

Biological Activities and Chelating Properties of New Benzoyl Derivatives of 2-Substituted Benzimidazoles

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ABSTRACT

Background and Objective: Increasing prevalence of bacterial infections as well as the resistance of some existing drugs necessitates the need for further research for compounds with more effective activities. Thus, this study synthesized benzoyl derivatives of 2-2-substituted benzimidazoles, evaluated their chelating properties and investigated the biological activities of the derivatives and their metal complexes.

Materials and Methods: The derivatives (L1, L2) and their metal (II) complexes were synthesized and characterized using UV-Vis, IR and NMR spectroscopies, metal analysis and magnetic susceptibility and conductance measurements and screened for antibacterial activity against six bacterial isolates: *Bacillus cereus* NCIB 6349, *Bacillus subtilis* NCIB 3610, *Bacillus stearothermophilus* NCIB 8222, *Serratia marcescens* NCIB 1377, *Klebsiella pneumoniae* NCIB 418, *Escherichia coli* (*E. coli*) NCIB 86.

Results: As ¹H-NMR, ¹³C-NMR and IR spectra confirmed the expected structures of the ligands. Spectral analyses of the ligands and the metal complexes showed the coordination of the ligands to the metal ions via the nitrogen and oxygen atoms in the benzoyl derivatives resulting in octahedral and tetrahedral geometries for L1 and L2, respectively. Some of the metal (II) complexes showed greater inhibitory effects against *E. coli* and *Bacillus stearothermophilus* than the reference streptomycin and ampicillin at 50 mg mL⁻¹. **Conclusion:** The study established L1 as a bidentate and L2 as a monodentate ligand. The metal complexes especially of L1 showed higher antibacterial activities against the tested micro-organisms than their corresponding ligands.

KEYWORDS

2-substituted benzimidazole, benzoyl derivatives, metal (II) complexes, chelating and biological properties, *Serratia marcescens*, *Bacillus cereus*

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INTRODUCTION

The increasing prevalence of bacterial infections across the globe, the limiting number of effective antimicrobial drugs as well as the resistance to some drugs continue to generate more interest and therefore the drive to search for more effective antimicrobial agents¹⁻³. These concerns have made the drive for the synthesis of more antimicrobial drugs that will inactivate various resistance mechanisms^{4,5}.



In modern drug discovery and medicinal chemistry, the benzimidazole nucleus has been proven to be a very significant pharmacophore for the development of new structural models for effective antimicrobial activity^{4,5}. Benzimidazole derivatives, as well as their metal complexes, have been of wide interest because of their diverse biological activities and clinical applications⁶. Substituted benzimidazoles have attracted more interest since it has been reported that the influence of the substitution at the 1, 2 and 5 positions of the benzimidazole ring is very important for the pharmacological effects⁷. Literature review further shows that 2-substituted benzimidazole derivatives are pharmacologically more important and hence the drive for the synthesis of more 2-substituted benzimidazoles⁸.

The 2-substituted benzimidazoles also have diverse applications in coordination chemistry, photo-physics, photo-chemistry and bioinorganic chemistry with the formation of stable complexes with various transition metals⁹.

Furthermore, the coordination chemistry of benzimidazoles and derivatives continues to attract enormous attention because of the fact that metal complexes have shown larger antimicrobial activities than the free ligands¹⁰ and also because of their interesting spectral, magnetic and structural properties¹⁰⁻¹⁶. The metal complexes of 2-substituted benzimidazole derivatives have also been found to exhibit inhibitory activities against a range of human tumor cells and as anticancer agents^{11,12}.

The immense therapeutic values of benzimidazole and its derivatives motivated this research work to design and synthesize new benzoyl derivatives of 2-substituted benzimidazole derivatives and their metal complexes and evaluate their antibacterial activities. Thus, the synthesis, characterization, chelating properties of new benzoyl derivatives of 2-substituted benzimidazoles namely N-(1H-benzo[d]imidazol-2-yl) benzamide (L1) and (2-methyl-1-H-benzo (d) imidazol-1-yl) (phenyl) methanone (L2), their metal (II) complexes and the antibacterial activities of the benzoyl derivatives and their metal complexes were determined.

MATERIALS AND METHODS

Study area: The research work commenced in August, 2018 at the Obafemi Awolowo University, Ile-Ife, Nigeria.

Reagents and Instrumentation: The reaction syntheses and purity were monitored by thin-layer chromatography (TLC), (Merck KGaA (Germany) plate). The ¹H and ¹³C-NMR spectra were recorded with Agilent -VNMR-400, (JOEL, United States), using TMS (Tetramethylsilane) as the internal standard and DMSO (Dimethyl Sulfoxide) as solvent. Infra-red spectra of the compounds were recorded on a Shimadzu FT-IR 8000 spectrophotometer (Shimadzu Cooperation Columbia, United States). The melting points were determined with a Gallenkamp melting point apparatus (SanYo, Cambridge United Kingdom). Ultraviolet/Visible absorption spectra were recorded using a Shimadzu UV-1700 spectrophotometer (Shimadzu Cooperation) Kyoto Japan) at room temperature. Conductance measurements were recorded using a hanna TDS conductivity meter (Pure Aqua, Inc. (Woonsocket, Rhode Island, United States of America) while the magnetic susceptibility measurements of the metal complexes were made at room temperature using Gouy Susceptibility Balance (Sherwood Scientific Ltd. (Cambridge United Kingdom).

Synthesis of N-(1H-benzo[d]imidazol-2-yl) benzamide (L1): The 2-aminobenzimidazole (0.5 g) was dissolved in 1 g of benzoyl chloride and 15 mL of ethanol was added. The solution was irradiated using microwave (Japan's Sharp Cooperation, Bergamo, Italy) irradiation for 2 min. The precipitate formed, filtered, washed with ice-cold water, recrystallized with absolute ethanol and dried in anhydrous calcium chloride, yielding 62% and melting point (m.p.) from 265-267°C as shown in Fig. 1.

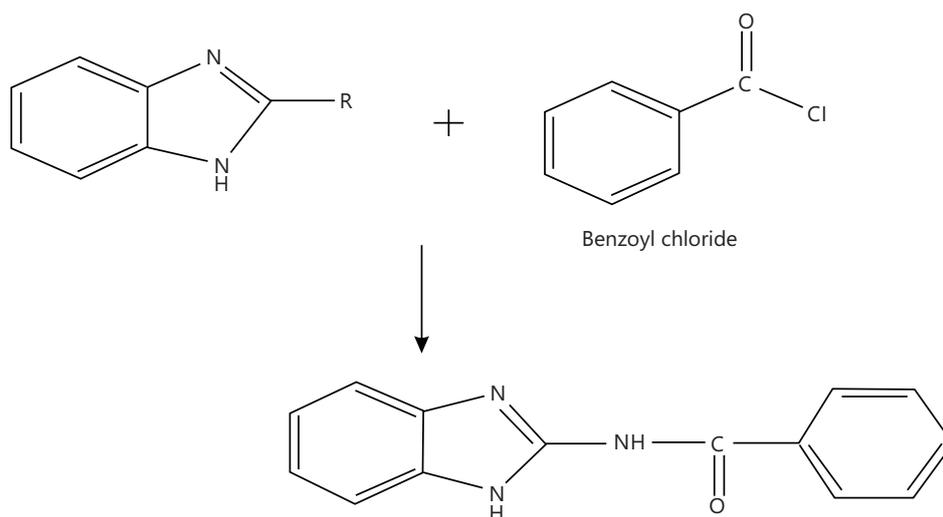


Fig. 1: Synthesis of L1 (R = NH₂)

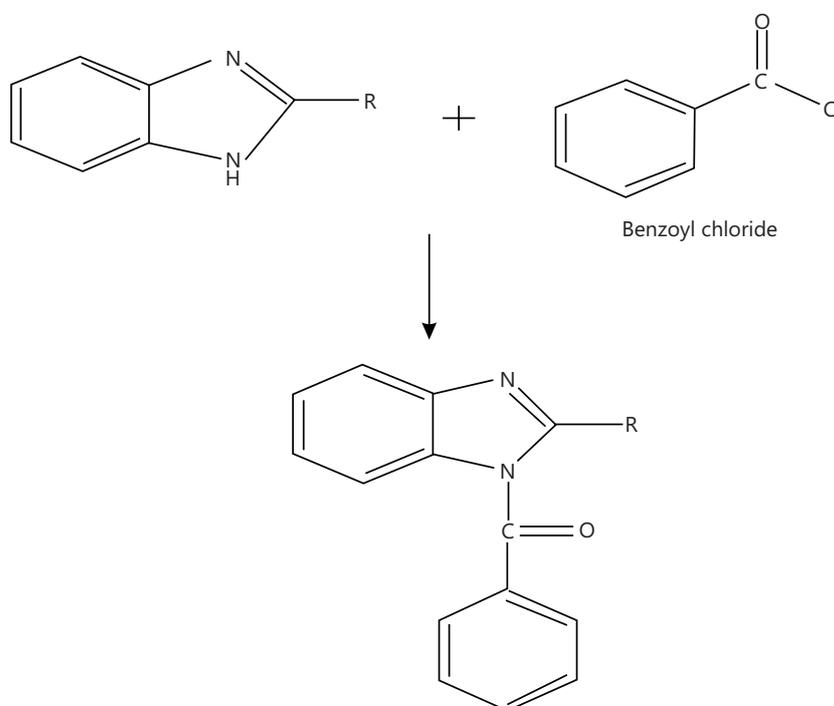


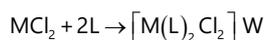
Fig. 2: Synthesis of L2 (R = CH₃)

Synthesis of 2-methyl-1-H-benzo (d) imidazol-1-yl) (phenyl) methanone (L2): The 2-methylbenzimidazole (0.5 g) was dissolved in 10 mL of 10% sodium hydrogen carbonate solution and 1 g of benzoyl chloride added to the solution. The reaction mixture was shaken vigorously in a stoppered test tube. The mixture was then acidified with (37%) dilute hydrochloric acid, filtered, washed with ice-cold water, recrystallized with absolute ethanol and dried in anhydrous calcium chloride, yielding 53%, m.p. 300-302°C as shown in Fig. 2.

Attempts were also made to use the 2-chloromethyl benzimidazole as the starting material but the intermediate product was the 2-methylbenzimidazole.

