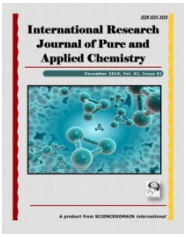

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Synthesis, Spectral, Thermal, *In-vitro* Antibacterial and Anticancer Activities of some Metal (II) Complexes of 3-(-1-(4-methoxy-6-methyl)-2- pyrimidinylimino)methyl-2-napthol

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Authors' contributions

This work was carried out in collaboration with all authors. AAO designed the study, wrote the protocol and the first draft of the manuscript. RK managed the analyses of the study and RS managed the cytotoxic studies. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

The synthesis, spectroscopic (IR, electronic, ^{1}HNMR and mass), magnetic, thermal and conductance measurements with *in-vitro* antibacterial and anticancer evaluation on Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of the Schiff base, 3-(-1-(4-methoxy-6-methyl)-2-pyrimidinylimino)methyl-2-napthol are reported. The ligand coordinates through the azomethine N and napthol O atoms, resulting in an N_2O_2 chromophore around the central metal atom. The room temperature magnetic moment, thermal, IR and electronic spectral measurements are consistent with the adoption of a 4-coordinate square planar/ tetrahedral geometry for the Co(II), Cu(II), Ni(II), Zn(II) and Pd(II) complexes; and a 6-coordinate octahedral geometry for the Mn(II) complex, with water occupying the fifth and sixth coordination sites. The complexes are magnetically dilute and non-electrolyte in DMSO. The *in-vitro* antibacterial studies show that the complexes are more active than the ligand and the Cu(II) complex exhibits a broad-spectrum antibacterial activity against *Enterococcus cloacae*, *Serratia liquefaciens*,

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Staphyloccus aureus, *Escherichia coli, Chromobacter violaceum, Klebsiella sp* and *Bacillus sp* with inhibitory zones range of 7.0-12.0 mm. The *in-vitro* cytotoxic studies show that the ligand is not active against HL-60 (Leukaemia) cells, but is resistant to 518A2 (Melanoma) cells with IC_{50} of about 70.03 µm. It is interesting to note that the Pd(II) complex exhibits super in-vitro anticancer activities against both 518A2(melanoma) and HL-60(Leukaemia) carcinomas with IC_{50} values of about 1.34 and 1.85 µM, which exceed Cisplatin activities of 35.0 and 3.5 µM in the same assay respectively.

Keywords: Anticancer activities; cis-platin; geometry; magnetically dilute; Schiff base.

1. INTRODUCTION

Recently, there has been renewed interest in metal (II) pyrimidinyl Schiff base chelates, due to their unique broad-spectrum anti-microbial, anti-HIV and anti–cancer activities. For instance, those derived from 4-amino-1, 3-dimethyl-2, 6-pyrimidinedione are potent antimicrobials, while condensed tricyclic pyrimidines showed anti-HIV activity. Furthermore, pyrimidinylamino benzenesulfonamido analogs exhibited high anti-tumour activity and low therapeutic index against murine S-180 carcinoma, while metal complexes of pyrimidinyl sulfanyl benzaimidazoles and ureas containing pyrimidinyl groups are potent anti-ulcer and antitumor agents (Abd El-Wahab, 2008; Ahmed et al., 2011; Cherayath et al., 1990; Enrique et al., 1992; Farghaly et al., 2011; Hueso-Urena et al., 2003; Huang et al., 2001; Jin et al., 2011; Khan and Asnani, 2011; Shamrokh et al., 2010; Sondhi et al., 2000). Our group have in the last seven years, been actively involved in syntheses, physicochemical and bioactivities of various Schiff base chelates with the aim of deriving Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) chelates, with broad-spectrum antimicrobial activities, which can be further developed into surface cleaning agents, while those with better anticancer activity than Cis-platin will be developed into anti-cancer drugs (Osowole and Akpan, 2012; Osowole and Daramola, 2012; Osowole et al., 2012; Osowole et al., 2009; Osowole et al., 2008; Osowole and Fagade, 2007; Osowole et al., 2005). Recently, we present our findings on the synthesis, characterisation and anticancer properties of the pyrimidinyl Schiff bases, 3-(-1-(4-methyl-6-chloro-2-pyrimidinylimino)methyl-2-napthol and 3-(-1-(4,6-dimethyl-2-pyrimidinyl imino) methyl-2-naphthol and their Mn(II), Co(II), Ni(II), Cu(II), Zn(II)/Pd(II) complexes (Osowole et al., 2011; Osowole et al., 2010). This work is thus an extension of the former study, in which the chloro substituent in the former Schiff base is replaced with the methoxy group with the sole aim of deriving metal complexes with better anticancer activities than Cis-platin. Their thermal, conductance, electronic and magnetic properties are also discussed. These complexes and the ligand are new, being reported by us for the first time (Ceyhan et al., 2011; da Silva et al., 2011; El-Ansary and Abdel- Kader, 2012; Gaber et al., 2001; Jin et al., 2011; Khan and Asnani, 2011; Khalil et al., 2002; Mounir et al., 1987; Obaleye et al., 2011; Osowole and Akpan, 2012; Osowole et al., 2012; Qiao et al., 2011; Soenmez and Sekerci, 2004).

2. EXPERIMENTAL

2.1 Chemicals

Reagent grade 2-amino-4-methoxy-6-methylpyrimidine and 2-hydroxy-1-napthaldehyde (Across) and hydrated manganese(II) nitrate, cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate, zinc(II) nitrate, palladium(II) chloride (Aldrich) were used as received. Solvents were purified by standard methods.

2.2 Physical Measurements

The elemental analyses for C, H and N were recorded on GmbH VarioEl analyser. Manganese, cobalt, nickel, copper, zinc and palladium were determined titrimetrically (Bassett et al., 1978). The ^{1}H NMR spectrum was recorded on a 300 MHz Oxford Varian NMR instrument in $CDCl_3$ at 295K. ^{1}H chemical shifts were referenced to the residual signals of the protons of $CDCl_3$ and are quoted in ppm. Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance at room temperature (27ºC) and diamagnetic corrections were calculated using Pascal's constants (Earnshaw, 1980). The reflectance spectra were recorded on a Perkin-Elmer λ20 spectrophotometer equipped with an integrating sphere, while infrared spectra were measured as KBr discs on a Bruker-IFS 66V spectrometer in the range 4000-400 cm^{-1}. Thermogravimetric analyses were done in static air, using a T6 Linseis thermal analyser with a heating rate of 10ºC/min in the range 30-700ºC, while electrolytic conductivities of the compounds in DMSO were determined using a MC-1, Mark V conductivity meter with a cell constant of 1.0 and melting points (uncorrected) were done using a Stuart scientific melting point apparatus smp3.

2.3 Synthesis

2.3.1 Preparation of 3-(-1-(4-methoxy-6-methyl)-2-pyrimidinylimino)methyl-2-napthol

The ligand, {[$C_{10}H_6$(OH)CH:N($C_6H_7N_2O$)]}, HL, was prepared by refluxing a mixture of 0.012 mol (1.67 g) of 2-amino-4-methoxy-6-methyl pyrimidine and 0.012 mol (2.07 g) of 2-hydroxy-1-napthaldehyde with 6 drops of acetic acid in 60 mL of ethanol for 6 h. The yellow product, formed on cooling to room temperature, was filtered and recrystallized from ethanol and dried *in vacuo* over anhydrous calcium chloride. The yield of the resulting Schiff base was 2.25 g (70%). ^{1}H nmr (ppm) δ11.0 (s, OH), δ 9.45 (d, 1H, HCN); 6.64-7.88 (m, 6H, $C_{10}H_6$); 6.25 (s, 1H, CH); 3.94 (s, 3H, OCH_3); 2.36 (s, 3H, CH_3).

