



SYNTHESIS, CHARACTERIZATION, AND ANTIBACTERIAL ACTIVITY OF METAL COMPLEXES OF 4-METHYL-*N'*-(4-NITROBENZYLIDENE) BENZOHYDRAZIDE

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Article Received on
20 October 2021,

Revised on 10 Nov. 2021,
Accepted on 30 Nov. 2021

DOI: 10.20959/wjpps202112-20770

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ABSTRACT

A series of 4-methyl-*N'*-(4-nitrobenzylidene) benzohydrazide metal complexes obtained from p-toluic acid hydrazide and p-nitro benzaldehyde were synthesized, characterized and screened for antibacterial activity. The ligand, 4-methyl-*N'*-(4-nitrobenzylidene) benzohydrazide and its metal complexes were characterized by melting point and decomposition temperature, elemental analysis, solubility, conductivity measurement, atomic absorption spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, magnetic susceptibility measurement, electronic and infrared spectroscopies, TGA/DTG and TOF-Mass spectroscopy. The results of the spectroscopic studies revealed that the ligand function as bidentate ligand, condensing

through Oxygen atom of the carbonyl group and Nitrogen atom of the azomethine group in the complexes. All metal complexes were paramagnetic except for Zn (II) complex was diamagnetic as expected. Furthermore, the elemental analysis, TOF-mass spectroscopy and conductivity measurement revealed a 1:2 metal to ligand confirmation and formulated masses of the complexes that were electrolytic in nature except for Cu (II) that was covalent. NMR spectrum further confirmed the structure of the ligand. The TGA/DTG of the ligand showed that the ligand was relatively stable. The antibacterial activities of the compounds against four isolates of microbes that is *Escherichia Coli* (*E. Coli*), *Klebsiella pneumoniae* (*K.pneumoniae*), *Staphylococcus pyogenes* (*s.pyogenes*) *salmonella typhi* (*S.typhi*) were studied.

The results of the antibacterial activity of the compounds revealed that the positive control was active against all bacterial strains while metal complexes showed higher activities against the bacterial strains except for *S.typhi* (which bio-metalated the compounds) than the ligand that showed no activity.

KEYWORDS: Schiff bases, Metal complexes, Antibacterial activity, Hydrazone derivatives, Thermal decomposition, Japp-Klingemann reaction.

1. INTRODUCTION

Hydrazones are a vital class of Schiff bases and are primarily obtained through the one pot condensation reaction involving a hydrazide (primary amine) and a carbonyl group (alkanal or alkanone).^[1] Hydrazones can also be obtained by the Japp-Klingemann reaction.^[2] Hydrazones serve as essential intermediate in heterocyclic chemistry.^[3,7] The hydrazone framework contains imine nitrogen with lone-pair of electrons viable for coordination to transition metal ions. The biological properties of the hydrazone ligands have been enhanced by the coordination of the transition metal ions to the ligands.^[4] Hence, hydrazones can be used in drug design and as ligands in coordination chemistry.^[5] The tautomerism in hydrazones and transition metal complexes has opened the way for these compounds to be used in biological fields such as antibacterial agents,^[6] anti-inflammatory agent,^[8] anti-cancer agents,^[9] and as antioxidants.^[10,11]

Toluic acid hydrazide has nitrogen and oxygen donor sites in the amine and carbonyl groups of its structure. Hence, it functions as a multidentate ligand. Similarly, *p*-nitro benzaldehyde can be prepared by acidic hydrolysis of 4-nitromethylbenzene and chromium(IV) oxide. Furthermore, due to its aldehydic oxygen donor site, *p*-nitro benzaldehyde and its derivatives have been used as ligand^[12] and in heterocyclic chemistry for synthesizing different compounds.^[7]

A detailed literature search showed that several hydrazone Schiff bases derived from either *p*-nitro benzaldehyde or *p*-toluic acid hydrazide and their metal complexes have been reported. However, no reports have been found on the Mn(II), Cu(II), and Zn(II) Schiff base derived from *p*-toluic acid hydrazide and *p*-nitro benzaldehyde. Therefore, in this study, we aim to synthesize, characterize, and screen the metal chelates of 4-methyl-*N'*-(4-nitrobenzylidene)benzohydrazide for possible potential antibacterial activities.

2. Experimental

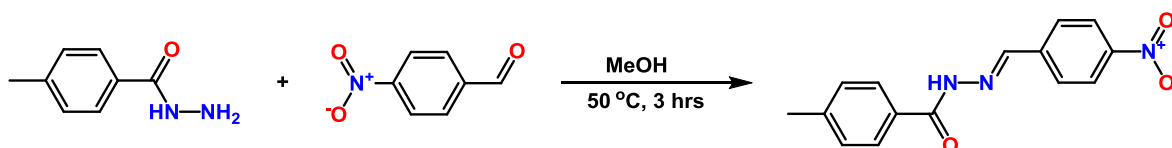
2.1 Materials, Reagents and Instrumentation details