Synthesis of the metal (II) complexes of L1 and L2: A mixture of L (2 mmol) and metal (II) salt, (1 mmol) in absolute ethanol (20 mL) was refluxed for 3 hrs. The precipitate filtered, washed with ice-cold water,

recrystallized with absolute ethanol and dried over anhydrous calcium chloride. The proposed equation for the metal complexes can be written as¹²:



Where:

M = Cu, Ni, Co, Mn and Zn

L = L1, L2

W = H₂O

Antibacterial study: The ligands and their metal complexes were screened for antibacterial activities. The test organisms included six strains of bacteria typed cultures of the National Collection of Industrial Bacteria (NCIB) namely, Gram positive: *Bacillus cereus* NCIB 6349, *Bacillus subtilis* NCIB 3610, *Bacillus stearothermophilus* NCIB 8222. Gram-negative: *Serratia marcescens* NCIB 1377, *Klebsiella pneumoniae* NCIB 418, *Escherichia coli*, NCIB 86. The sensitivity testing of the compounds was determined using the agar well diffusion method¹⁷. Zones of inhibition and the effects of the compounds on bacterial strains were compared with those of standard antibiotics, ampicillin and streptomycin.

RESULTS

Physico-chemical characteristics: The ligands are white in colour and all the complexes possess a variety of colours ranging from white to deep green. The purity of the compounds was ascertained by melting point and TLC. The percentage yield of the ligands and metal complexes ranged from 51.47-67.87%. The melting points of the ligands are between the range of 265-267 °C for L1 and 300-302 °C for L2 while most of the complexes have melting points beyond 300 °C except for some complexes of copper and zinc which decomposed at temperatures between 228 and 286 °C. The colours, percentage yields and melting points of the ligands and the complexes as well as the Percentage Metal Analyses of the complexes of L1 and L2 are presented in Table 1.

Conductivity measurements: The molar conductivities for the complexes measured in methanol and DMF are shown in Table 1. They are in the range (6.94-21.10 Ω⁻¹ cm² mol⁻¹) for L1 and 27.40-71.40 Ω⁻¹ cm² mol⁻¹ for L2.

¹H-NMR and ¹³C-NMR: The ¹H-NMR spectrum of ligand L1 (Fig. 3) gave peaks at δ_{ppm} 8.37-8.03 (d, 2 H) and a multiple at δ_{ppm} 7.73-7.38 (7 H) while the ¹³C-NMR spectrum (Fig. 4) shows signals at 112-145 and 166.47 ppm. The signal at 40.0 ppm is due to the solvent.

Table 1: Physico-chemical and analytical data for the ligands and their complexes

Compounds	Colour	Yield (%)	Melting points (°C)	Molar conductance (Ω ⁻¹ cm ² mol ⁻¹)	Metal found (%) (calculated)
L1	White	62.00	265-267	-	-
[Cu (L1) ₂ Cl ₂].2H ₂ O	Deep green	58.00	284-286	19.09	9.85 (9.57)
[Ni (L1) ₂ Cl ₂]	Dirty green	57.27	>350	14.14	9.71 (9.76)
[Co (L1) ₂ Cl ₂]	Pink	55.09	>320	11.42	9.75 (9.37)
[Mn (L1) ₂ Cl ₂]	Yellow	67.87	>326	6.94	9.15 (11.70)
[Zn (L1) ₂ Cl ₂]	White	52.07	228-232	21.10	10.70 (11.14)
L2	Dirty white	53.30	300-302	-	-
[Cu (L2) ₂ Cl ₂].2H ₂ O	Light green	62.05	296-298	71.40	9.57 (10.00)
[Ni (L2) ₂ Cl ₂].2H ₂ O	Green	56.52	305-307	47.60	9.46 (9.64)
[Mn (L2) ₂ Cl ₂]	Yellow	51.47	276-278	40.40	9.18 (9.54)
[Zn (L2) ₂ Cl ₂]	White	57.78	293-295	27.40	10.74 (11.71)

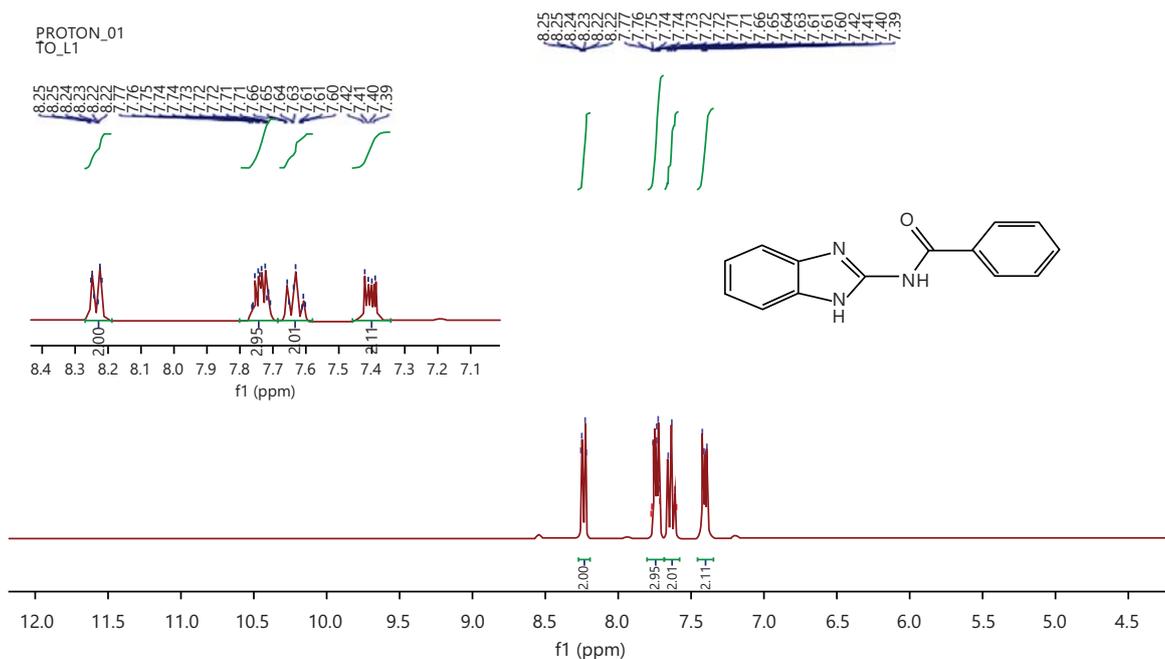


Fig. 3: ¹H NMR spectrum of L1

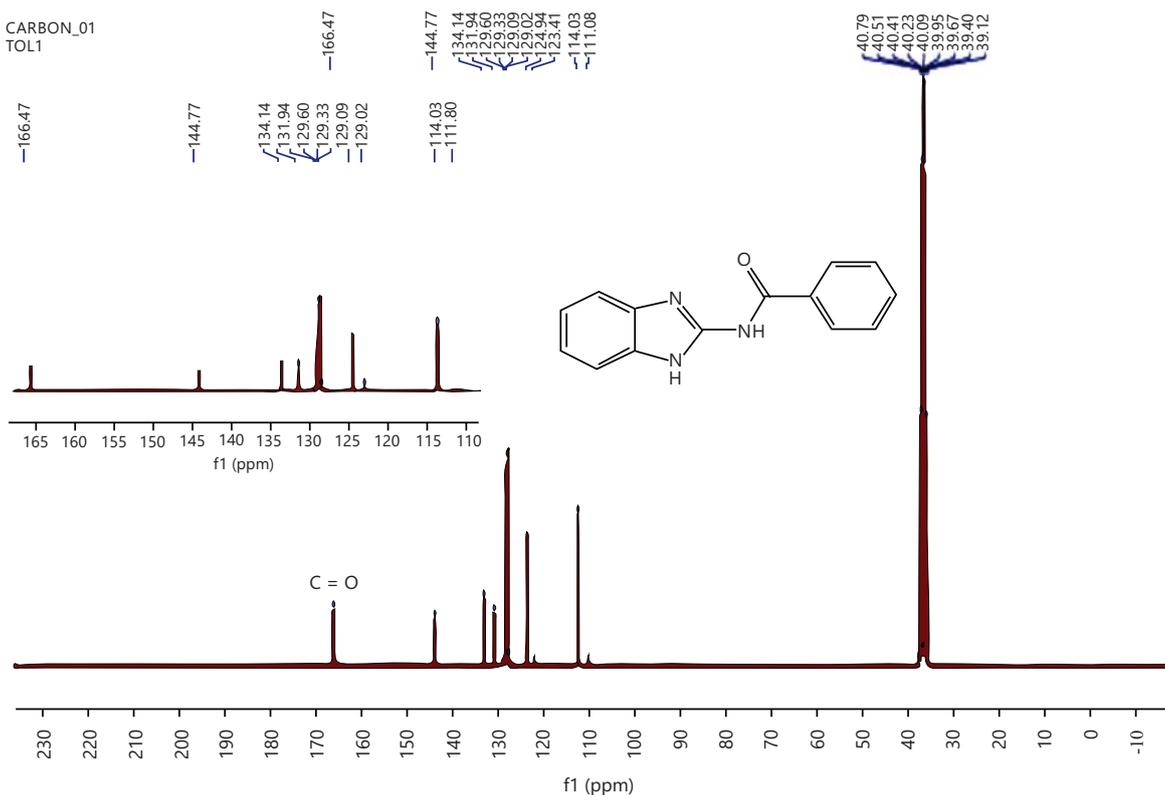


Fig. 4: ¹³C NMR spectrum of L1

Similarly, the ¹H NMR spectrum of ligand L2 (Fig. 5) gave peaks at 7.62-7.59 and 2.49 ppm while the ¹³C-NMR spectrum (Fig. 6) gave signals at 126.04-134.63, 165.92 and 39.96 ppm. The signal at 40.0 ppm is that of the solvent.