2.3.2 Preparation of the metal(II) complexes (M = Mn, Co, Ni, Cu, Zn)

A solution of the metal(II) nitrates (0.69 mmol, 0.12-0.20 g) in 20 mL ethanol was added to a stirring solution of the ligand (1.37 mmol, 0.40 g) in 30 mL ethanol at room temperature (26ºC), followed by the gradual addition of triethylamine (1.37 mmol, 0.17 mL). The resulting homogeneous solution was further refluxed for 6 h at 50ºC, during which the products formed. These were later filtered, washed with ethanol and dried in *vacuo* over anhydrous $CaCl_2$. Similar procedure was used to isolate the Pd(II) complex from its chloride salt.

2.4 Biological Studies

2.4.1 Antibacterial studies

The assay was carried out on the ligand and its metal(II) complexes using Agar diffusion technique. The surface of the agar in a Petri dish is uniformly inoculated with 0.3 mL of 18 hours old culture of *E. cloacae*, *S. liquefaciens*, *S. aureus*, *E. coli*, *C. violaceum, Klebsiella sp* and *Bacillus sp*. 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 the bench for 30 min before incubation at 37ºC for 24 h, after which inhibitory zones (in mm) were taken as a measure of antimicrobial activity. The minimum inhibitory concentration (MIC) was determined by the introduction of six different concentrations (1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg/mL) of the compound into six wells bored into the agar. The lowest concentration of each compound that inhibited growth of the test organism was taken as the minimum inhibitory concentration. The experiments were conducted in duplicates and gentamycin was used as the reference drug.

2.4.2 Anticancer studies

The human HL-60 leukaemia cells were obtained from the German National Resource centre for Biological materials (DSMZ), Braunschweig and the human 518A2 melanoma cells were cultured at the Department of Oncology and Haematology, Medical Faculty of the Martin-Luther University, Halle, Germany.

2.4.2.1 Cytotoxicity (MTT) Assay

MTT [3(4, 5-dimethylthiazol-2-yl)2, 5-diphenyltetrazoliumbromide] was used to identify viable cells which are capable of reducing it in their mitochondria by succinate dehydrogenase to a violet formazan product.

2.4.2.2 Cell lines and culture condition

HL-60 ($0.5x10^6$ cells/mL) and 518A2 ($1.7 x10^5$ cells/mL) cells were seeded out and cultured for 24 h. Incubation (5% CO_2, 95% humidity, 37ºC) of cells following treatment with the test compounds was continued for 24, 48 and 72 h. Blank and solvent controls were incubated under identical conditions. A 5 mg/mL stock solution of MTT in phosphate-buffered saline (PBS) was then added to a final concentration of 0.05%. After 2 h the precipitate of formazan crystals was redissolved in a 10% solution of sodium dodecylsulfate (SDS) in DMSO containing 0.6% acetic acid in the case of the HL-60 cells. For the adherent melanoma (518A2) cells, the microplates were swiftly turned to discard the medium prior to adding the solvent mixture. The microplates were gently shaken in the dark for 30 min and left in the incubator overnight, to ensure a complete dissolution of the formazan. Finally the absorbance at wavelength 570 nm and 630 nm (background) was measured using an ELISA plate reader. All experiments were carried out in quadruplicate, and the percentage of viable cells quoted was calculated as the mean ± SD with respect to the controls set to 100%. Blank tests have shown that DMSO used in the preparation of the test compound does not have any effect on the cancer cell lines.

3. RESULTS AND DISCUSSIONS

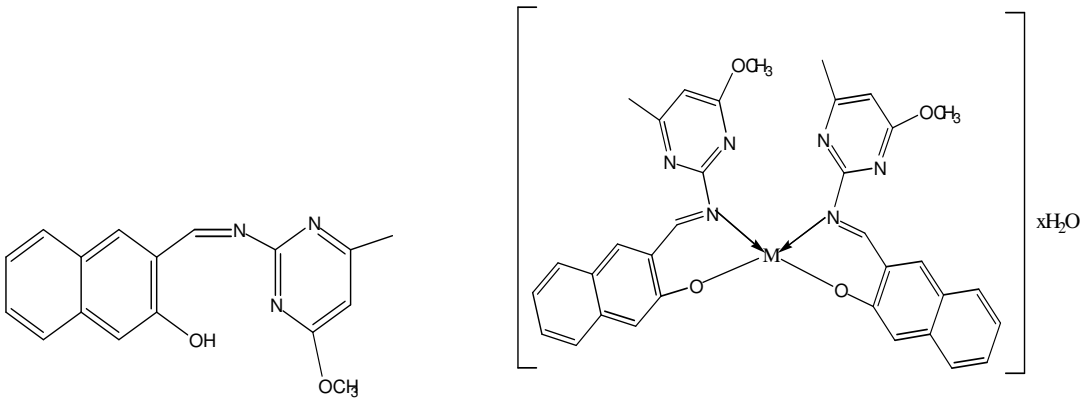
The reaction of the ligand with the metal(II) nitrates (Mn, Co, Ni, Cu, and Zn) gave coloured complexes in moderate-good yields (40-70%) according to equations 1 and 2.

$$M(NO_3)_2.2H_2O + 2HL \rightarrow [ML_2]xH_2O + 2HNO_3 + bH_2O \quad .....(1)$$

(*when M = Mn{x = 2, b = 0}, Co, Zn{ x = 1, b = 1}; Ni{x = 3/2, b =0.5}, Cu{x = ½, b = 1.5}*)

$$PdCl_2 + 2HL \rightarrow [PdL_2] + 2HCl \quad .....(2)$$

The decomposition patterns obtained from TGA curve, shows a good correlation between experimental and calculated percentages of CHN. This confirms the proposed formulation of the complexes (Fig. 1). Similarly, the ligand melts in the range 185-186ºC, while the complexes have high melting points in the range 264-322ºC, with the exception of the Pd(II) complex with a low melting point in the range 158-160ºC. This observation further corroborates coordination. Non-formation of suitable crystal prevents the measurement of single X-ray diffraction. The analytical data, colours, % yields, melting points and room temperature magnetic moments of the complexes are presented in Table 1.



(A) (B)

Fig. 1. The proposed structure for the ligand (A) and complexes (B)

3.1 Mass Spectra and Conductance Measurements

The mass spectra of ligand and the complexes show peaks attributed to the molecular ions m/z at 293 $[L]^+$; 639 $[ML_2\text{-}2H]^+$; 643 $[CoL_2\text{-}2H]^+$; 643 $[NiL_2\text{-}2H]^+$; 647 $[CuL_2\text{-}3H]^+$; 648 $[ZnL_2\text{-}3H]^+$ and 690 $[PdL_2+H]^+$.

The molar conductances of the complexes are ranged 10.0-22.0 $\Omega^{-1}cm^2\ mol^{-1}$ in DMSO, showing they were non-electrolytes, a value of 70.0-90.0 is expected for a 1:1 electrolyte (Geary, 1971).

Table 1. Analytical data for the compounds

Compound (Empirical formula)	F. M	m/z	Color	μeff	% Yield	Λ_m^*	M.P(ºC)	Analysis (Calculated)			
								%C	%H	%N	% M
HL ($C_{17}H_{15}N_3O_2$)	293.32	293	Yellow	-	60	-	185-186	70.08 (69.61)	4.96 (5.15)	14.33 (14.33)	-
[$MnL_2.2H_2O$] ($MnC_{34}H_{32}N_6O_6$)	675.60	639	Brown	5.67	40	15.0	305-307	60.56 (60.45)	4.71 (4.77)	12.32 (12.44)	8.10 (8.13)
[CoL_2]H_2O ($CoC_{34}H_{30}N_6O_5$)	661.62	643	Brick Red	4.47	60	10.0	303-304	61.48 (61.17)	4.40 (4.57)	12.73 (12.70)	9.03 (8.91)
[NiL_2]3/2H_2O ($NiC_{34}H_{31}N_6O_{5.5}$)	679.64	643	Orange	3.30	60	18.0	320-322	61.12 (60.89)	4.20 (4.67)	12.31 (12.37)	8.67 (8.64)
[CuL_2]½H_2O ($CuC_{34}H_{29}N_6O_{4.5}$)	657.18	647	Brown	1.84	70	13.0	264-266	62.18 (62.14)	3.94 (4.44)	12.31 (12.79)	9.65 (9.67)
[ZnL_2]H_2O ($CuC_{34}H_{30}N_6O_5$)	667.67	648	Yellow	0.11	70	17.0	290-292	61.50 (61.17)	4.20 (4.53)	12.51 (12.59)	9.80 (9.74)
[PdL_2] ($PdC_{34}H_{28}N_6O_4$)	688.62	690	Brown	D	70	22.0	158-160	59.55 (59.30)	4.06 (4.09)	12.34 (12.20)	15.08 (15.10)