Toluic acid hydrazide, 4-nitrobenzaldehyde, manganese(II) sulfate monohydrate, copper(II) nitrate trihydrate and zinc(II) sulfate heptahydrate, absolute ethanol, methanol, distilled water, chloroform, and dimethylsulfoxide were of analytical grade and were obtained from Aldrich, BDH, and Merck Chemicals, and were used without further purification. The molar conductivity measurements of 1×10^{-3} M solutions of the complexes in DMSO were carried out at room temperature using electrochemical analyzer CONSORT C933 and magnetic susceptibilities were measured at room temperature using mercury tetrathiocyanatocobaltate (II) as the calibrant on a Cahn RM-2 electrobalance. The UV-Visible spectra of the ligand and the complexes were recorded as DMSO solution on the Perkin-Elmer 21 spectrophotometer in the range $900-190 \text{ cm}^{-1}$. 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 metal complexes was determined via complexometric titration using EDTA and atomic absorption method using Buck Scientific model 210. The ^1H and ^{13}C NMR spectra were registered using Bruker DRX (500 MHz). The mass spectra of the ligand and metal complexes were recorded on the Waters micromass LCT Premier TOF-MS. The TGA-DTA spectra were obtained using Shimadzu instruments (Shimadzu TGA-Q50 thermobalance).

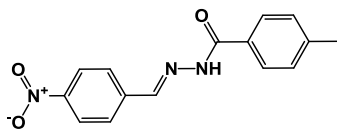
2.2 Synthesis

2.2.1 Synthesis of ligand

The protocol was carried out in accordance with Festus, Mohareb and Soderberg *et al.*^[13,14] with slight modifications. A mixture of toluic acid hydrazide (2.9 mmol, 4.0 g in 50 mL methanol) and 4-nitrobenzaldehyde (2.9 mmol, 4.03 g in 50 mL methanol) was refluxed while stirring for 3 hours at 50°C . The formed solid product was filtered off, washed with methanol several times followed by re-crystallization from warm methanol and finally dried under vacuum (Scheme 1).



Scheme 1: Synthesis of 4-methyl-*N'*-(4-nitrobenzylidene)benzohydrazide, L.

4-Methyl-*N'*-(4-nitrobenzylidene)benzohydrazide (L):

(*E*)-4-methyl-*N'*-(4-nitrobenzylidene)benzohydrazide
Chemical Formula: C₁₅H₁₃N₃O₃
Exact Mass: 283.10
Molecular Weight: 283.29
Elemental Analysis: C, 63.60; H, 4.63; N, 14.83; O, 16.94

Color: Cream yellow.

Yield: 93.08 %

M.p.: 242-244 °C.

FT-IR (KBr, ν , cm⁻¹): 3189 (N-H), 1780 (C=O), 1609 (C=N).

¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 12.06 (s, 1H, NH), 8.55 (s, 1H, CH=N), 8.31 (d, 2H, Ar-H), 8.29 (d, 2H, Ar-H), 7.99 (d, 2H, Ar-H), 7.97 (d, 2H, Ar-H), 2.39 (s, 3H, Ar-Me).

¹³C NMR (125 MHz, DMSO-*d*₆, δ , ppm): 163.20 (1C, C=N), 147.77 (1C, C=O), 142.18-127.73 (12C, Ar-C), 144.93 (3C, Ar-Me)

MS (EI, *m/z* (%)): 283 (M+1)

UV/Vis (DMSO, nm): 294, 357.

2.2.2 Synthesis of metal(II) complexes

The protocol was carried out in accordance with Bharate and Shane *et al.*^[15,16] with slight modifications as follows. A 1:2 mixture of the metal salts (1.8 mmol for Mn (II), Cu(II), and Zn(II)) and the ligand (1.0 g, 3.5 mmol) is mixed in 40 mL of ethanol. The mixture was stirred for 3 hours on a magnetic stirrer hotplate at 50 °C. Afterwards, triethylamine (TEA) was added as buffer and the reaction mixture was adjusted to a pH of 8. Different shades of colored precipitates were filtered off and washed with ethanol and finally dried over silica gel in a desiccator (Figure 1).

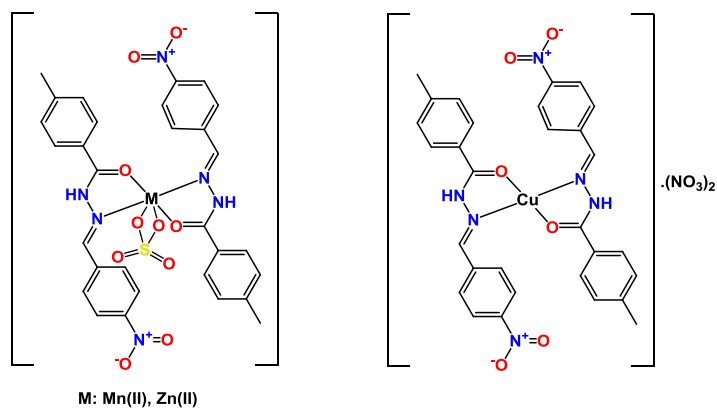
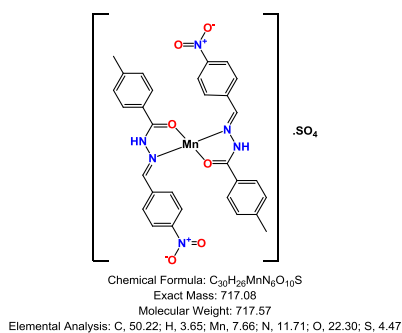


Figure 1: Proposed structures of the metal complexes.