Infrared spectra: The infrared spectra of L1 and its complexes (Fig. 7-12) show absorption bands at 3175-3475 cm⁻¹ for N-H, bands at 1626-1701, 1556-1626 and 1313-1340 cm⁻¹ for C = O, C = N and C-N

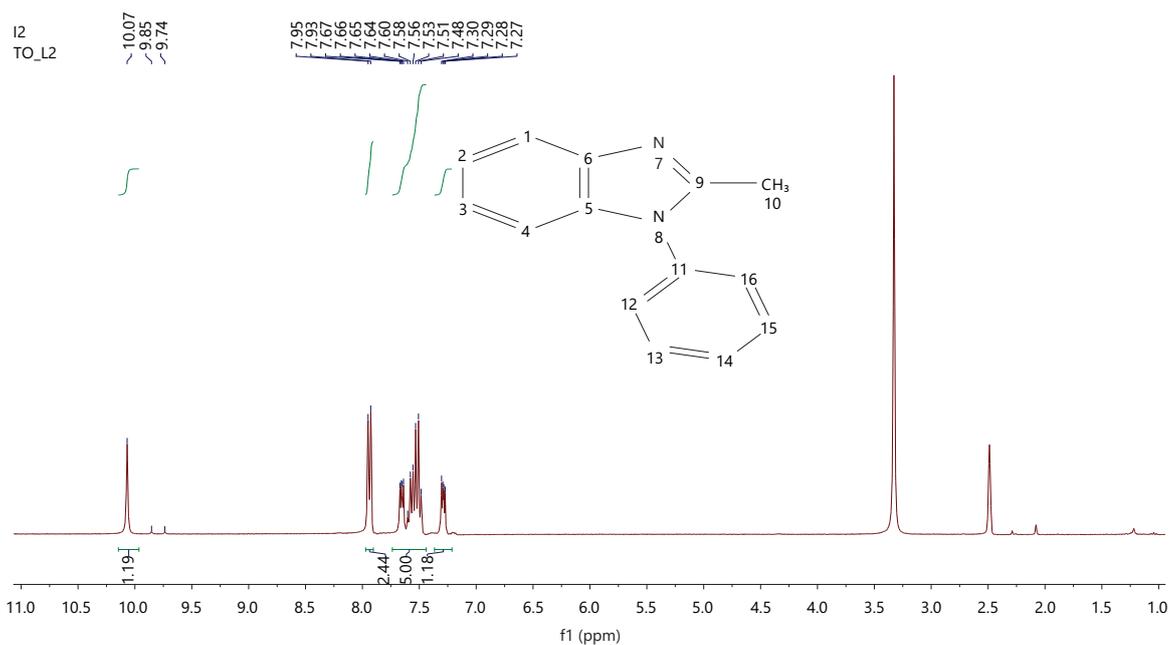


Fig. 5: ¹H NMR spectrum of L2

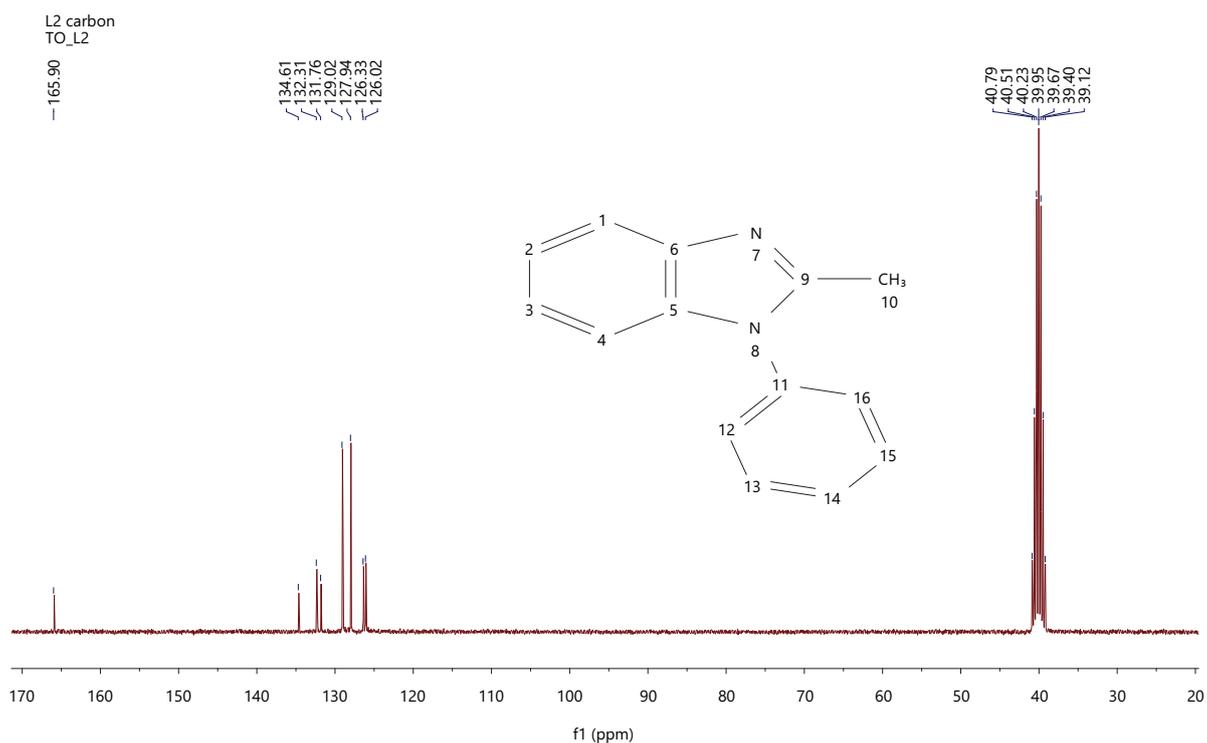


Fig. 6: ¹³C NMR spectrum of L2

Table 2: Important infrared spectral bands (cm⁻¹) of the benzoyl derivative, L1 and metal (II) complexes

Frequency of compounds	ν (NH)	ν (C = O)	ν (C = N)	ν (C-N)	ν (C = C)	ν (M-O)	ν (M-N)
L1	3475	1701	1626	1340	1600	-	-
[Cu (L1) ₂ Cl ₂].2H ₂ O	3460	1678	1633	1313	1589	669	526
[Ni (L1) ₂ Cl ₂].2H ₂ O	3417	1649	1579	1317	1556	632	434
[Co (L1) ₂ Cl ₂].2H ₂ O	3175	1655	1556	1315	1578	617	472
[Mn (L1) ₂ Cl ₂].2H ₂ O	3292	1674	1565	1341	1564	631	443
[Zn (L1) ₂ Cl ₂].2H ₂ O	3474	1626	1601	1340	1466	678	444

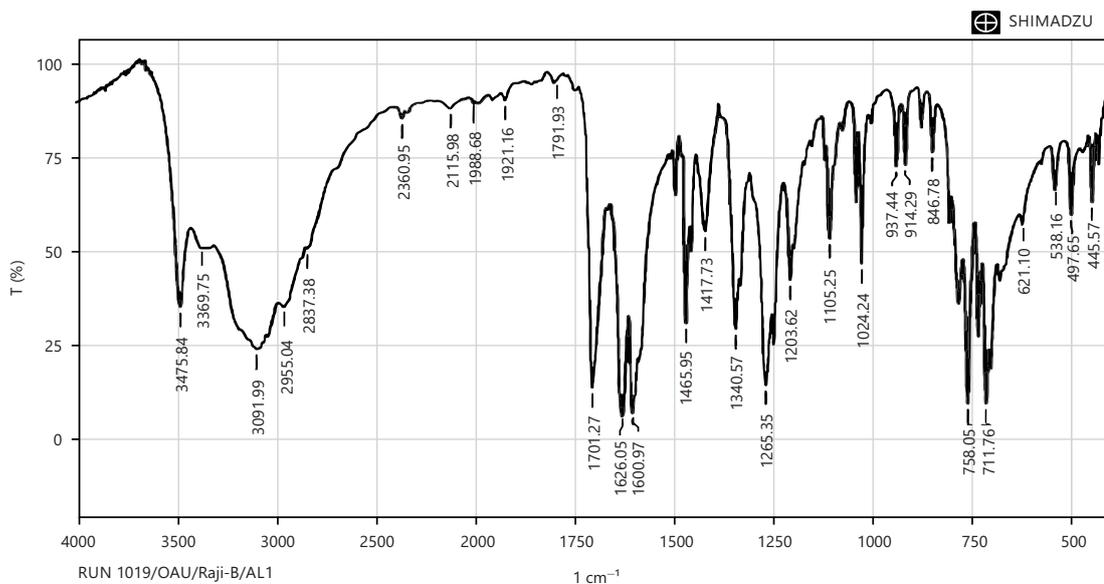


Fig. 7: IR spectrum of L1

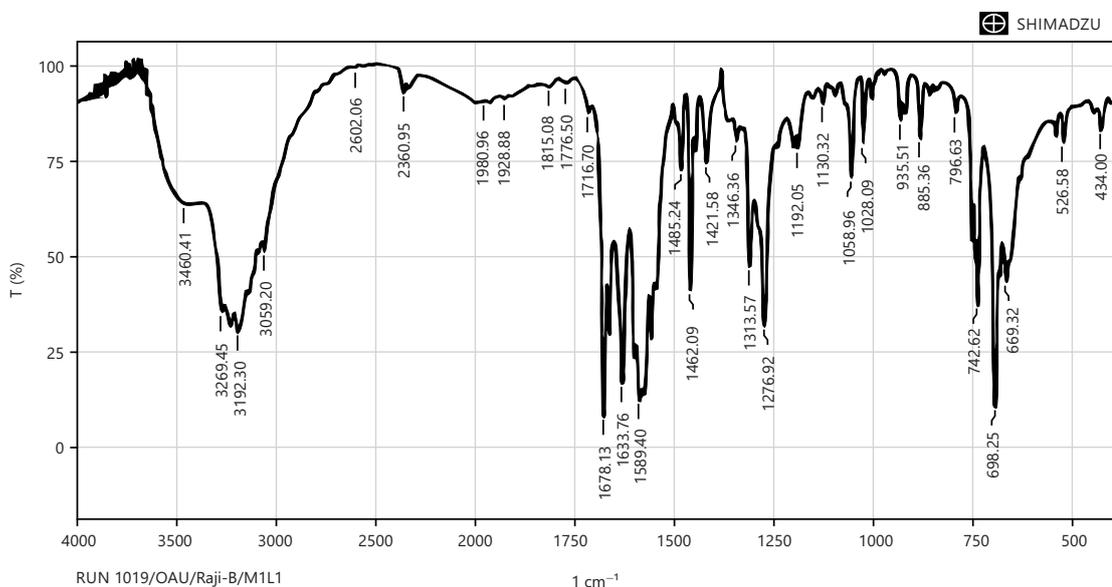


Fig. 8: IR spectrum of $(\text{Cu} (\text{L1})_2\text{Cl}_2) \cdot 2\text{H}_2\text{O}$

vibrational frequencies, respectively (Table 2). There were shifts in the stretching frequencies of C = O, C = N and C-N in the imidazole units of the benzimidazole rings in the spectra for the metal complexes, (Table 2 and Fig. 8-12). There were also downward shifts in the N-H stretching vibrational frequencies from 3475 cm^{-1} of the ligand, L1 to 3460, 3417, 3175, 3292 cm^{-1} for Cu (II), Ni (II), Co (II) and Mn (II) complexes, respectively (Table 2). In addition, there are appearances of new bands at 434-526 and 617-678 cm^{-1} for the L1 complexes.

