomer 1 and isomer II, the strong band due to v(N-H) shifted to a higher frequencies in isomer I to 3217.33 cm^{-1} and 3224.65 cm^{-1} in isomer II indicative of nitrogen atom of the amino group of the ligand, HL to the Ni(II) complexes[28]. Similarly, the band due to *v*(C=O) in the ligand, HL shifted to a lower frequencies in the Ni (II) complexes indicative of the carbonyl group Oxygen atom complexing to the Ni(II) complexes. The bands due to *v*(C=N) in azomethine group remained unchanged in the Ni (II) complexes, showing no complexation of the azomethine nitrogen atom to the Ni(II) complexes[29]. More so, the new bands due to *v*(M-O) and *v*(M-N) observed in the range of 445.87-425.94 cm^{-1} and 585.24-540.93 cm^{-1} which were absent in ligand, HL spectrum further indicated coordination between ligand and Ni(II) salt[30].

2.6Nuclear Magnetic Resonance (NMR) Spectroscopy Difference of the Isomeric Mixture

The ^{1}H NMR spectrum of Ni(II) complex isomer I, being paramagnetic usually gives broad bands[31]as shown in fig 3.0, hence ^{2}H NMR is commonly used instead of ^{1}H NMR of the paramagnetic species. The ^{1}H NMR spectrum of Ni(II) complex isomer II revealed the number of peaks expected in the proposed structure of the complex in Figure 8.