[MnL₂SO₄]

Color: Yellow.

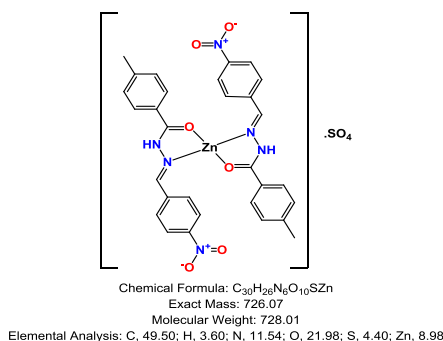
Yield: 55 %.

M.p.: 280-284 °C.

FT-IR (KBr, ν , cm^{-1}): 3193 (N-H), 1652 (C=O), 1557 (C=N), 431 (Mn-N), 502 (Mn-O).

Anal. calcd. for $C_{30}H_{26}MnSN_6O_{10}$: C, 50.22; H, 3.65; N, 11.71, Mn, 7.66. Found, C, 50.96; H, 4.45; N, 12.61, Mn, 7.90%

$\Lambda_m(\square^{-1}m^2mol^{-1})$: 29.



[ZnL₂SO₄]

Color: Cream yellow.

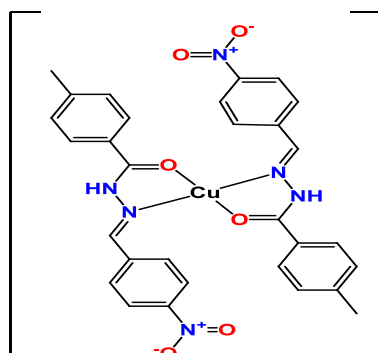
Yield: 54%.

M.p.: 294-296 °C.

FT-IR (KBr, ν , cm^{-1}): 3183 (N-H), 1651 (C=O), 1588 (C=N), 421(Zn-N), 510 (Zn-O).

Anal. calcd. for $\text{C}_{30}\text{H}_{26}\text{ZnSN}_6\text{O}_{10}$: C, 49.50; H, 3.60; N, 11.54; Zn, 8.98. Found: C, 45.77; H, 4.58; N, 11.35, Zn, 8.90%.

$\Lambda_m(\square^{-1}\text{m}^2\text{mol}^{-1})$: 49.



Chemical Formula: $\text{C}_{30}\text{H}_{26}\text{CuN}_8\text{O}_{12}$
 Exact Mass: 753.10
 Molecular Weight: 754.13
 Elemental Analysis: C, 47.78; H, 3.48; Cu, 8.43; N, 14.86; O, 25.46

$[\text{CuL}_2] \cdot (\text{NO}_3)_2$

Color: Light yellow.

Yield: 68%.

M.p.: 270-272 °C.

FT-IR (KBr, ν , cm^{-1}): 3194 (N-H), 1652 (C=O), 1592 (C=N), 426 (Cu-N), 520 (Cu-O).

Anal. calcd. for $\text{C}_{30}\text{H}_{26}\text{CuN}_8\text{O}_{12}$: C, 47.78; H, 3.48; N, 14.86, Cu, 8.43. Found, C, 48.10; H, 4.06; N, 12.39; Cu, 9.02%.

$\Lambda_m(\square^{-1}\text{m}^2\text{mol}^{-1})$: 136.

2.3 Antibacterial assay

Antibacterial actions of the ligand and its' metal complexes were investigated by the Agar-Well Diffusion method with little modification following the procedure previously reported^[15,17] Muller Hinton Agar plates were prepared, and the 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 dry to ensure complete diffusion with the agar

surface and the agar plates were then incubated at 37 °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.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The ligand and its metal complexes were air-stable solids, non-hygroscopic, and of different shades of colors due to *d-d* transitions.^[18,19,20] Ligand (L) was decomposed at 242-244 °C, and all complexes were decomposed in the range of 270-296 °C confirming coordination.^[15] The elemental analysis and the quantitative analysis showed good closeness with the calculated percentage of the constituent's elements confirming the formulation of the complexes and the stoichiometric ratio of the metal salts and the ligand was 1:2.^[21]

The ligand and its metal complexes were generally soluble in DMSO but were slightly soluble in chloroform, methanol, ethanol, water, and DMF and this is due to their polymeric states.^[15] Hence, their molar conductance was taken in DMSO at room temperature. The values obtained were in the range of 29, 49, and 136 $\Omega^{-1}\text{m}^2\text{mol}^{-1}$ typical of non-electrolytes and electrolytes for the Mn(II), Zn(II), and Cu(II) complexes, respectively.^[22] Mn(II), Zn(II), and Cu(II) complexes isolates were tested qualitatively for sulphate and nitrate groups gave negative for Mn(II) and Zn(II) confirming absence of counter ions and positive for Cu(II) complex with colored precipitate showing counter ions formation^[23] as shown in Figure 1.

The electronic absorption spectral data and magnetic moment values of the ligand and its transition metal complexes as shown in Table 1. The electronic spectra of the compounds were characterized by absorption maxima between 365 nm, 218-296 nm and 196 nm attributed to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and charge transfer (CT) transitions, respectively.^[24]

Table 1: Electronic and magnetic data of the ligand and its metal complexes.