The infrared spectra of L2 and its complexes, (Fig. 13-17) show stretching vibrations bands at $3056\text{-}3132 \text{ cm}^{-1}$ for C-H, bands at $1651\text{-}1658 \text{ cm}^{-1}$ for C = O. There were also bands at $1525\text{-}1530$ and $1280\text{-}1393 \text{ cm}^{-1}$ (Table 3). There is appearance of new bands at $472\text{-}521 \text{ cm}^{-1}$ for the L2 complexes.

Electronic spectra and magnetic moments: Electronic spectra of the ligands and the complexes were recorded in DMSO. There were bands at 231 and 299 nm for L1 and 228 nm for L2. (Table 4 and Fig. 18, 19).

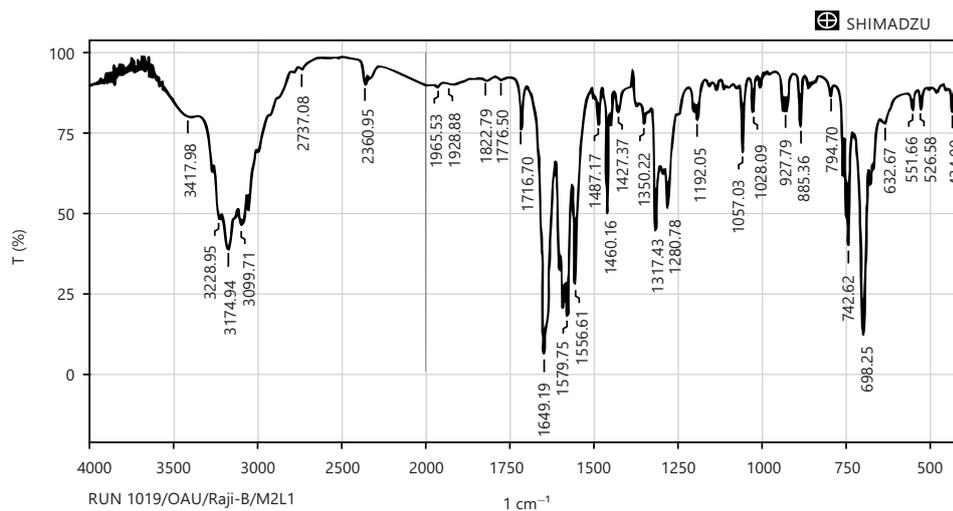


Fig. 9: IR spectrum of $[\text{Ni}(\text{L}1)_2\text{Cl}_2]$

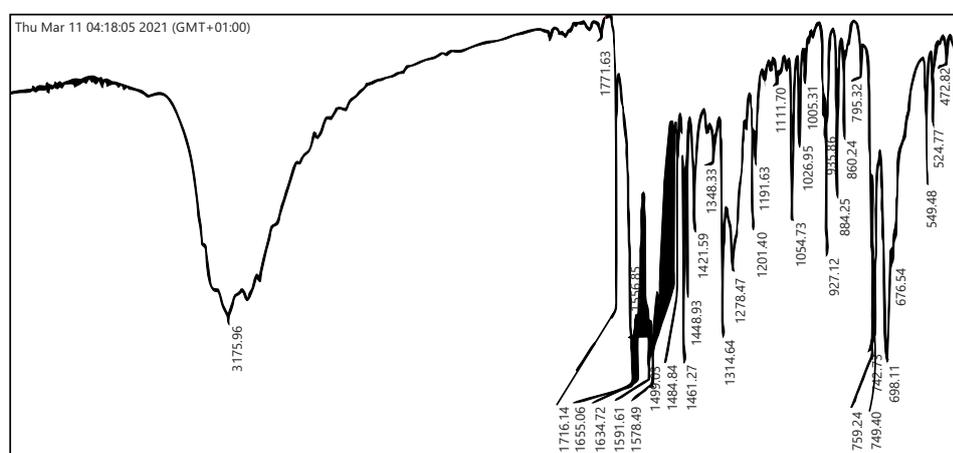


Fig. 10: IR spectrum of $[\text{Co}(\text{L}1)_2\text{Cl}_2]$

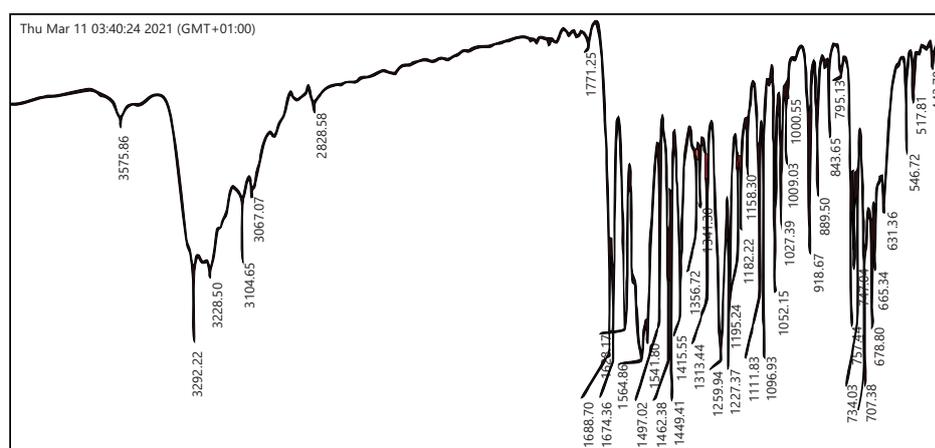


Fig. 11: IR spectrum of $[\text{Mn}(\text{L}1)_2\text{Cl}_2]$

The electronic absorption spectra of Cu (II) complexes of L1 and L2 displayed one broad band with a slight shoulder at 768 and 783 nm, respectively (Fig. 20 and 21). The copper (II) complexes of L1 and L2 also gave magnetic moment values of 2.05 and 1.16 BM, respectively (Table 4).

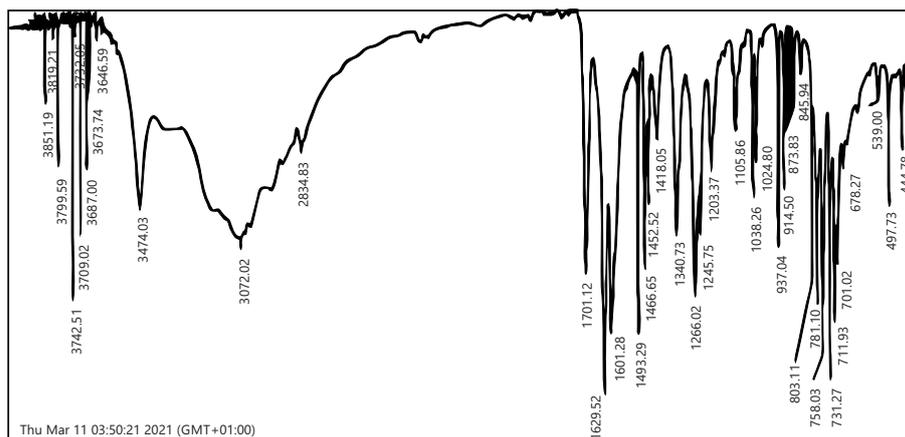


Fig. 12: IR spectrum of [Zn(L1)₂Cl₂]

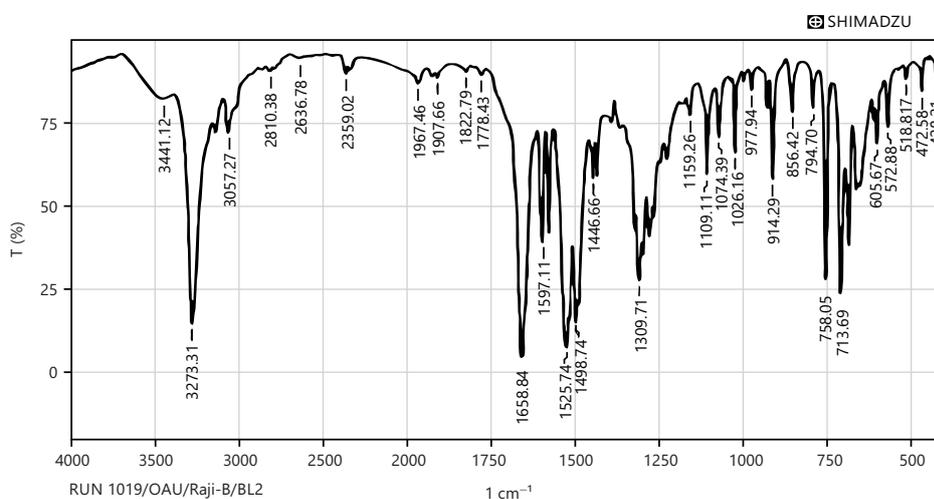


Fig. 13: IR spectrum of L2

Table 3: Important infrared spectral bands (cm⁻¹) of the benzoyl derivative, L2 and metal (II) complexes

Frequency of compounds	ν (C-H)	ν (C = O)	ν (C-Hsp ²)	ν (C = C)	ν (C = N)	ν (C-N)	ν (M-O)
L2	3057	1658	3273	1597	1526	1310	-
CuL2	3132	1654	3271	1577	1530	1393	521
NiL2	3057	1655	3273	1527	1528	1310	473
MnL2	3056	1656	3272	1498	1525	1323	519
ZnL2	3056	1651	3271	1578	1529	1280	472

L2: 2-methyl-1-H-benzo (d) imidazol-1-yl) (phenyl) methanone

Table 4: Electronic spectra and magnetic moments of ligands and their Cu (II), Ni (II), Co (II), Mn (II) and Zn (II) complexes

Compounds	Intra-ligand transition (nm)	Ligand field transition (nm)	Magnetic moment μ eff (BM)	Proposed geometry
L1	231,299	-	-	-
[Cu(L1) ₂ Cl ₂].2H ₂ O	233,321	768	2.05	Octahedral
[Ni(L1) ₂ Cl ₂].2H ₂ O	232,303	453,504,645	2.00	Octahedral
[Co(L1) ₂ Cl ₂].2H ₂ O	234,306	497,646,764	4.86	Octahedral
[Mn(L1) ₂ Cl ₂].2H ₂ O	233,300	493,783	1.35	Octahedral
[Zn(L1) ₂ Cl ₂].2H ₂ O	301	-	Diamagnetic (0.35)	Octahedral
L2	228	-	-	-
[Cu(L2) ₂ Cl ₂].2H ₂ O	292	783	1.16	Tetrahedral
[Ni(L2) ₂ Cl ₂].2H ₂ O	267	613,779	2.12	Tetrahedral
[Mn(L2) ₂ Cl ₂].2H ₂ O	270	596,773	2.0	Tetrahedral
[Zn(L2) ₂ Cl ₂].2H ₂ O	277	-	Diamagnetic (0.66)	Tetrahedral