$^*\Omega^{-1}\ cm^2\ mol^{-1}$; F. m = Formula mass; D = Diamagnetic; M.P = Melting point

3.2 ^{1}HNMR Spectra

The ligand napthyl ring protons resonate as a multiplet at δ 6.64-7.88 ppm (m, 6H, $C_{10}H_6$). The phenolic proton is observed as a singlet at 11.0 ppm (s, 1H, OH) and the imine proton resonates as a doublet at δ 9.45 ppm (d, 1H, H=CN), while the pyrimidine ring proton is seen as a singlet at δ 6.25 ppm (s, 1H, $CH_{pyrimidine}$). The methoxy and methyl protons resonate as singlets at 3.94 (s, 3H, OCH_3) and 2.36 (s, 3H, CH_3) ppm respectively.

In the Zn(II) complex spectrum, the napthyl ring protons and the imine proton signal are shielded at δ δ 7.01-8.21 ppm (m, 6H, $C_{10}H_6$) and δ 10.64 ppm (s, 1H, H=CN) respectively . The phenolic proton is conspicuously absent, indicating the involvement of OH in chelation. The pyrimidine ring proton (s, 1H, $CH_{pyrimidine}$), methoxy(s, 3H, OCH_3) and methyl protons (s, 3H, CH_3) are seen at 6.23, 3.61 and 2.24 ppm respectively. These protons are all downfield shifted indicative of deshielding due to the coordination of the imine nitrogen atom (Sharma and Srivastava, 2006).

The Pd(II) complex spectrum, shows that the the napthyl ring protons and the imine proton signal are shielded at δ 6.70-7.96 ppm (m, 6H, $C_{10}H_6$) and δ 9.53 ppm (d, 1H, H = CN) respectively. The phenolic proton is conspicuously absent, indicating the involvement of OH in chelation. Similarly, the upfield shifts of the pyrimidine ring, methyl and methoxy protons to 6.33, 2.43 and 4.01 ppm are indicative of shielding. These shifts are affirmative of coordination through the imine nitrogen atom (Sharma and Srivastava, 2006).

3.3 Infrared Spectra

The relevant infrared data are presented in Table 2. The assignments of the infrared bands are made by comparing the spectra of the compounds with reported literature on similar systems (Cherayath et al., 1990; Huang et al., 2001; Sondhi et al., 2000; Sonmez and Haciyusufoglu, 2006). The *ν*OH band of the ligand is seen at 3437 cm^{-1} and its absence in the complexes is due to the involvement of the napthol *O* in bonding to the metal ions. The broad band at 3500 cm^{-1}, in all the metal complexes with the exception of the Pd(II) complex is assigned to *ν*OH coordinated/hydrated water. The uncoordinated C=N stretching vibrations in the ligand are observed as three bands at 1627-1538 cm^{-1} (Khalil et al., 2002; Gaber et al., 2001). These bands are four in the metal complexes and suffered bathochromic shifts to 1626-1519 cm^{-1} in the Schiff base complexes, thus confirming the involvement of the imine *N* atom in coordination to metal (II) ion. Furthermore, the observance of three to four bands of *ν*C=N bands in this work is indicative of the absence of geometric isomerism in the complexes. It has been documented that metal complexes in Cis-isomeric form usually have a single *ν*C=N bands while those in trans-isomeric form have two *ν*C=N bands (Nejo et al., 2009a, 2009b).The δC—H vibration of the ligand is observed at 976 cm^{-1} and suffers bathochromic shift to 843-748 cm^{-1} in the complexes due to the pseudo-aromatic nature of the chelates (Osowole et al., 2005). Further evidence of coordination is the observance of bands due to *ν*(M—O) and *ν*(M—N) at 499-423 and 596-504 cm^{-1} respectively in the complexes. These bands are absent in the spectra of the ligands (Gaber et al., 2001; Mounir et al., 1987).

3.4 Electronic Spectra and Room Temperature Magnetic Moments

The Mn(II) complex shows three weak bands expectedly at 11.88, 15.85 and 22.88 kK respectively, typical of 6-coordinate octahedral geometry and are assigned as $^6A_{1g} \rightarrow {}^4T_{1g}$,

$^6A_{1g} \rightarrow {}^4T_{2g}$ (G), $^6A_{1g} \rightarrow {}^4E_g$(G) transitions. The effective magnetic moment of Mn(II) complexes are expected to be close to the spin-only value of 5.90 B.M. since the ground term is $^6A_{1g}$ and as such there is no orbital contribution. Consequently, an observed moment of 5.67 B.M. for this complex indicates that it is high spin, and complementary of octahedral geometry (Abu-elwafa and Isa, 1989; Lever, 1980).

The Co(II) complex, displays two bands at 13.80 and 19.34 kK assigned to $^4A_2 \rightarrow {}^4T_1$(F), ($\nu_2$), and $^4A_2 \rightarrow {}^4T_1$(P), ($\nu_3$) transitions of a tetrahedral geometry (Abd El-Wahab, 2008; Hueso-Urena et al., 2003). The observed moment of 4.47 B.M is supportive of tetrahedral geometry, since moments in the range 4.2-4.6 B.M is usually observed for tetrahedral Co(II) compounds (Sonmez and Sekerci, 2004).

The reflectance spectra of the Ni(II) complex showed absorption bands at 14.00 and 23.28 kK assigned to $^3T_1$(F) $\rightarrow$ $^3A_2$, (ν_2) and $^3T_1$(F) $\rightarrow$ $^3T_1$(P), (ν_3) transitions, in a tetrahedral environment (Osowole et al., 2008). Generally, square planar Ni(II) complexes are diamagnetic, while tetrahedral complexes are paramagnetic with moments in the range 3.20-4.10 B.M. respectively. This complex has a moment of 3.30 B.M. and hence it is tetrahedral (Gaber et al., 2001).

The observance of two bands at 15.00 and 24.00 kK in the Cu(II) complex indicates square planar geometry with the assignment of the bands as $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions, because tetrahedral Cu(II) complexes usually have a single absorption band below 10.0 kK. A moment of 1.9-2.2 B.M. is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry, expectedly higher than the spin only moment due to orbital contribution and spin-orbit coupling (Khalil, 2002). The Cu(II) complex, has a moment of 1.84 B.M. and is consequently mononuclear.

The Zn(II) complex showed M→L CT transitions at 22.17 kK, as no d-d transition is expected. An observed moment of 0.11 B.M. for this complex confirms that it is essentially diamagnetic and tetrahedral (Osowole et al., 2005).

The spectrum of the Pd(II) complex shows two absorption bands at 14.51 and 21.83 kK, typical of square planar geometry which are assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$ transitions. This complex is expectedly diamagnetic (Cherayath et al., 1990).

The ligand bands (Table 2) are bathochromic/ hypsochromic shifted in the complexes, indicative of coordination, with three band maxima between 27.00-30.00, 31.85-35.26 and 42.00-50.00 kK assigned to n- π*, π-π* and charge transfer transitions respectively (Mounir et al., 1987).