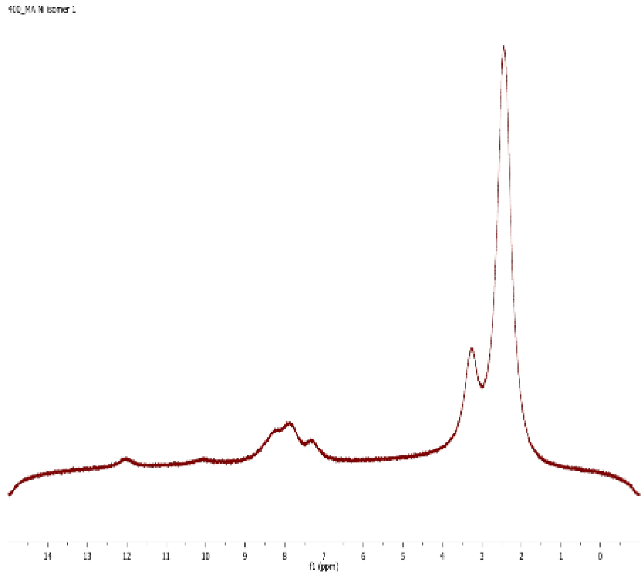

Fig 3. ^{1}H NMR spectrum of $[Ni(HL)_2]SO_4$ ISOMER 1

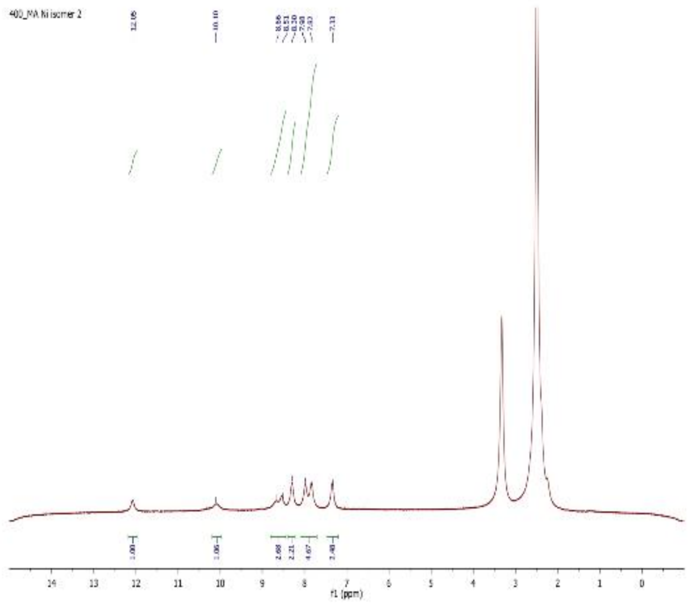

Fig 4. ^{1}H NMR Spectrum of $[Ni(HL)_2]SO_4$ ISOMER 11

Table 4. FTIR Spectral data of the metal complexes and the ligand

Sample	*v*(N-H)	*v*(C=O)	*v*(C=N)	*v*(M-O)	*v*(M-N)
HL	3189.53	1780	1609.53 1587.88	-	-
$[Ni(HL)_2]SO_4$ isomer 1	3217.33	1651.51	1610.28 1589.77	445.87	585.24
$[Ni(HL)_2]SO_4$ isomer 11	3224.65	1651.12	1610.26 1584.38	438.10	540.93

2.7 Mass Spectroscopy

The mass spectral peaks of the metal (II) complexes and the mass spectrum of the ligand, HL revealed different base peaks. A base peak at m/z 218 amu was observed from the spectrum Ligand, HL relative to its formula weight of 283.3. The mass spectra of the Ni(II) complexes isomer I and isomer II showed base peaks at m/z 630 amu and 684 amu respectively relative to the formula weight of 721.3 as shown in figure 5 and 6.

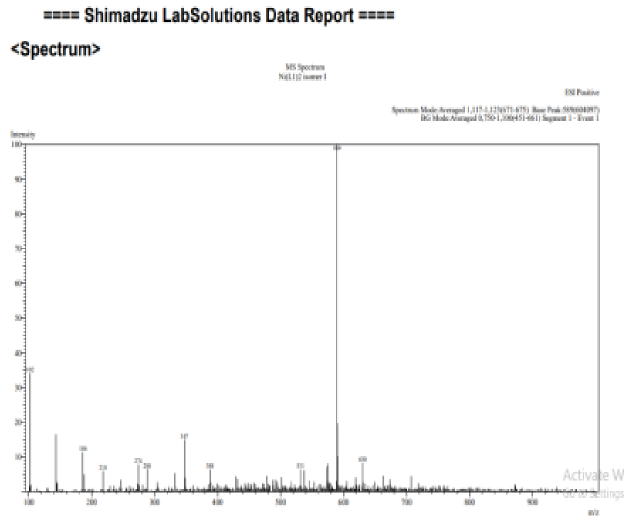

Fig 5. Mass spectrum of $[Ni(HL)_2]SO_4$ ISOMER I

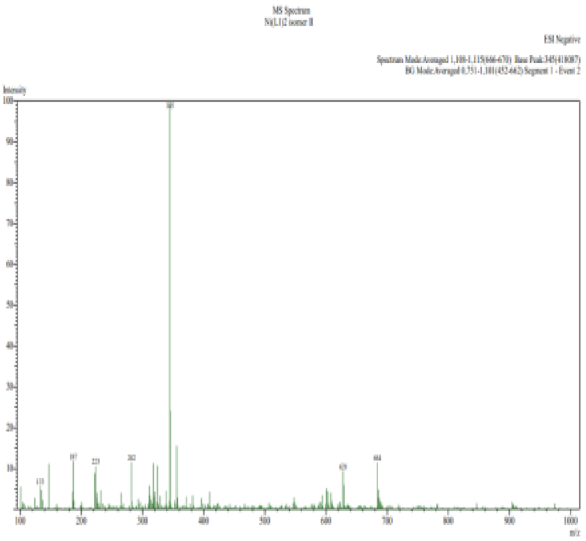

Fig 6. Mass spectrum of $[Ni(HL)_2]SO_4$ ISOMER II

2.8 Antibacterial Activities of the Isomeric Mixture of Nickel(II) Complexes

The antibacterial studies of the ligand, HL and its isomeric Nickel (II) complexes, presented in Table 5. From the results, it showed that all the tested organisms bio-metalated all the samples except *k.pneumoniea* which could not inhibit the isomeric Ni(II) complex isomer I[32]. Ni(II) complex isomer I showed better activity against *k.pneumoniea* than Ni(II) complex isomer II.