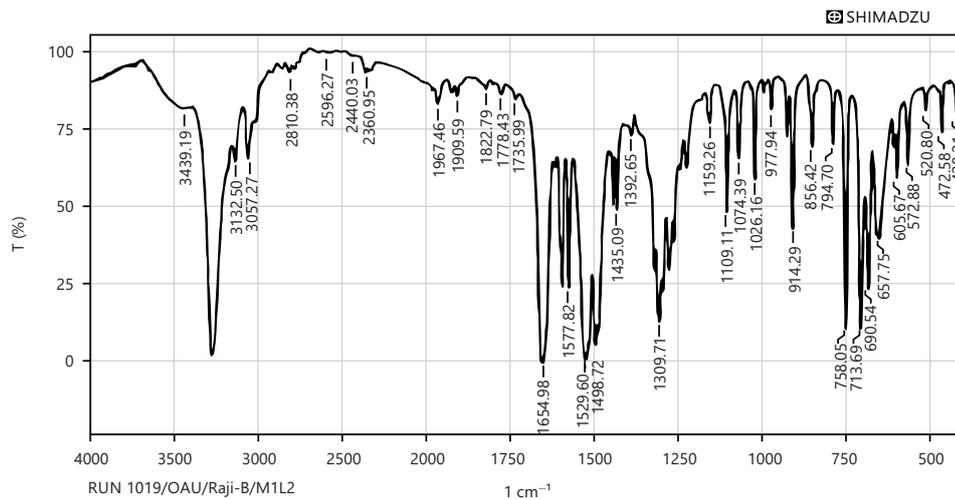


Fig. 14: IR spectrum of [Cu(L2)₂Cl₂].H₂O

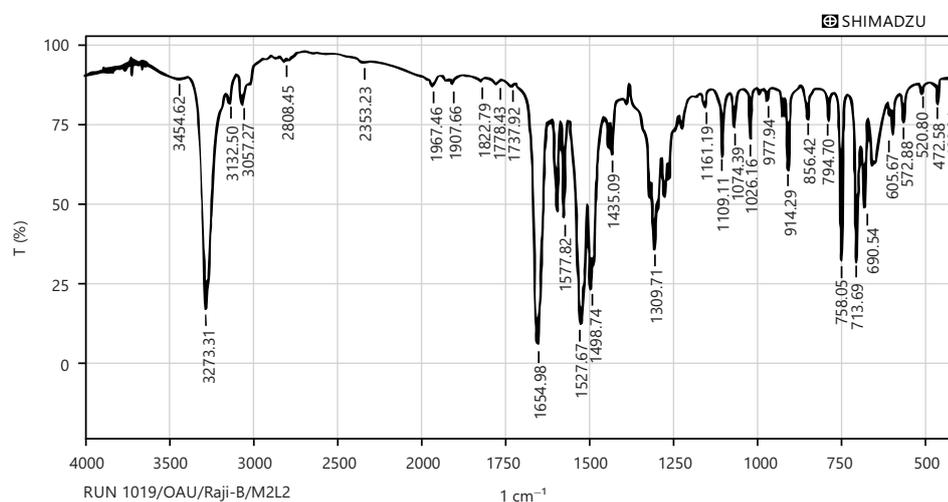


Fig. 15: IR spectrum of [Ni(L2)₂Cl₂].H₂O

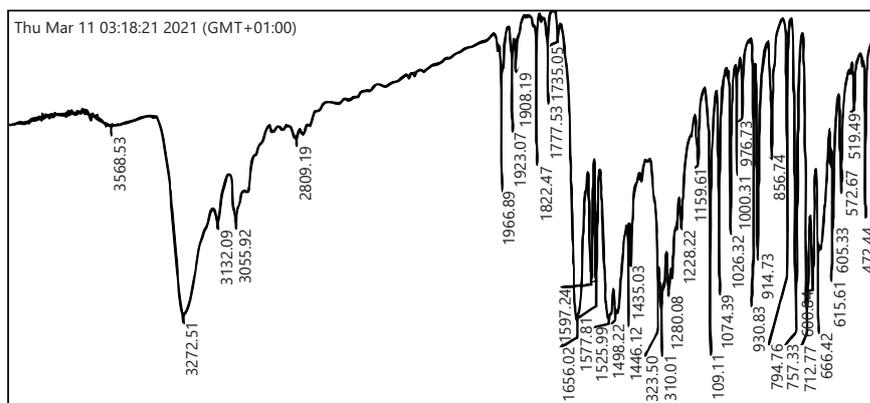


Fig. 16: IR spectrum of [Mn(L2)₂Cl₂]

The visible spectrum for Ni (II) complex of L1 displayed three bands at 453, 504 and 645 nm, (Fig. 22 and Table 4). The magnetic moment values for the Ni (II) complexes were found to be 2.00 and 2.12 BM for L1 and L2, respectively.

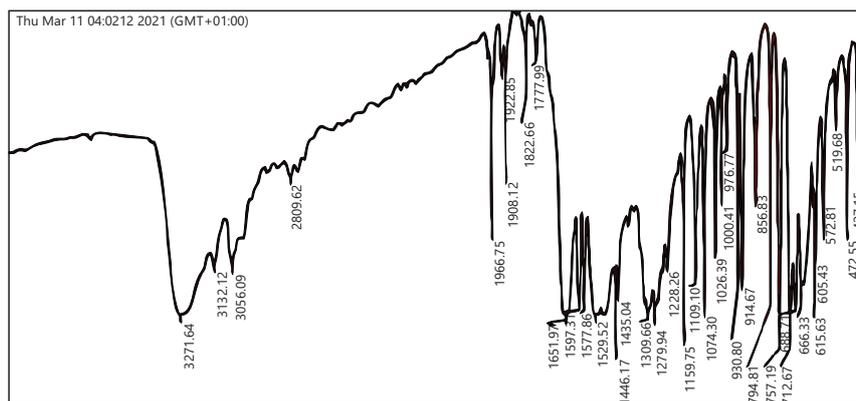


Fig. 17: IR spectrum of [Zn(L2)2Cl2]

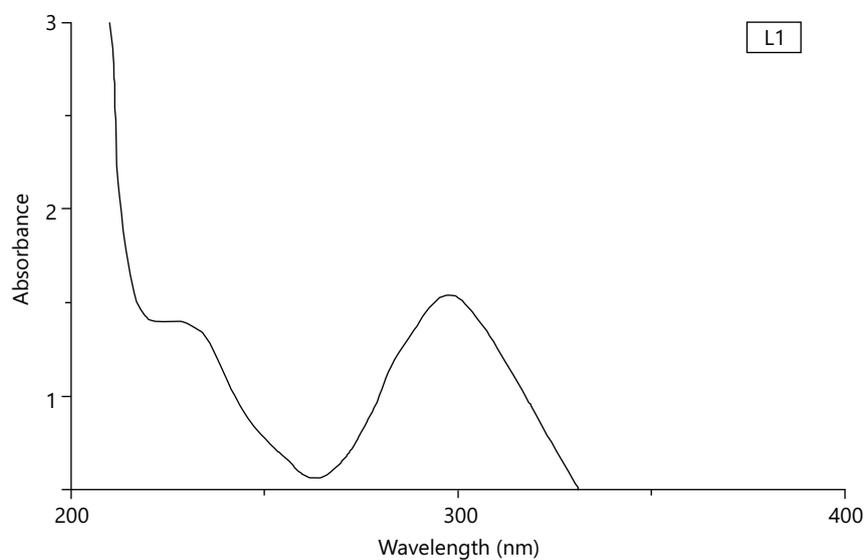


Fig. 18: UV spectrum of L1

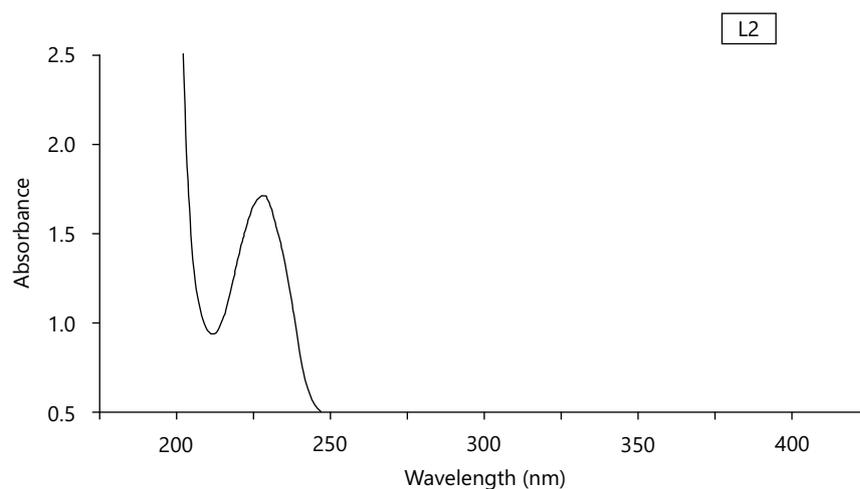


Fig. 19: UV spectrum of L2

The visible spectrum for Ni (II) complex of L1 displayed three bands at 453, 504 and 645 nm, (Fig. 22 and Table 4). The magnetic moment values for the Ni (II) complexes were found to be 2.00 and 2.12 BM for L1 and L2, respectively.