Sample	μ_{eff} (B.M.)	Band (nm), assignment
Ligand	-	365 $n \rightarrow \pi^*$; 218-296 $\pi \rightarrow \pi^*$; 196 CT
[MnL ₂ SO ₄]	5.58	679 ${}^6A_{1g} \rightarrow {}^4T_{1g}$; 463 ${}^6A \rightarrow {}^4T_{2g}(G)$; 427 ${}^6A_{1g} \rightarrow {}^4E_g(G)$
[CuL ₂](NO ₃) ₂	2.18	772 ${}^2B_{1g} \rightarrow {}^2A_{1g}$; 491 ${}^2B_{1g} \rightarrow {}^2E_{1g}$
[ZnL ₂ SO ₄]	Dia	834 L \rightarrow MCT; 506 L \rightarrow MCT; 428 L \rightarrow MCT

The Mn(II) complex spectra showed three absorption bands at 679 nm, 463 nm and 427 nm assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ transitions, respectively, consistent with octahedral geometry. The observed magnetic moment of 5.58 B.M. was indicative of ferromagnetic octahedral^[23] since the effective magnetic moment of 5.5-6.0 B.M. is expected for Mn(II) complexes of 6-coordinate octahedral geometry.^[25]

The two absorption bands revealed in the spectrum of the Cu (II) complex at 772 nm and 491 nm assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}$ indicative of a distorted square geometry. This distortion is due to Jahn-Teller.^[26] This is further corroborated by an observed magnetic moment of 2.18 B.M.

The Zn (II) complex exhibited bands at 834 nm, 506 nm and 428 nm typical of octahedral geometry assigned to metal \rightarrow ligand charge transfer since *d-d* transitions were not expected. The magnetic moment of the Zn (II) complex was diamagnetic due to the fully filled 3*d*-orbital with electrons.^[27]

The IR bands at 3189 cm^{-1} , 1609 cm^{-1} and 1588 cm^{-1} were assigned as $\nu(\text{N-H})$, $\nu(\text{C=O})$ and $\nu(\text{C=N})$ in azomethine group, for the free ligand, respectively.^[28,29] The strong band due to $\nu(\text{C=N})$ shifted to lower frequencies in the spectra of Mn(II) and Zn(II) complexes indicative of coordination of the azomethine nitrogen to Mn(II) and Zn(II) ion while the $\nu(\text{N-H})$ band in the spectrum of the Cu(II) complex remained unshifted significantly corroborating non-coordination of the azomethine nitrogen to the Cu(II) ion. The bands corresponding to $\nu(\text{C=O})$ on coordination to Mn(II), Zn(II), and Cu(II) complexes shifted to a lower and higher frequency, respectively, indicative of the bonding of the carbonyl oxygen to the metal ions, and the band corresponding to $\nu(\text{C=N})$ in azomethine, on complexation shifted to a higher frequency in the Cu(II) complex spectra, showing the coordination of the azomethine nitrogen to the Cu(II) ion.^[30] The bands due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ were observed in the range more than $422\text{-}432\text{ cm}^{-1}$, These bands were absent in the spectrum of the ligand, a further indication of coordination.

Nuclear magnetic resonance spectroscopy, being a powerful tool in the elucidation of organic and inorganic compounds, is used to confirm the structure of the ligand in this study. The proton NMR spectrum for the ligand revealed that the first hydrogen on nitrogen bonding to the iminic nitrogen, H^1 appears as a singlet downfield at a chemical shift of δ 12.06 ppm. The hydrogen labeled H^2 on the iminic carbon appears as a singlet peak at δ 8.55 ppm while the

third and the fourth hydrogen atoms H³ and H⁴ shows a doublet peak at δ 8.31 ppm. Next, the hydrogen atoms on the aromatic ring labeled H⁵ and H⁶ appear as a doublet peak at δ 8.29 ppm. The hydrogen atoms labeled H⁷ and H⁸ on the toluene aromatic ring appear as doublet peaks at δ 7.99 ppm while hydrogen atoms labeled H⁹ and H¹⁰ appear as a doublet at δ 7.97 ppm and the methyl group on the toluene aromatic ring shows a singlet at δ 2.39 ppm Figure 2.

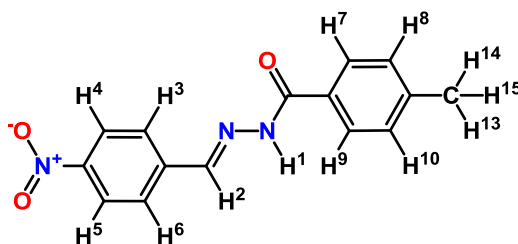


Figure 2: Proton structure of ligand.

The mass spectrum of the ligand gave a base peak at m/z 283 relative to its formula weight of 283 amu. The mass spectrum of the Mn(II) complex showed a base peak at m/z 717 amu corresponding to the formula weight of 718 amu. Likewise, the mass spectrum of the Cu(II) complex gave a base peak at m/z 753 amu same to the formula weight of 754 amu. The mass spectrum of the Zn(II) complex gave a base peak at m/z 726 amu corresponding to the formula weight of 728 amu.