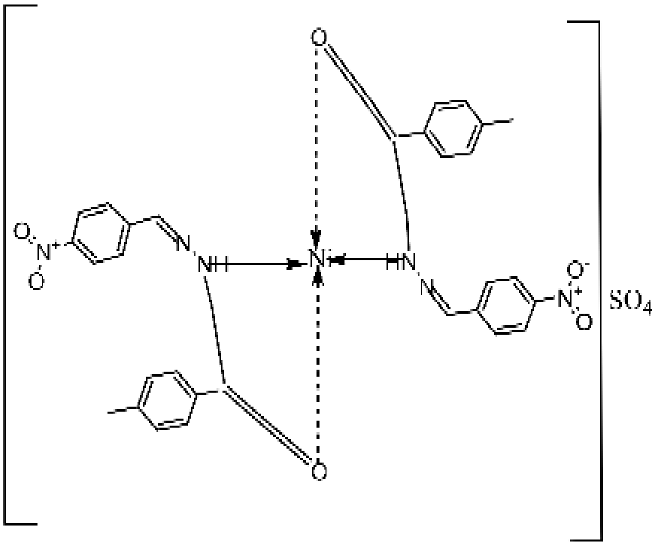

Fig 7. Proposed structure of $[Ni(HL)_2]SO_4$ isomer I

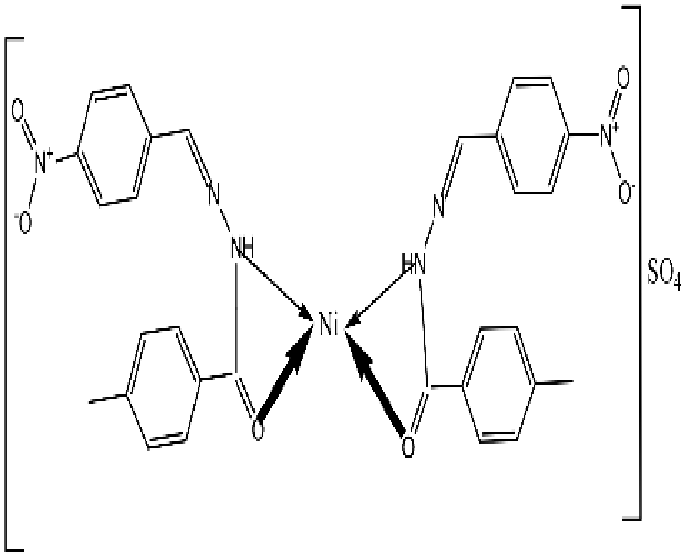

Fig 8. Proposed structure for $[Ni(HL)_2]SO_4$ isomer II

3.0 Conclusion

In this paper the preparation of the hydrazone ligand, HL derived from the reaction between p-toluic acid hydrazide and 4-nitrobenzaldehyde and its isomeric Nickel complexes have been showcased. The ligand coordinates with nickel ions via its N and O indicates bidentate nature of the ligand. This is supported by IR data. The molar conductance of Ni(II) complex isomer I and isomer II shows its covalent nature and the basis of electronic and magnetic data, the Ni(II) complex isomer I and isomer II show that isomer I is paramagnetic while isomer II is diagmagnetic with a 4-coodinate geometry.

Table 5. Antibacterial activities of the ligand,HL and the complexes.

Ligand/Complexes		Strep. pyogenes (mm)	K. pneumoniea (mm)	S. typhi. (mm)	E. coli (mm)
Ligand, HL (mg/ml)	80	-	-	-	-
	100	-	-	-	-
	120	-	-	-	-
$[Ni(HL)_2]SO_4$ isomer I (mg/ml)	80	-	12.0	-	-
	100	-	14.4	-	-
	120	-	16.2	-	-
$[Ni(HL)_2]SO_4$ isomer II (mg/ml)	80	-	10.0	-	-
	100	-	12.4	-	-
	120	-	15.2	-	-
Tetracycline (20 mg/ml)		17.4	24.4	16.4	12.4

The isomeric Ni(II) complexes show good viable antibacterial properties.

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Disclosure Statement

Conflict of interests: The authors declare that they have no conflict of interest.

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