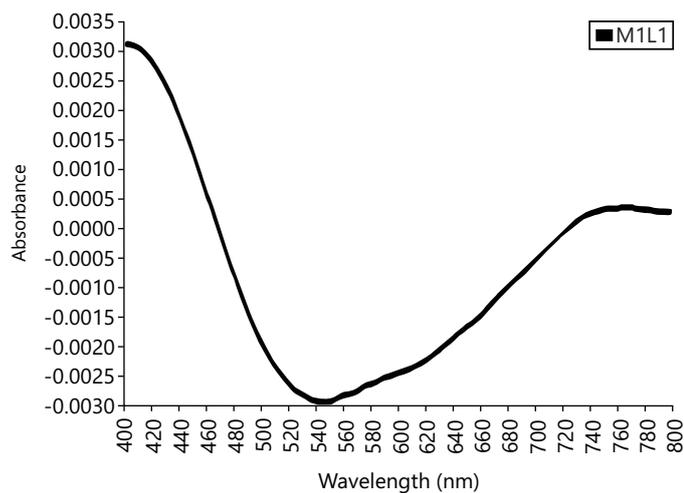


Fig. 20: Visible spectrum of [Cu (L1)₂Cl₂]

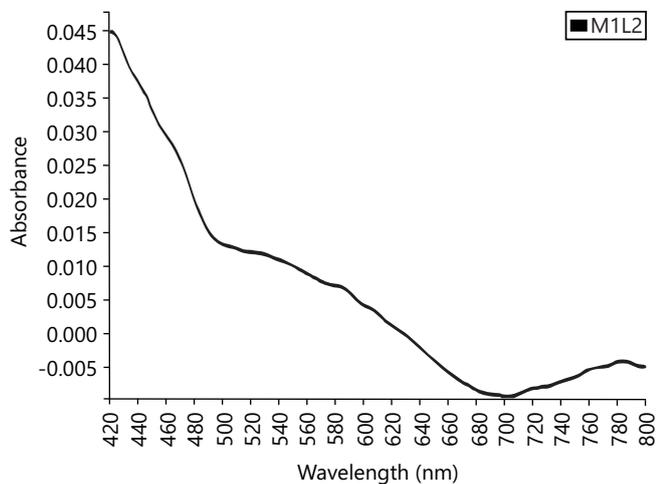


Fig. 21: Visible spectrum of [Cu (L2)₂Cl₂]

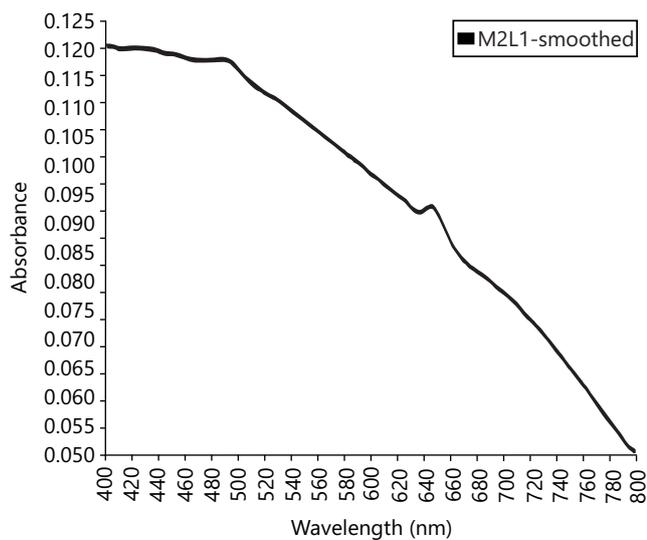


Fig. 22: Visible spectrum of [Ni (L1)₂Cl₂]

The complex of Co (II) L1, (Fig. 23) shows 3 electronic transitions at 497, 646 and 764 nm in the visible region while the Mn (II) Complex of L1 and Mn (II) complex of L2, (Fig. 24 and 25), respectively show weak

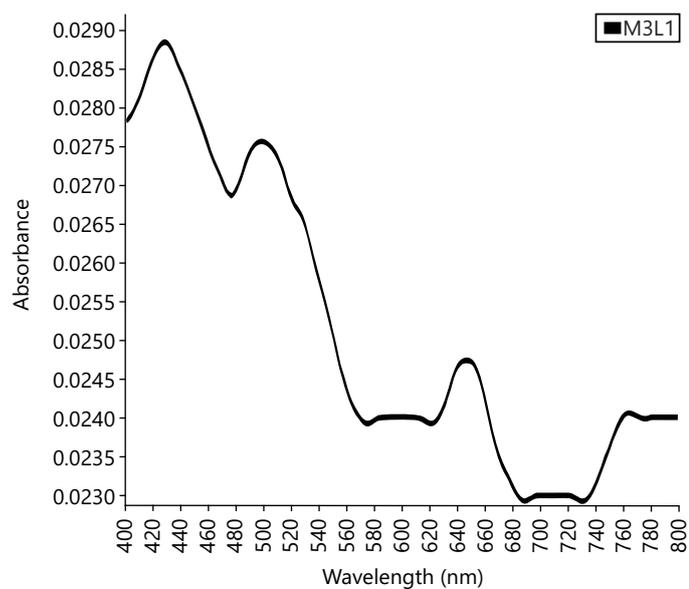


Fig. 23: Visible spectrum of [Co(L1)₂Cl₂]

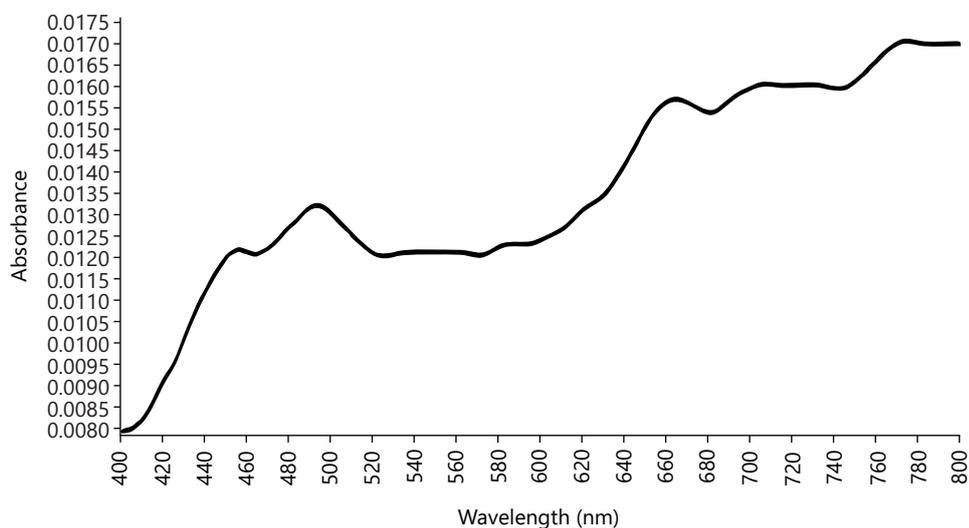


Fig. 24: Visible spectrum of [Mn(L1)₂Cl₂]

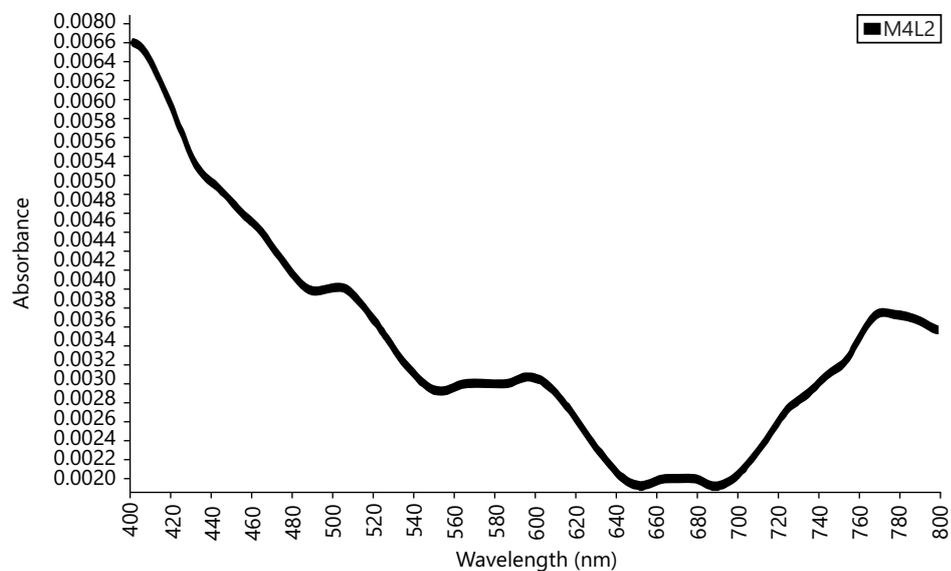


Fig. 25: Visible spectrum of [Mn(L2)₂Cl₂]