The melting point, stability, structure, and decomposition characteristics of the synthesized ligand are studied on TGA and DTG thermal analytical method (Table 2). The TGA of the ligand was run in the temperature range between 25 to 900 °C via nitrogen atmosphere. The TGA curve shows two stages of thermal decomposition. In the first stage, the thermal degradation of the ligand takes place between 245-300 °C with mass loss 25.5 % (calculated mass loss of 32.12 %) with DTG peak showing exothermic process at 282 °C. The second stage of the TGA curve in the range between 430-625 °C indicates the thermal decomposition of the ligand, L¹ with mass loss 74.5 % (calculated mass loss of 67.88 %) with DTG peak at 492 °C indicative of an exothermic process.

Table 2: TGA/DTG data of the ligand.

Compound	Step	Temp. range (° C)	DTG Max(°C)	Thermal effect	Mass loss% Exp (Obs)	Assignment	Residue
L ¹ (C ₁₅ H ₁₃ N ₃ O ₃)	1 st	245-300	282	Exo	25.5(32.12)	C ₇ H ₇	
	2 nd	430-525	492	Exo	74.5(67.88)	C ₆ H ₄ NO ₃	

3.2 Antibacterial activities

The antibacterial activities of the metal complexes against different isolates of bacteria are presented in Table 3. Zn (II) complex was active against *S. pyogenes*, *K. pneumoniae*, and *E. coli* in varying concentrations range. Mn (II) complex was active against *K. pneumoniae* and *E. coli* in changing concentrations from 100-120 mg/mL.^[31]

Table 3: Antibacterial activity of the ligand and its metal complexes (mm).

Ligand/Complexes	<i>S. pyogenes</i> (mg/mL)		<i>K. pneumoniae</i> (mg/mL)		<i>S. typhi</i> (mg/mL)		<i>E. coli</i> (mg/mL)	
	100	120	100	120	100	120	100	120
Ligand			-	-	-	-	-	-
[MnL ₂ SO ₄]			12.4	14.2	-	-	14.0	16.4
[CuL ₂](NO ₃) ₂			-	-	-	-	-	-
[ZnL ₂ SO ₄]	12.4	15.6	11.4	13.6			12.0	14.5
Tetracycline 20 (mg/mL)	23.5		22.0		20.4		25.5	

“-“ : not active.

Supplementary materials

Operator: Ewera Donatus
 Experimental Date/Time: 07/11/2020 08:41:26 AM
 Instrument Configuration: MS 4900
 Inlet: My inlet
 Internal Sample id: ABUAD/CPE/MS0832/L1:E\CORINOV20NOV063E
 Ionization mode: EI+
 Scan: 11
 Base m/z: 135.99.54 FS
 Subtract (Data Correct Base (Baseline correction method))

Sample Comment: Dart
 Office2 Volt: 5 (V)
 Office1 Volt: (5V)
 Pusher Bias Volt: 0.55 (V)
 Detector volt: 2300 (V)
 RT: 88
 TIC: 9406421
 Client: Consults