Table 2. Relevant infrared and electronic spectral data of the complexes

Compound	*v*OH	*v*(C=N)		*v*Ph/C—O	δC-H	v(M—N)	*v*(M—O)	Electronis spectral (kK)
HL	3437s	1627s	1597s	1444s	976s	-	-	28.00 32.00 40.00
		1538s		1362s				47.00
[$MnL_2.2H_2O$]	3500b	1618s	1605s	1293s	833s	593m	493m	11.88 15.85 22.88
		1587s	1532s	1183s	748s	545m	441s	27.55 32.15 41.07
[CoL_2]H_2O	3400b	1617s	1603s	1291m	832s	592s	499m	13.80 19.34 27.05
		1553s	1531s	1186m	750s	555m	443m	35.26 41.81
[NiL_2]3/2H_2O	3500b	1621s	1579s	1280m	836s	560m	486m	14.00 23.28 27.03
		1540s	1519s	1140m	751m	527m	423m	31.85 48.33
[CuL_2]½H_2O	3500b	1615s	1589s	1288m	835s	596m	498m	15.00 24.00 27.00
		1554s	1531s	1186m	751s	532m	446m	30.00 43.00
[ZnL_2]H_2O	3500b	1616s	1603s	1288m	838s	596m	498m	22.17 28.00 33.00
		1589s	1533s	1185m	751s	550m	446m	42.00 50.00
[PdL_2]	-	1626s	1600s	1250m	843s	555m	446m	14.51 21.83 30.00
		1558s	1530s	1188m	762s	504m	429m	40.00 50.00

S = strong, m = medium, 1kK = 1000 cm^{-1}

3.5 Thermal Studies

The decomposition stages, temperature ranges, percentage losses in mass and assignment of decomposition moieties are given in Table 3. The thermal degradation of the ligand, HL occurred in three steps. The first stage is the loss of 0.75 mole of nitrogen and 1.5 moles of hydrogen, with mass losses of (obs.=8.03 %, calc.=8.18%) within a temperature range of 30-200ºC. The next stage involves the loss of the organic fraction, $C_{10}H_{10}O$, within a temperature range of 200-400ºC, with mass losses of (obs.=50.30 %, calc.=49.78%). The final stage is the loss of the organic moiety, $C_7H_2N_{1.5}O$, with mass losses of (obs.=41.67 %, calc.=41.93%) within the temperature range 400-500ºC.

The Mn(II) complex decomposed in three stages. Stage one is between 30-210ºC, which indicates the loss of the organic moiety, $C_6H_{10}NO_2$, and two molecules of water, with mass losses of (obs.=26.25%, calc.=24.26%). The second stage is within a temperature range of 210-350ºC and is attributed to the loss of the organic moiety, $C_4H_8NO_2$, with mass losses of (obs.=17.18%, calc.=15.09%). The final stage is the loss of the organic moiety, $C_{24}H_{10}N_4$, between 350-700ºC with mass losses of (obs.=54.39%, calc.=52.37%) leaving behind Mn residue.

The decomposition of the Co(II) complex occurs in three steps. The first step is within a temperature range of 30-190ºC and corresponds to the loss of a mole of water and 1.5 mole of oxygen, with mass losses of (obs.=10.00%, calc.=9.98%). The successive decomposition occurs within a temperature range of 190-360°C and equals the loss of the organic moiety, $C_8H_8N_2$, with mass losses of (obs.=19.92%, calc.=19.95%). The final stage is the loss of the organic moiety, $C_{26}H_{20}N_4O$, between 360-700°C with mass losses of (obs.=60.18%, calc.=61.07%). The final product is cobalt.

The TGA curve of the Ni(II) complex reveals three steps decomposition. The first step corresponds to the loss of water and NO_2 with mass losses of (obs. = 10.0%, calc.=9.68%) between 30-190ºC. The second is within the temperature range 190-360ºC, attributed to the loss of the organic moiety, $C_9H_9N_2$, with mass losses of (obs.=21.54%, calc.=21.95%). The final stage is within a temperature range of 360-700ºC and corresponds to the loss of the organic moiety, $C_{25}H_{19}N_3O_2$, with mass losses of (obs.=59.32%, calc.=59.42%). The remaining fraction is Ni residue.

The Cu(II) complex decomposes in four stages. The first involves the loss of 0.5 mole of water, a mole of H_2 and a mole of O_2 with mass losses of (obs.=6.73%, calc.=6.55%) between 30-100ºC. The second is within a temperature range of 100-230ºC and corresponds to the loss of N_2O, with mass losses of (obs.=6.49%, calc.=6.70%). The third phase is within 230-350°C and corresponds to the loss of the organic moiety, C_9H_9O, with mass losses of (obs.=20.24%, calc.=20.26%).The final stage is within a temperature range of 350-700ºC and corresponds to the loss of the organic moiety, $C_{25}H_{17}N_4$, with mass losses of (obs.=58.02%, calc.=56.82%). The remaining fraction is Copper.

The Zn(II) complex decomposes in three stages. The stage one is between 30-210ºC, which indicates the loss of a mole of water and 0.5 mole of nitrogen, with mass losses of (obs.=3.54%, calc.=3.74%). The second stage is within a temperature range of 210-390ºC, which corresponds to the loss of the organic moiety, $C_8H_8O_4$, with mass losses of (obs.=24.66%, calc.=25.19%). The final stage is between 390-700ºC and is attributed to the loss of the organic moiety, $C_{26}H_{20}N_5$, with mass losses of (obs.=60.07%, calc.=60.28%), leaving behind the zinc residue.

The Pd(II) complex decomposes in two phases. The first phase is between 30-300ºC and is assigned to the loss of the organic fragment, $C_{20}H_{20}N_5$, with mass losses of (obs.=47.90%, calc.=49.00%). The final phase is within a temperature range of 300-700ºC which corresponds to the loss of the organic moiety $C_{14}H_8O_4N$, with mass losses of (obs.=37.61%, calc.=36.87%) leaving behind the palladium residue. Thus, the decomposition patterns corroborate the proposed formulation of the complexes and it suggests the use of these complexes as metal source in metal organic chemical vapour deposition (Ngo et al., 2003).

Table 3. Thermal data for the complexes

Compound	Temperature range(ºC)	TG weight loss Calc.	(%) Obs.	Assignments
HL	30-200	8.18	8.03	¾N_2 + 3/2H_2
($C_{17}H_{15}N_3O_2$)	200-400	49.78	50.30	$C_{10}H_{10}O$
	400-500	41.93	41.67	$C_7H_2N_{1.5}O$
[ML_2.2H_2O]	30-210	24.26	26.25	$C_6H_{10}NO_2$ + 2H_2O
($MnC_{34}H_{32}N_6O_6$)	210-350	15.09	17.18	$C_4H_8NO_2$
	350-700	52.37	54.39	$C_{24}H_{10}N_4$
				Mn (residue)
[CoL_2]H_2O	30-190	9.98	10.00	1.5O_2 + H_2O
($CoC_{34}H_{30}N_6O_5$)	190-360	19.95	19.92	$C_8H_8N_2$
	360-700	61.07	60.18	$C_{26}H_{20}N_4O$
				Co(residue)
[NiL_2]3/2 H_2O	30-190	9.68	10.00	NO_2 + 1.5H_2O
($NiC_{34}H_{31}N_6O_{5.5}$)	190-360	21.95	21.54	$C_9H_9N_2$
	360-700	59.42	59.32	$C_{25}H_{19}N_3O_2$
				Ni (residue)
[CuL_2]½H_2O	30-100	6.55	6.73	½H_2O + H_2+O_2
($CuC_{34}H_{29}N_6O_{4.5}$)	100-230	6.70	6.49	N_2O
	230-350	20.26	20.24	C_9H_9O
	350-700	56.82	58.02	$C_{25}H_{17}N_4$
				Cu (residue)
[ZnL_2]H_2O	30-210	3.75	3.54	½N_2 + H_2O
($CuC_{34}H_{30}N_6O_5$)	210-390	25.19	24.66	$C_8H_8O_4$
	390-700	60.28	60.07	$C_{26}H_{20}N_5$
				Zn (residue)
[PdL_2]	30-300	47.90	49.00	$C_{20}H_{20}N_5$
($CuC_{34}H_{28}N_6O_4$)	300-700	36.87	37.61	$C_{14}H_8NO_4$
				Pd(residue)

Obs. = observed, Calc. = calculated

3.6 Antibacterial Activities

The antibacterial activities of the ligand and its complexes against *E. cloacae*, *S. liquefaciens*, *E. coli*, *S. aureus*, *C. violaceum*, *Klebsiella sp* and *Bacillus sp* are presented in Table 4. The ligand has no activity at all, and *Pseudomonas sp* is mostly resistant to the metal complexes.