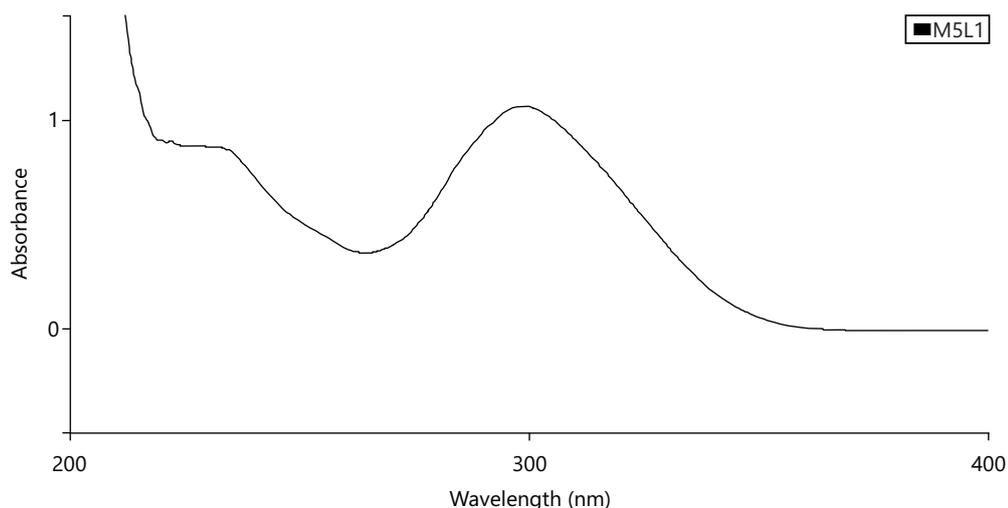


Fig. 26: Ultraviolet spectrum of $[Zn(L1)_2Cl_2]$

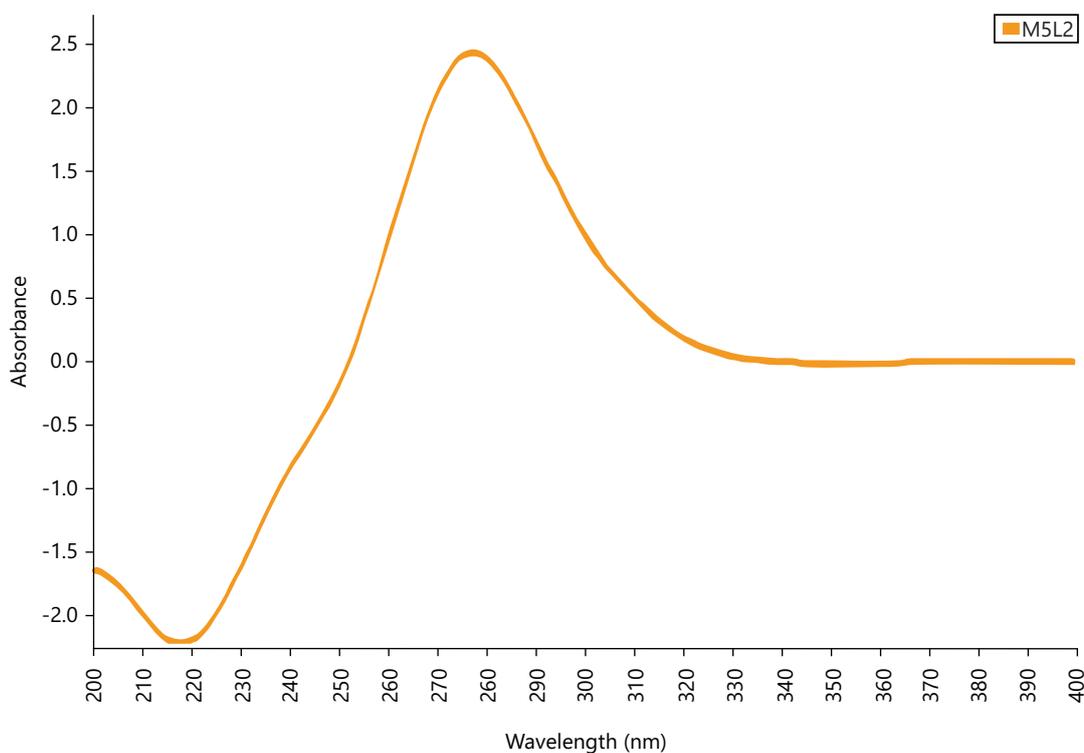


Fig. 27: Ultraviolet spectrum of $[Zn(L2)_2Cl_2]$

bands at 493, 783 nm for L1 and 596 and 773 nm for L2, respectively. The magnetic moment values for the cobalt and Manganese complexes are shown in Table 4.

For the zinc complexes, bands at 237-299 nm were obtained in the ultraviolet region, (Fig. 26 and 27).

Proposed structures of the metal (II) complexes: The structures of the metal (II) complexes based on data from elemental analysis, FT-IR spectroscopic study, magnetic measurements, UV-Vis spectroscopy and molar conductivities are octahedral geometry for metal (II) L1 complexes and tetrahedral geometry for metal (II) L2 complexes are proposed in Fig. 28 and 29, respectively.

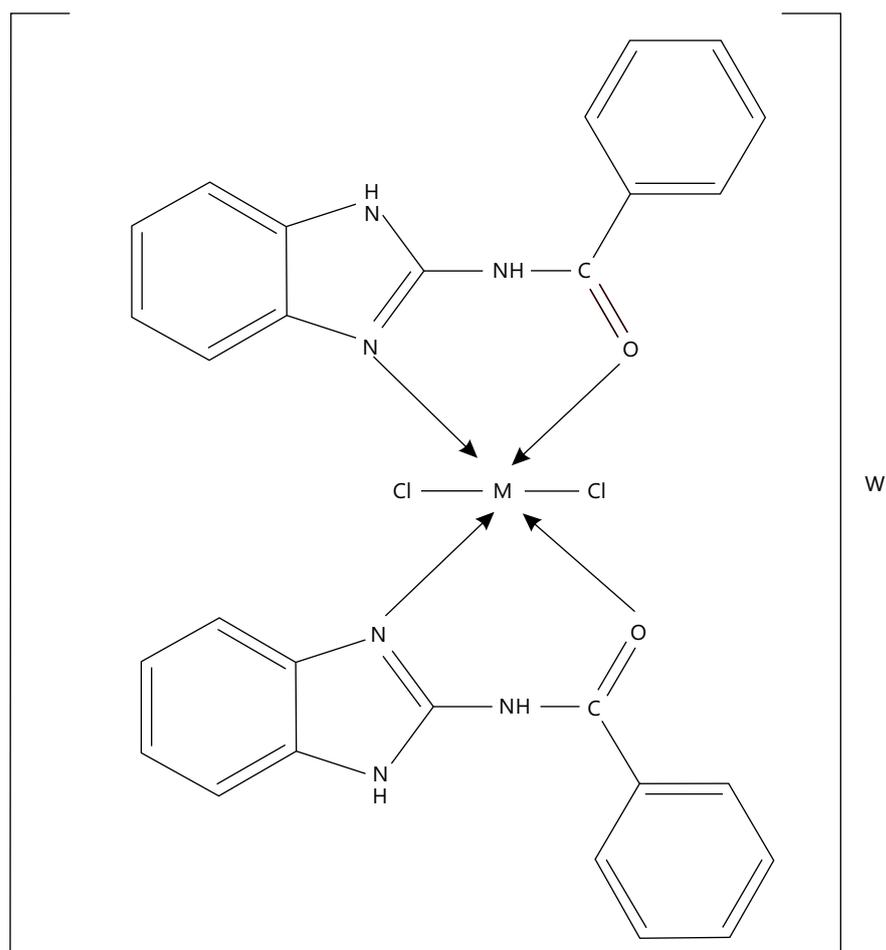


Fig. 28: Proposed structure for Cu (II), Co (II), Ni (II), Mn (II) and Zn (II) complexes of N-(1H-benzo[d]imidazol-2-yl) benzamide, (ML1)

M = Cu, Co, Ni, Mn and Zn, W = 2H₂O

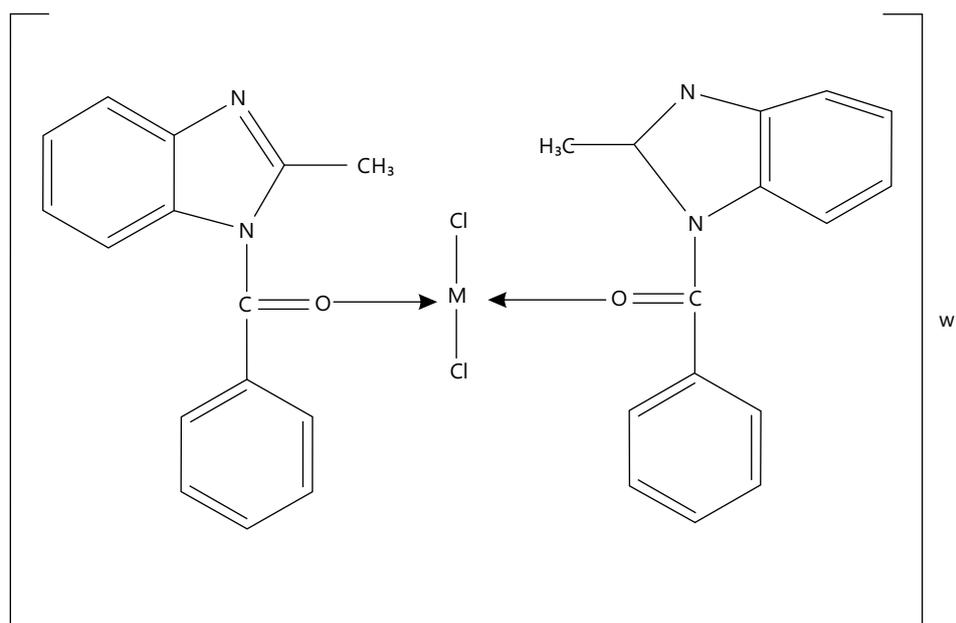


Fig. 29: Proposed structure for Cu (II), Ni (II), Mn (II) and Zn (II) complexes of (2-methyl-1H-benzo(d)imidazol-1-yl)(phenyl)methanone, (ML2)

M = Cu, Ni, Mn and Zn, W = H₂O

Table 5: Diameter of zones of inhibition of N-(1H-benzo [d] imidazol-2-yl) benzamide (L1) and metal complexes on selected bacteria isolates (mm)

Bacteria	Concentrations at 50 mg mL ⁻¹						Positive strep	Control ampil
	L1	CuL1	NiL1	CoL1	MnL1	ZnL1		
<i>K. Pneumonia</i>	13	9	10	8	0	0	15	28
<i>Escherichia Coli</i>	8	13	22	32	16	20	28	18
<i>Bacillus Cereus</i>	9	0	0	0	0	9	24	15
<i>Bacillus Stearothermophilus</i>	20	16	18	27	17	15	25	12
<i>Serratia Marcescens</i>	8	9	0	17	9	6	26	13
<i>Bacillus Subtilis</i>	8	11	0	15	9	0	26	NA
Negative Control	+++	+++	+++	+++	+++	+++	+++	+++

+++ : No zone of inhibition was produced (there was no growth around the well), STREP: Streptomycin, AMPIL: Ampicillin and NA: Not applicable

Table 6: Diameter of zones of inhibition of (2-methyl-1-H-benzo (d) imidazol-1-yl) (phenyl) methanone (L2) and metal complexes on selected bacteria isolates (mm)

Bacteria	Concentrations at 50 mg mL ⁻¹					Positive strep	Control ampil
	L2	CuL2	NiL2	MnL2	ZnL2		
<i>K.Pneumonia</i>	0	0	0	0	0	15	28
<i>Escherichia Coli</i>	0	0	0	9	0	28	18
<i>Bacillus Cereus</i>	0	0	0	0	0	24	15
<i>Bacillus Stearothermophilus</i>	13	15	15	14	14	25	12
<i>Serratia Marcescens</i>	0	9	0	0	0	26	13
<i>Bacillus Subtilis</i>	0	0	0	0	0	26	NA
Negative Control	+++	+++	+++	+++	+++	+++	+++

+++ : No zone of inhibition produced (there was no growth around well) STREP: Streptomycin, AMPIL: Ampicillin and NA: Not applicable

Antibacterial activity: The results of the antibacterial activity at 50 mg mL⁻¹ against six bacteria with reference to streptomycin and ampicillin are given in Table 5 and 6, respectively. The L1 and its metal complexes have considerable effects on almost all the bacteria as evident in Table 5. At 50 mg mL⁻¹, *Klebsiella pneumoniae* was found to be resistant to L1, MnL1 and ZnL1 complexes, similar to *Bacillus cereus*. The CoL1 possessed a greater inhibitory effect (32 mg mL⁻¹) against *Escherichia coli* and *Bacillus stearothermophilus* than the reference streptomycin (28 mg mL⁻¹) and ampicillin (18 mg mL⁻¹).