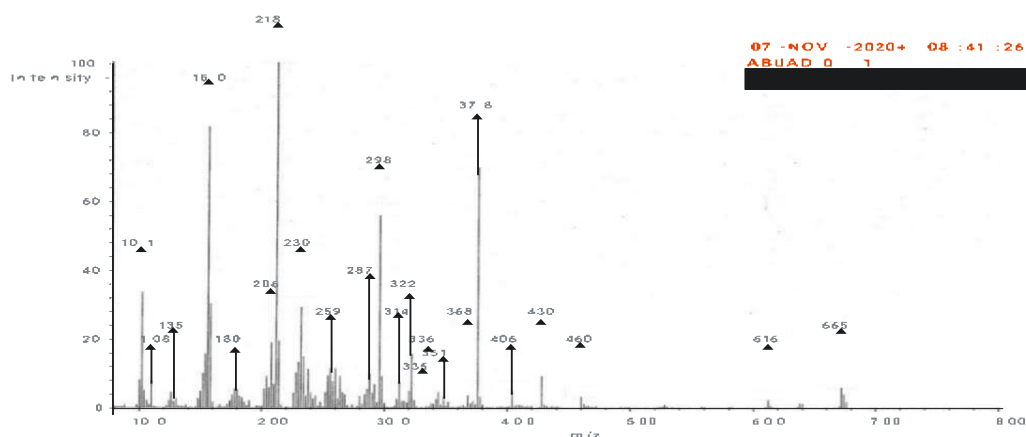
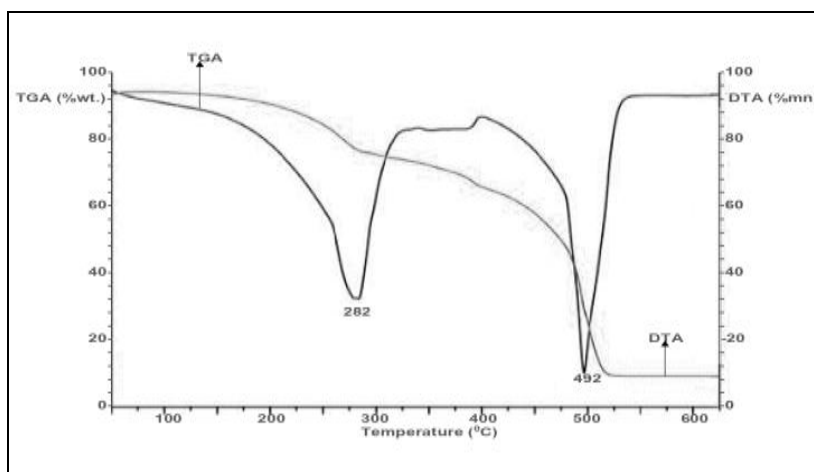
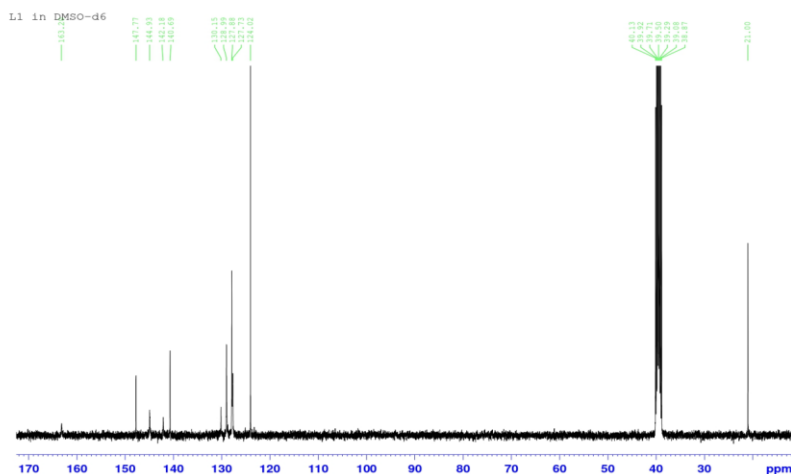
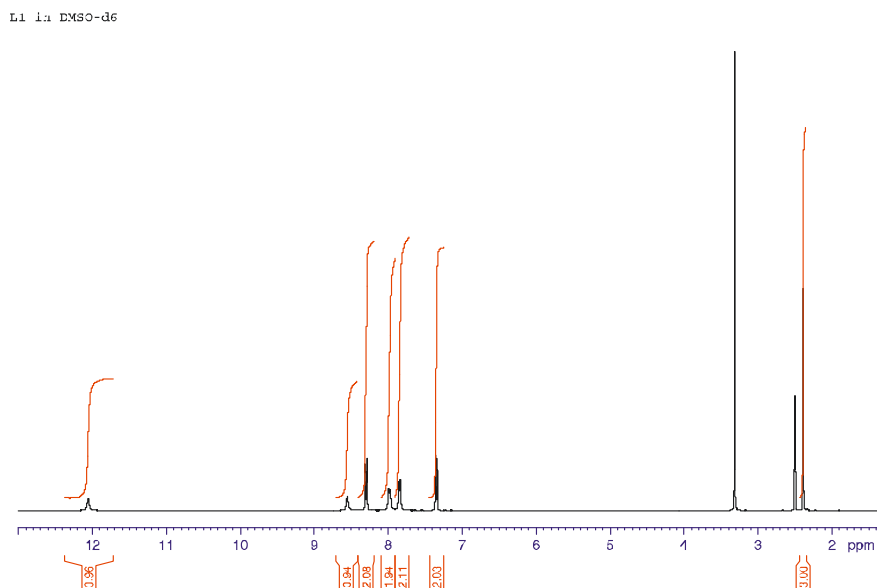


Fig. S1: GCMS Spectrum of L¹



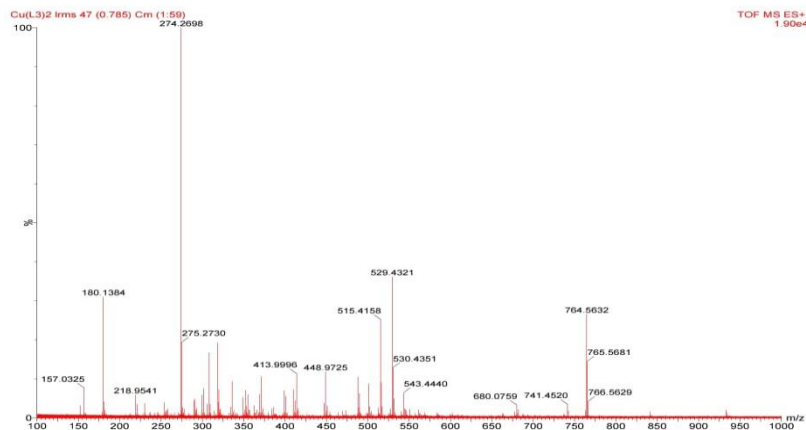


Fig. S5: Mass spectrum of Mn Complex.