Table 4. Zones of inhibition (in mm) of the compounds against various microbes

Compounds	*S. liquefaciens*	*E. coli*	*E. cloacae*	*C. violaceum*	*S. aureus*	*Bacillus sp*	*Klebsiella sp*	*Pseudomonas sp*
HL	R	R	R	R	R	R	R	R
$[MnL_2.2H_2O]$	13.0±0.2	9.0±0.4	12.0±0.3	R	R	R	R	R
$[CoL_2]H_2O$	7.0±0.1	7.0±0.0	7.0±0	9.0±1.0	R	R	R	R
$[NiL_2]3/2H_2O$	8.0±0.7	9.0±0.2	8.0±0.1	10.0±1.1	7.0±0.1	R	R	R
$[CuL_2]½H_2O$	11.0±0.4	10.0±0.1	12.0±0.1	9.0±1.0	10.0±0.1	7.0±0.1	12.0±0	R
$[ZnL_2]H_2O$	12.0±0.4	8.0±0.6	9.0±0.1	R	8.0±0.1	7.0±0.2	7.0±3.0	7.0±0
$[PdL_2]$	9.0±0.3	8.0±0.1	R	7.0±0	10.0±0.4	R	R	R
+ Gentamycin	26.0±1.0	45.0±1.2	40.0±0.1	43.0±1.6	40.0±0.8	28.0±1.2	30.0±1.3	40.0±1.6

R = Resistant, E. cloacae = Enterococcus cloacae, S. liquefaciens = Serratia liquefaciens, Bacillus sp, Klebsiella sp, E. Coli = Escherichia coli, S. aureus = Staphyloccus aureus, C. violaceum = Chromo bacter violaceum

This is attributed to its very versatile nutritional capability, adaptability to various hydrocarbon rings and the possession of pump mechanism which ejects metal complexes as soon as they enter the cell (Pelczar et al., 1996). Similarly, *Bacillus sp* and *Klebsiella sp* are resistant to all the metal complexes with the exception of the Cu(II) and Zn(II) complexes whose activities are 7.0, 12.0, 7.0 and 7.0 mm respectively. The resistance of the *Klebsiella sp* is attributed to its ability to produce extended-spectrum beta-lactamases (ESBL) which inactivates the compounds and the resistance of *Bacillus sp* is a consequence of its thick peptidoglycan layer which is less permeable to the metal complexes (Abd El-Wahab, 2008). In addition, *E. cloacae* is sensitive to all the complexes, with the exceptions of the Pd(II) complexes and an inhibitory zone range of 7.0-12.0 mm. Similarly, *C. violaceum* is sensitive to all the complexes with the exception of the Mn(II) and Zn(II) complexes with inhibitory zones range of 7.0-10.0 mm. Furthermore, *E. coli* and *S. liquefaciens* are sensitive to all the complexes with inhibitory zones range of 7.0-10.0 and 7.0-13.0 mm respectively. In all cases, the metal complexes are more active than the ligand expectedly due to chelation, which reduced the polarity of the metal atom, mainly because of partial sharing of its positive charge with donor groups of the ligand and possible π-electron delocalisation on the aromatic rings. This increased the lipophilic character, favouring its permeation into the bacterial membrane, causing the death of the organisms (Thangadurai and Natarajan, 2001). A look at the antibiotic, gentamycin, activities (26.0-45.0 mm) against the various bacterial isolates relative to the metal complexes (7-19 mm) showed that the activities of the latter are much lower, with optimum activity being about half of gentamycin with $[MnL_2.2H_2O]$ against *S. liquefaciens.* The Cu(II) complex has a broad-spectrum activity like gentamycin against the organisms used, although much lower.

3.7 Anticancer Studies

The growth inhibitory effects of the ligand, and its Cu(II) and Pd(II) complexes on the Cis-platin (CDDP) resistant 518A2 (Melanoma) and (CDDP) sensitive HL-60(Leukemia) cell lines are presented in Table 5. The ligand, HL (63.91-80.03 µM) is about twice as resistant as CDDP (35.0 µM) against Melanoma cells throughout the duration of the experiment. Similarly, the copper(II) complex is resistant to the melanoma cells throughout the experimental hours, with an IC_{50} value of about 34.09 µM which is comparable to CDDP activity of 35.0 µM. On the contrary, the Pd(II) complex exhibited super activity against the melanoma cells throughout the duration of the experiment, being about thirty times more active than CDDP, with an IC_{50} value of about 1.34 µM.

Table 5. IC_{50} values of the ligand and its complexes against melanonoma (518A2) and leukaemia (HL60) cells

Complexes	IC_{50} [µM] Melanoma cells(518A2)			IC_{50} [µM] Leukaemia cells (HL60)		
	24h	48h	72h	24h	48h	72h
CDDP	35	ND	ND	3.5	ND	ND
H_2L	66.16±18.98	63.91±8.55	80.03±6.96	>100	>100	>100
$[CuL_2]$	33.69 ±0.43	30.79±0.01	37.78±1.31	20.01	28.37	35.49
$[Pd(L)_2]$	1.59±0.01	1.42±0.18	1.01±0.39	1.90	1.85	1.86

<5 µM = super active; 5-10 µM = strongly active; 11-19 µM = moderately active; 20-30 µM = weakly active; >30 µM = resistant; > 100 µM = not active; CDDP = Cis-platin; ND = Not determined.

The ligand has no activity at all against HL-60 Leukemia cells, while the Cu(II) complex has weak activity at 24 and 48 h, with IC_{50} values of 20.01 and 28.37 µM, which are a sixth; and

an eighth as sensitive as CDDP respectively. Further exposure till 72 h shows it became resistant with an IC_{50} value of 35.49 µM. Interestingly, the Pd(II) complex has almost constant, super activity approximately 1.87 µM throughout the duration of experiment, which is about twice as active as CDDP (3.5 µM). The Mn(II), Co(II), Ni(II) and Zn(II) complexes are not screened in this study.

It is evident from the cytotoxic studies, that $[PdL_2]$ has the best anticancer activity against both Melanoma (518A2) and HL60 (Leukemia) carcinomas *in-vitro* with IC_{50} values of about 1.34 and 1.85 µM respectively, which is thirty times more active than, and twice as active as CDDP. The increased activity of $[PdL_2]$ against the growth of 518A2 (Melanoma) and HL-60(Leukemia) cells is of interest in the development of tumor therapeutics and suggests further investigations in this area.

Furthermore, in comparison with our earlier study (Osowole et al., 2010) it was observed that on changing from the chloro substituent to methoxy (present study), the activity of the Cu(II) complex against the melanoma cells increases from nil activity to resistant ($IC_{50,}$ 33.69 µM at 24 h). However, the reverse is observed with leukemia cells at 24 h i.e. the activity of the Cu(II) complex decreases from moderately active (IC_{50}, 14.04 µM) to weakly active (IC_{50}, 20.01 µM). However at 48 h and 72 h, the chloro complex is less active, with IC_{50} values of 75.33 µM and 39.29 µM, than its methoxy analog which is weakly active at 48 h (IC_{50}, 28.37 µM) and resistant at 72 h (IC_{50}, 35.49 µM). In addition, the anticancer activities of the Pd(II) complex on both the melanoma and leukemia cells are lower in the chloro complex than its methoxy analog throughout the duration of the experiment. e.g. with melanoma cells, activity increased from thrice sensitivity ($IC_{50,}$ 10.68 µM at 24 h) to about twenty fold (IC_{50}, 1.59 µM at 24 h) that of CDDP (IC_{50}, 35 µM at 24 h). Likewise, with the leukemia cells, activity increased from weakly active ($IC_{50,}$ 20.56 µM at 24 h) to strongly active (IC_{50}, 1.90 µM at 24 h).