Most of the bacterial isolates showed significant resistance against L2 and its metal complexes, (Table 6). However, CuL2, NiL2, MnL2 and ZnL2 showed higher activity against *Bacillus stearothermophilus* than the reference ampicillin.

DISCUSSION

The ligands are white in colour. The colours of the complexes arise from d-d transitions or charge transfer transitions. Most of the metal complexes have melting points beyond 300°C. These relatively high melting points of the metal complexes are characteristics of coordination compounds¹⁸. The Percentage Metal Analyses of the complexes of L1 and L2 showed good correlations between the experimental and theoretical values. All these physicochemical properties are summarized in Table 1.

The molar conductivities for the complexes in the range of 6.94-21.10 Ω⁻¹ cm² mol⁻¹ for ML1 and 27.40-71.40 Ω⁻¹ cm² mol⁻¹ for ML2 indicate that the complexes are non-electrolytic in nature. The values are presented in Table 1. The results were consistent and corresponded with the literature¹⁸.

The peaks for the protons at δ_{ppm} 8.37-8.03 (d, 2H) in the ¹H NMR spectrum of ligand L1, (Fig. 3) are due to benzimidazole protons while the multiplet at δ_{ppm} 7.73-7.38 (7H) are due to the aromatic protons. Signals at 112-145 ppm in the ¹³C-NMR spectrum (Fig. 4) are for the carbon on both the benzimidazole

and the aromatic ring while the signal at 166.47 ppm, (a large down-field shift) is for carbonyl carbon. The signal at 40.0 ppm is due to the solvent. Similarly, $^1\text{H-NMR}$ spectrum of ligand L2 (Fig. 5) shows peaks for benzimidazole protons between 7.62-7.59 ppm. The signal at 2.49 ppm corresponds to the alkyl proton. The $^{13}\text{C-NMR}$ spectrum (Fig. 6) shows signals at 126.04-134.63 ppm for the carbon on the benzimidazole and phenyl part of the ring. The 165.92 ppm is for the carbonyl carbon which is down-field due to both sp^2 hybridization and to the double bond to oxygen. The signal for the alkyl carbon appeared upfield with a chemical shift of 39.96 ppm with that of the solvent at 40.0 ppm. The assignments of the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopic data were in agreement with the proposed molecular structures¹⁹.

The shifts in the stretching frequencies of N-H, C = O, C = N and C-N in the imidazole units of the benzimidazole ring on coordination of L1 with metal ions, Fig. (8-12) are indications of the involvement of these groups in the coordination of L1 to the metal ions. These were similar to those obtained by Sadeek *et al.*²⁰, Raducka *et al.*²¹ and Srivastva *et al.*²². The downward shifts in the N-H stretching vibrational frequencies from 3475cm^{-1} of the ligand, L1 to 3460, 3417, 3175, 3292cm^{-1} for Cu (II), Ni (II), Co (II) and Mn (II) complexes, respectively (Table 2) are indications of coordination through the imidazole nitrogen of the imidazole ring. These changes were similar to those found in the literature^{20,21}. The stretching vibrations bands in the infrared spectrum of L2 and its complexes, (Fig. 13-17) at $3056\text{-}3273\text{cm}^{-1}$ could be attributed to C-H, bands while those at $1651\text{-}1658\text{cm}^{-1}$ are for C = O. The bands at $1525\text{-}1530$ and $1280\text{-}1393\text{cm}^{-1}$ (Table 3) are characteristics of C = N and C-N vibrational frequencies, respectively²³.

Metal-ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of ligands to metal ions. Thus, further evidence of coordination of L1 and L2 with metal ions is shown by the appearance of new weak bands at $434\text{-}526$ and $617\text{-}678\text{cm}^{-1}$ which can be assigned to Metal-nitrogen (M-N) and metal-oxygen (M-O) vibrations, respectively for L1 complexes and bands at $472\text{-}521\text{cm}^{-1}$ assigned to metal-oxygen (M-O) vibration for L2 complexes. These were consistent with values obtained in the literature^{20,24}.

The electronic bands at 231 and 299 nm in the UV spectrum of L1 and 228 nm in the UV spectrum of L2, (Table 4 and Fig. 18, 19) correspond to $n\rightarrow\sigma^*$, $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the major chromophores, -N-H, -C = N and C = C present in the ligand molecules. Shifts in the position of the bands were observed on coordination to the metal ions. The slight shoulders at 768 and 783 nm in the electronic absorption spectra of Cu (II) complexes of L1 and L2, respectively, are due to the Jahn-Teller effect Fig. (20 and 21). This is characteristic of Cu (II) complexes in an octahedral or tetrahedral environment with $^2\text{Eg}\rightarrow^2\text{T}_2\text{g}$ transition²⁵.

The magnetic moment values of 2.05 and 1.16 BM for the copper (II) complexes of L1 and L2, respectively indicate their mononuclear nature with one unpaired electron and suggest a distorted Octahedral and Tetrahedral geometries, respectively as calculated spin only magnetic moment for copper is 1.73 BM. This shows that it is paramagnetic²⁶.

The visible spectra for the Ni (II) complex of L1, (Fig. 22) displayed three bands at 453, 504 and 645 nm which can be attributed to the d-d electronic transitions $^3\text{A}_{2\text{g}}(\text{F})\rightarrow^3\text{T}_{2\text{g}}(\text{F})$, $^3\text{A}_{2\text{g}}(\text{F})\rightarrow^3\text{T}_{1\text{g}}(\text{F})$ and $^3\text{A}_{2\text{g}}(\text{F})\rightarrow^3\text{T}_{1\text{g}}(\text{P})$, respectively. Furthermore, μ_{eff} of Ni (II) d^8 was found to be 2.00 and 2.12 BM for L1 and L2, respectively. These supported the octahedral and tetrahedral geometries of the Ni (II) complexes²⁶.

The 3 electronic transitions, 497, 646 and 764 nm in the visible region for Co (II) complex of L1 (Fig. 23) are most likely due to $^4\text{T}_{1\text{g}}\rightarrow^4\text{T}_{2\text{g}}$, $^4\text{T}_{1\text{g}}\rightarrow^4\text{A}_{2\text{g}}$ and $^4\text{T}_{1\text{g}}\rightarrow^4\text{T}_{1\text{g}}(\text{P})$, respectively. These transitions correspond to Co (II) in an octahedral complex. The 4.86 BM magnetic moment value for $[\text{Co}(\text{L1})_2\text{Cl}_2]$ also suggests an Octahedral arrangement^{26,27}. Octahedral Mn (II) complex of L1 and Tetrahedral Mn (II) complex of L2,

Fig. (24 and 25) show weak bands at 493, 783 nm for L1 and 596, 773 nm for L2, respectively. The 1.35 and 2.0 BM magnetic moment values for MnL1 and MnL2 complexes indicate paramagnetism in octahedral and tetrahedral environments, respectively^{25,28}.

For the zinc complexes, the bands, 237-299 nm in the ultraviolet region are due to charge transfer Fig. (26 and 27). The almost zero magnetic moment values for the Zn complexes (Table 4) confirm that they are diamagnetic²⁹.

Thus, the structures of the metal (II) complexes based on data from elemental analysis, FT-IR spectroscopic study, magnetic measurements, UV-Vis spectroscopy and molar conductivities are octahedral geometry for metal (II) L1 complexes and tetrahedral geometry for metal (II) L2 complexes. The metal-ligand coordination modes observed in this work were similar to those found by Téllez *et al.*¹⁵ in the study of the coordination behaviour of benzimidazole, 2-substituted benzimidazoles and benzothiazoles towards transition metal ions. The results of the antibacterial activities of L1 and its metal complexes at 50 mg mL⁻¹ against six bacteria with reference to streptomycin and ampicillin presented in Table 5 indicate that L1 and its metal complexes have considerable effects on the bacteria. At 50 mg mL⁻¹, *Klebsiella pneumoniae* was found to be resistant to L1, MnL1 and ZnL1 complexes. Similarly, *Bacillus cereus* CoL1 possessed a greater inhibitory effect (32 mg mL⁻¹) against *Escherichia coli* and *Bacillus stearothermophilus* than the reference streptomycin (28 mg mL⁻¹) and ampicillin (18 mg mL⁻¹). Most of the bacterial isolates showed significant resistance against L2 and its metal complexes, (Table 6). However, CuL2, NiL2, MnL2 and ZnL2 showed higher activity against *Bacillus stearothermophilus* than the reference ampicillin. The improved activities of the metal complexes may be due to the nature of the metal ion and can also be attributed to an increase in cell permeability which eventually facilitates absorption through the lipid of the selected microorganisms^{23,26}.

A literature survey revealed the importance of the substitutions at 1, 2 and 5 positions of the benzimidazole ring for their pharmacological activities^{7,8}. The antimicrobial activities of a series of benzimidazole-pyrazole hybrids have also been correlated with the various groups present on the molecule and their pharmaceutical properties discussed. At the same time, the role of electron withdrawing group in improving antimicrobial activities was supported by the studies of Kumar *et al.*³⁰. Studies have also shown that metal complexes are more active compared to the uncomplexed ligands^{31,32}.

Thus, as the search for more effective antimicrobial agents continues, more research work is expected for more explorations along these directions as well as examining the effect of different functional groups and substituents in the design of additional benzimidazole derivatives with antimicrobial activities.

CONCLUSION

This study synthesized two benzoyl derivatives of 2-substituted benzimidazoles, L1 and L2 and established their chelating properties and the anti-bacterial activities of both the ligands and the metal complexes. L1 acts as a bidentate ligand bonding through imidazole nitrogen and carbonyl oxygen resulting into octahedral geometry while L2 acts as a monodentate ligand through the carbonyl oxygen resulting in tetrahedral geometry. The metal complexes showed higher anti-bacterial activities than their ligands but CoL1 possessed a greater inhibitory effect against *Escherichia coli* and *Bacillusstearothermo philus* than the reference streptomycin and ampicillin. The anti-bacterial activities could further be explored by incorporating other substituents on the 2-substituted benzimidazole group.

SIGNIFICANCE STATEMENT

The study has added to the existing literature, the synthesis of two benzoyl derivatives of 2-substituted benzimidazoles namely N-(1H-benzo[d]imidazol-2-yl) benzamide (L1) and (2-methyl-1-H-benzo (d)

imidazol-1-yl) (phenyl) methanone (L2). It also provided information on the chelating properties of the derivatives which are also essential as metal complexes of derivatives showed better activity than the ligands. Furthermore, the findings on the antibacterial activities of the benzoyl derivatives and the metal complexes are very beneficial in pharmacological applications.

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