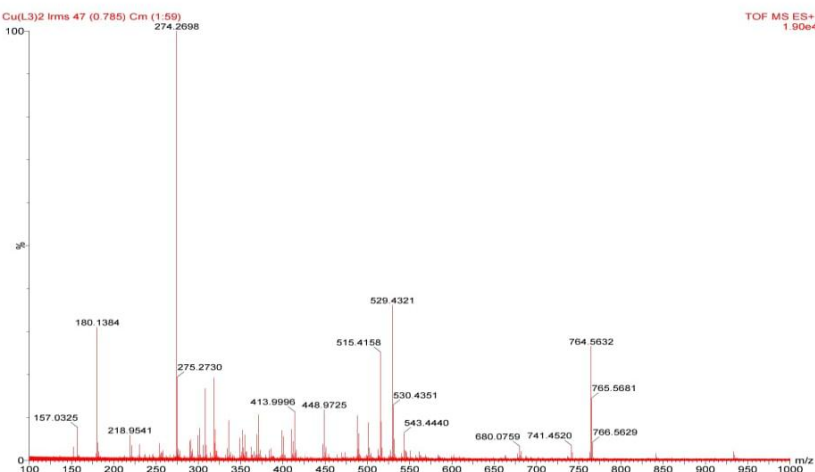


Fig. S6: Mass spectrum of Cu complex.

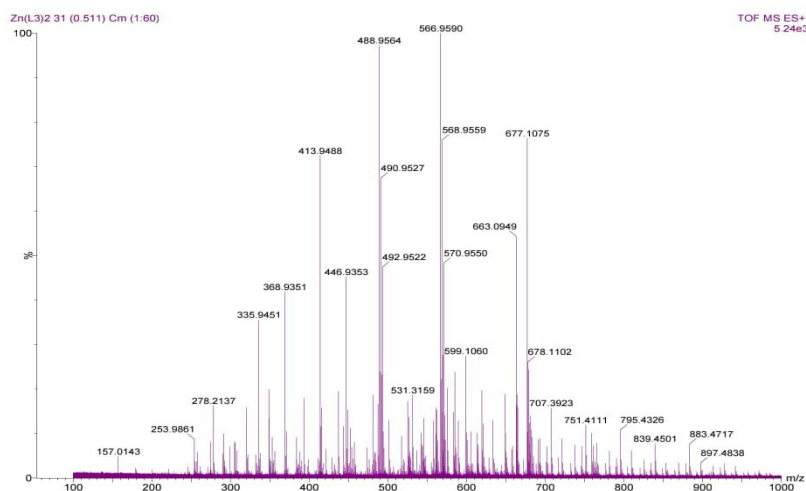


Fig. S7: Mass Spectrum of Zn(II) complex.

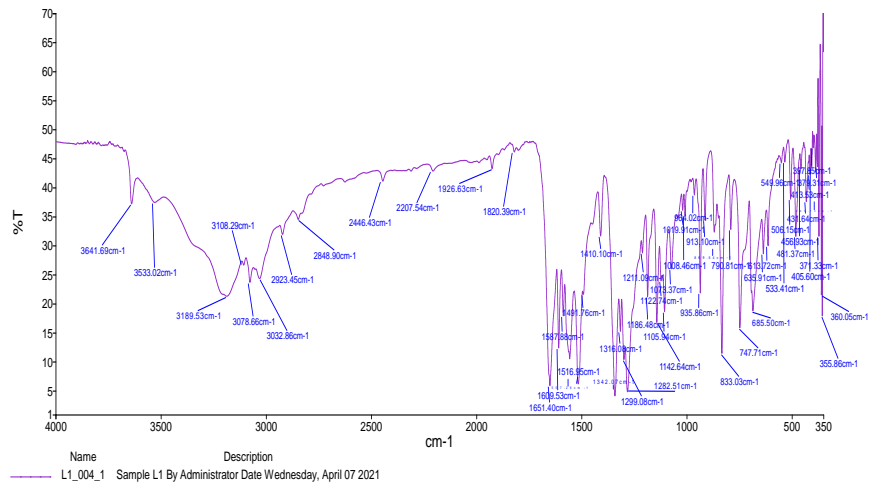


Fig. S8: FT-IR Spectrum of 4-methyl-N'-(4-nitrobenzylidene) benzohydrazide, L.