Thus, we conclude that the presence of electron releasing methyl and a weak electron withdrawing methoxy at the 4^{th} and 6^{th}positions of this series of pyrimidinyl Schiff base instead of the strong electron withdrawing chloro substituent led to enhanced anti-cancer activities in the metal complexes.

4. CONCLUSION

The Schiff base, 3-(-1-(4-methoxy-6-methyl)-2-pyrimidinylimino)methyl-2-napthol coordinates to the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) ions using the azomethine N and napthol O atoms. The assignment of a 4-coordinate square planar/ tetrahedral geometry for the Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes and a 6-coordinate octahedral geometry for the Mn(II) complex is corroborated by magnetic, thermal, infrared and electronic spectral measurements. The *in-vitro* antibacterial studies show that the Cu(II) complex has broad-spectrum antibacterial activities against *E. cloacae*, *S. liquefaciens*, *S. aureus*, *E. coli, C. violaceum, Klebsiella sp* and *Bacillus sp* with inhibitory zones range of 7.0-12.0 mm, while the *in-vitro* cytotoxic studies show that the Pd(II) complex exhibits super *in-vitro* antitumor against both 518A2(melanoma) and HL-60(Leukaemia) carcinomas with IC_{50} of about 1.34 and 1.85 µM respectively, which is about thirty times more active than and twice as active as CDDP.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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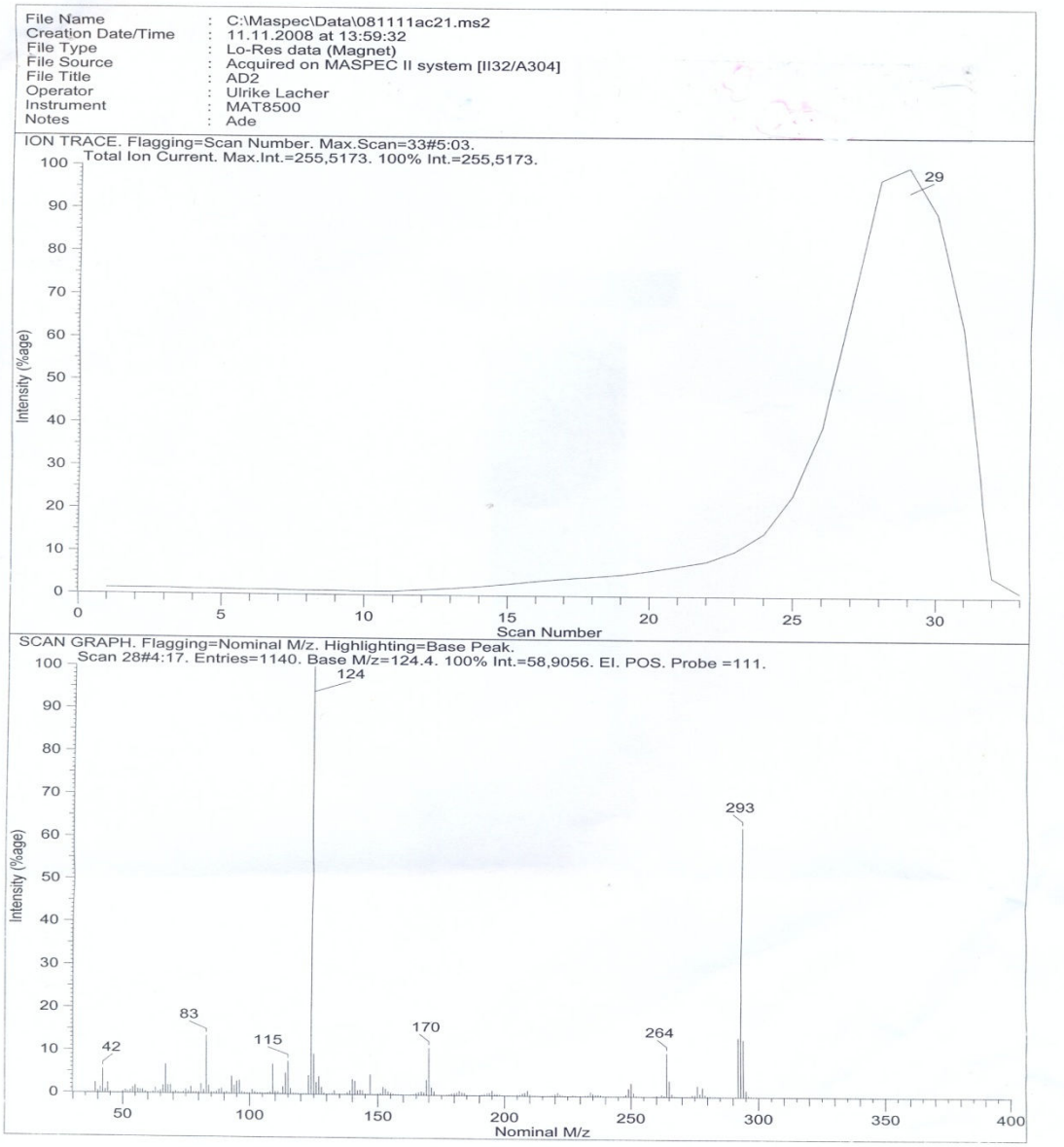
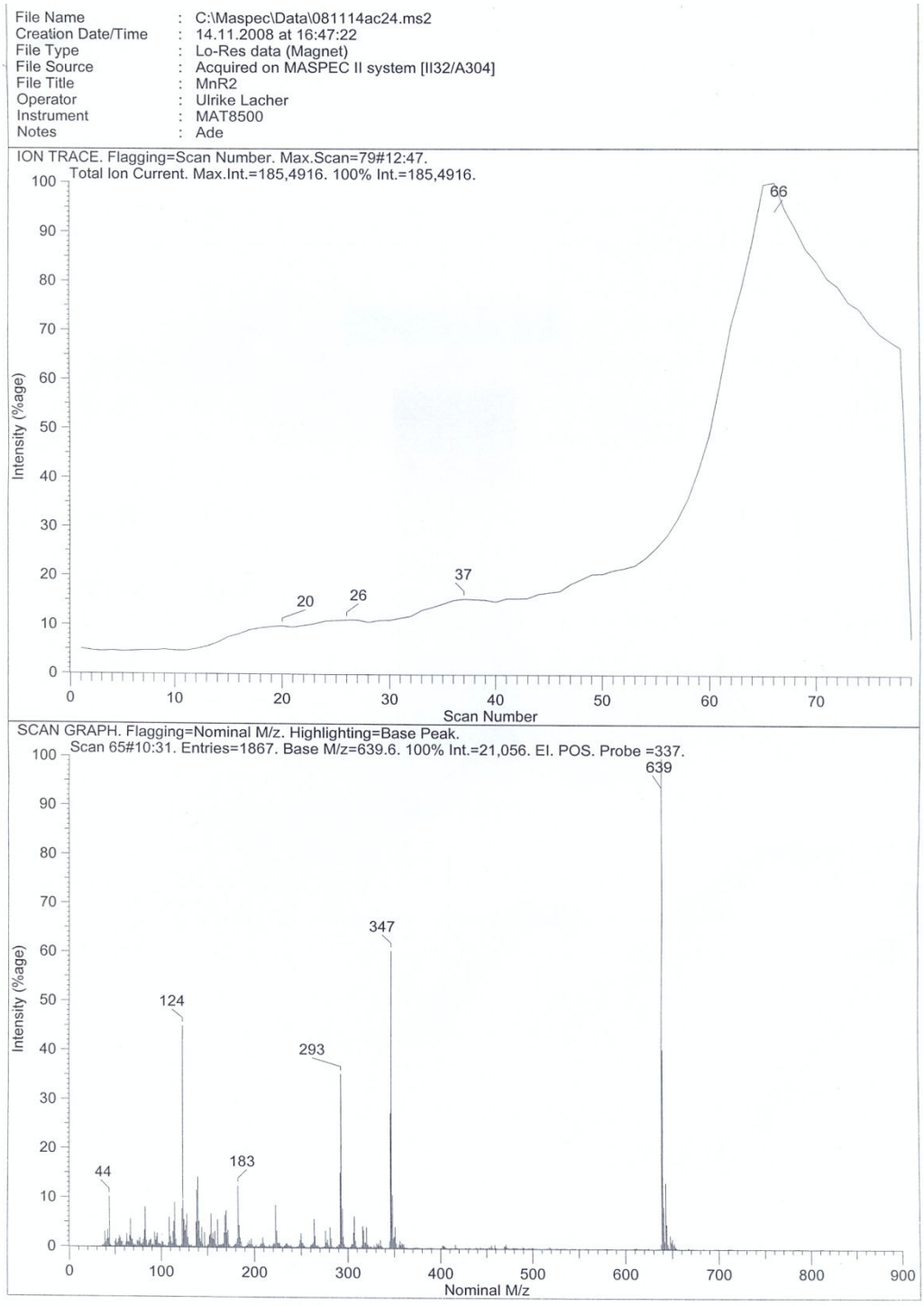
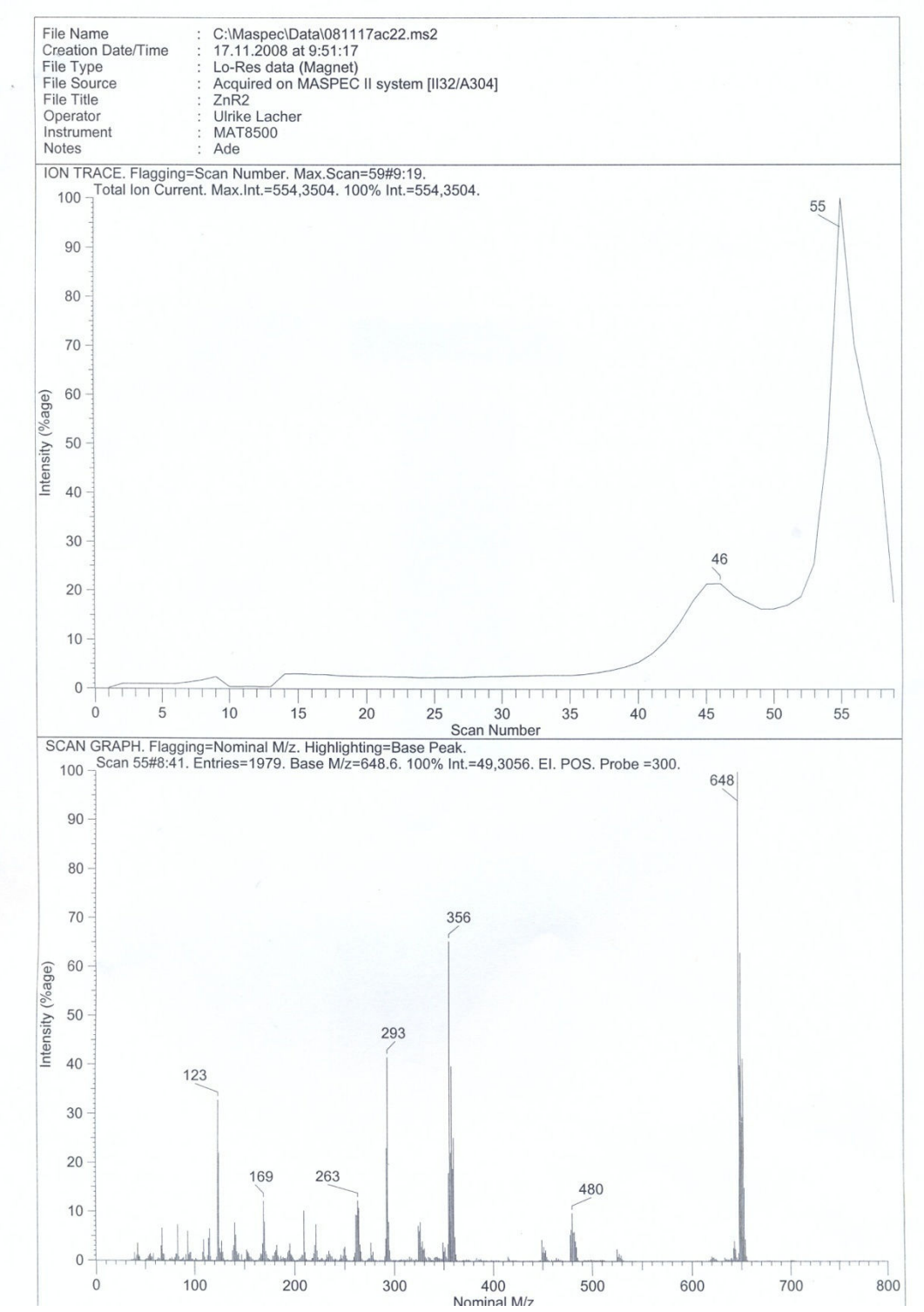
SUPPLEMENTARY DATA