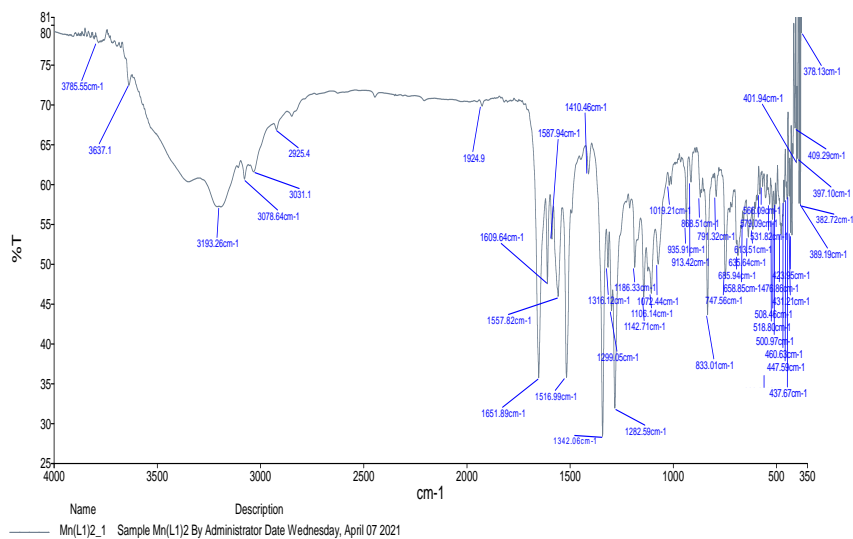
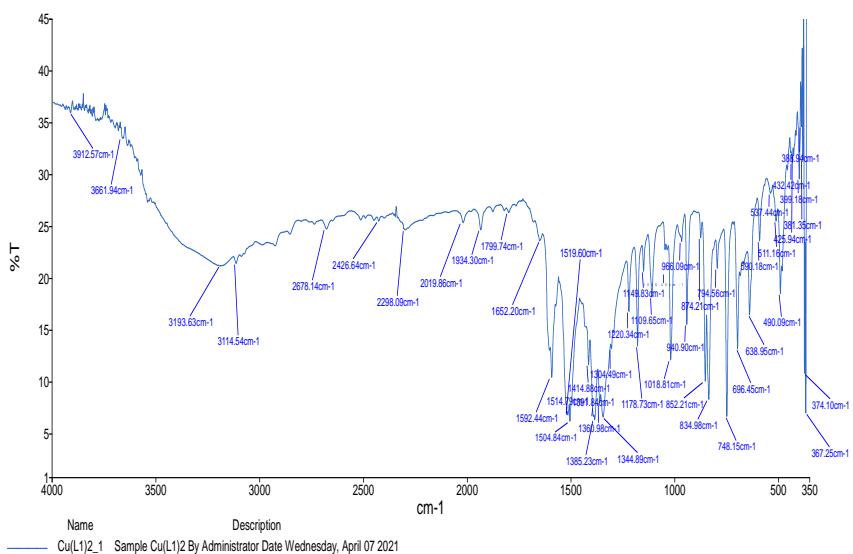
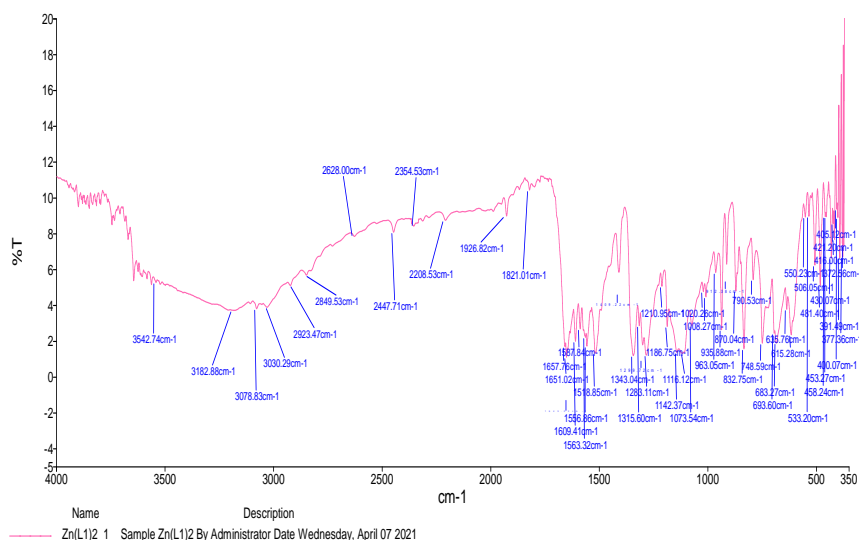


Fig. S9: FT-IR Spectrum of Mn complex.



FT-IR Spectrum of Cu complex.



4. CONCLUSION

In this paper, the preparation of the hydrazone ligand, L derived from condensation of *p*-toluic acid hydrazide and 4-nitrobenzaldehyde and its Mn(II), Cu(II), and Zn(II) complexes have been described. The hydrazone coordinates with metal ions through its N and O indicating bidentate nature of the ligand. This is supported by FT-IR data. The molar conductances show the Mn(II) and Zn(II) complexes are covalent while the Cu(II) complex is electrolytic in nature. The proposed geometries for Mn(II) and Zn(II) complexes are octahedral while the Cu(II) complex is square planar, amidst available spectroscopic data and magnetic moment data. In general, the complexes have better antibacterial activities than the ligand.

ACKNOWLEDGEMENTS

The authors thank the Federal University of Technology, Akure, Nigeria for the provision of laboratory facilities and acknowledged the support from European Journal of Chemistry.

Disclosure statement

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

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

CR
CRediT authorship contribution statement

Conceptualization: Malumi Emmanuel Olusola; Methodology: Owolabi Bodunde Jose; Software: Gurgur Emmanuel; Validation: Okoronkwo Afamefuna Elvis; Formal Analysis: Malumi Emmanuel Olusola; Investigation: Oyetayo Victor Olusegun; Resources: Malumi Emmanuel Olusola; Data Curation: Malumi Emmanuel Olusola; Writing - Original Draft: Malumi Emmanuel Olusola; Writing - Review and Editing: Malumi Emmanuel Olusola; Visualization: Malumi Emmanuel Olusola; Funding acquisition: Malumi Emmanuel Olusola; Supervision: Okoronkwo Afamefuna Elvis; Project Administration: Malumi Emmanuel Olusola.

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