Appendix 1. Mass spectrum of the ligand



Appendix 2. Mass spectrum of the Mn(II) complex



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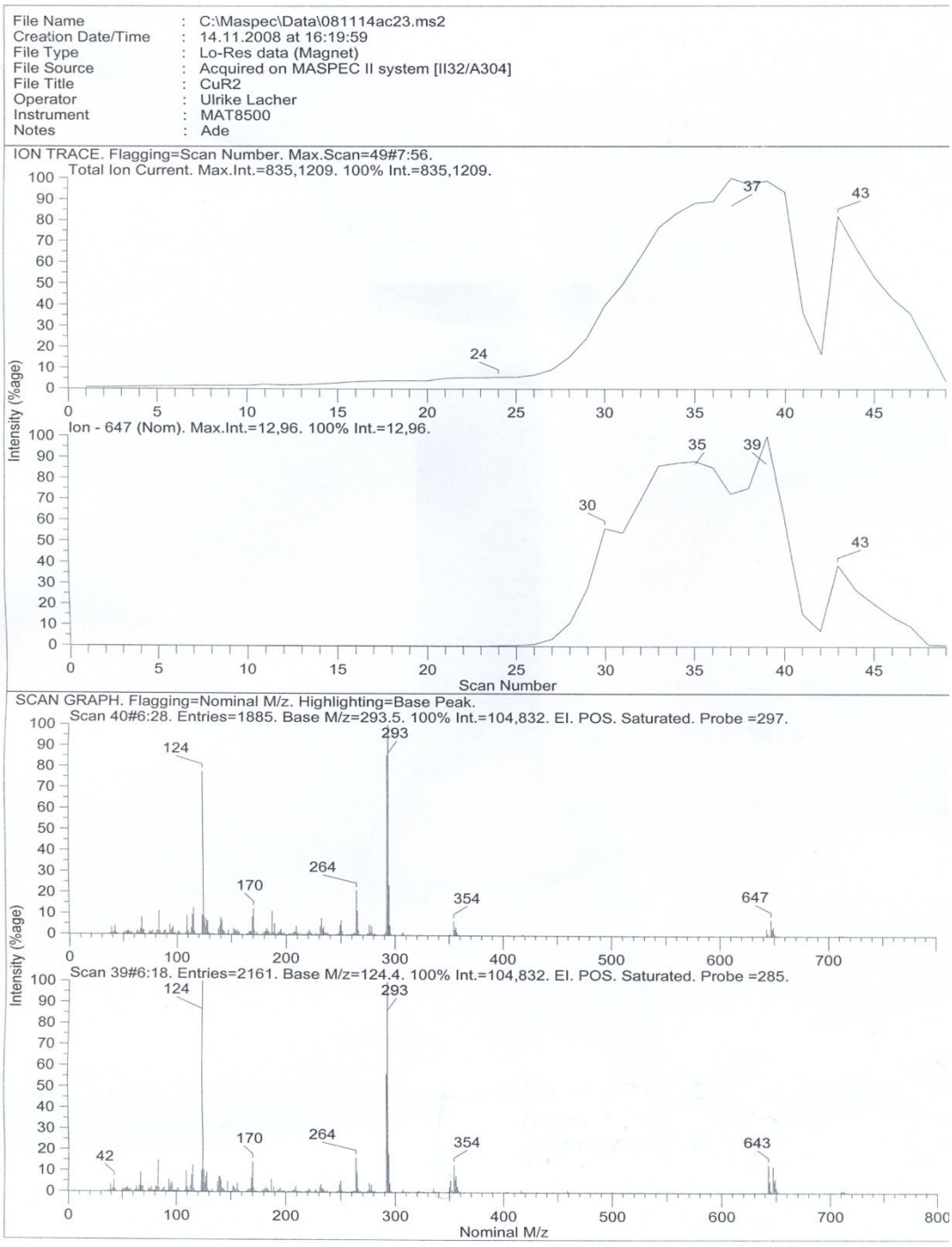
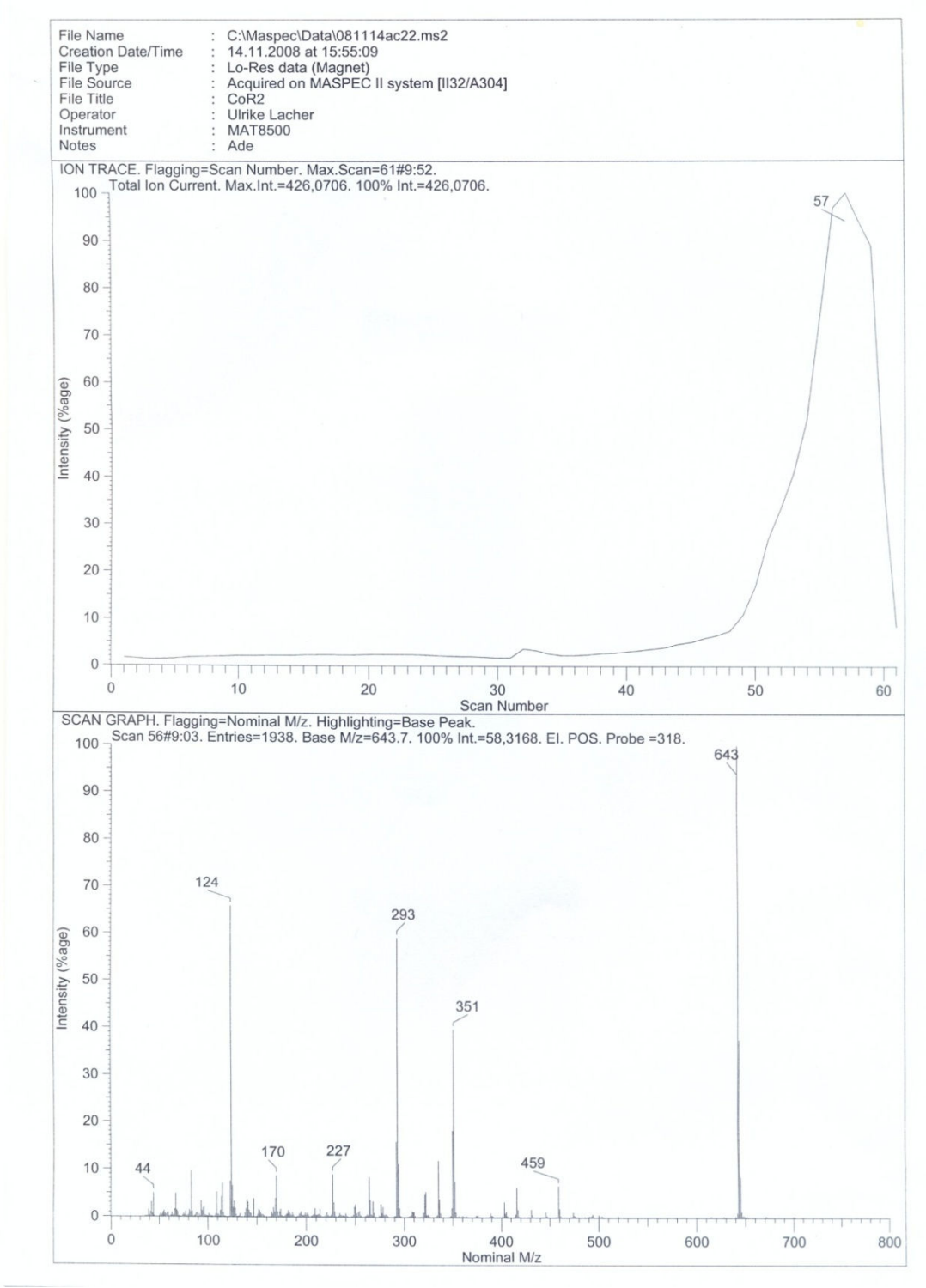
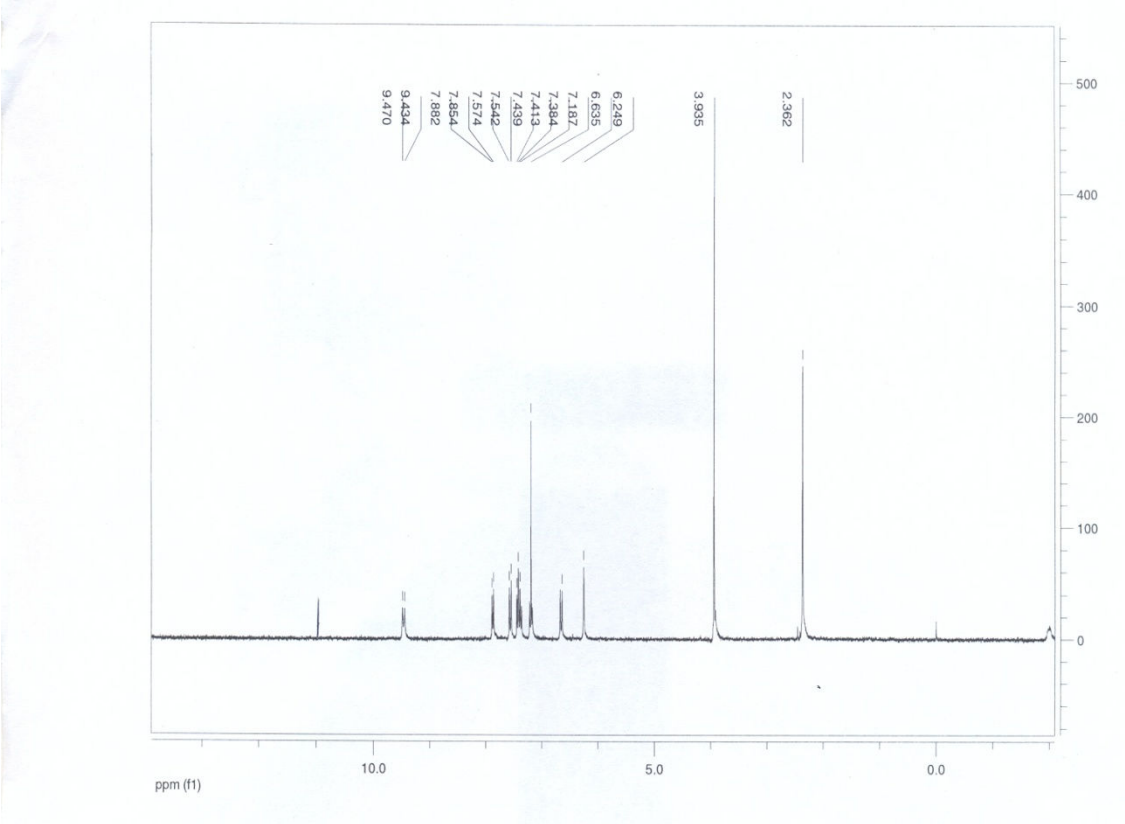


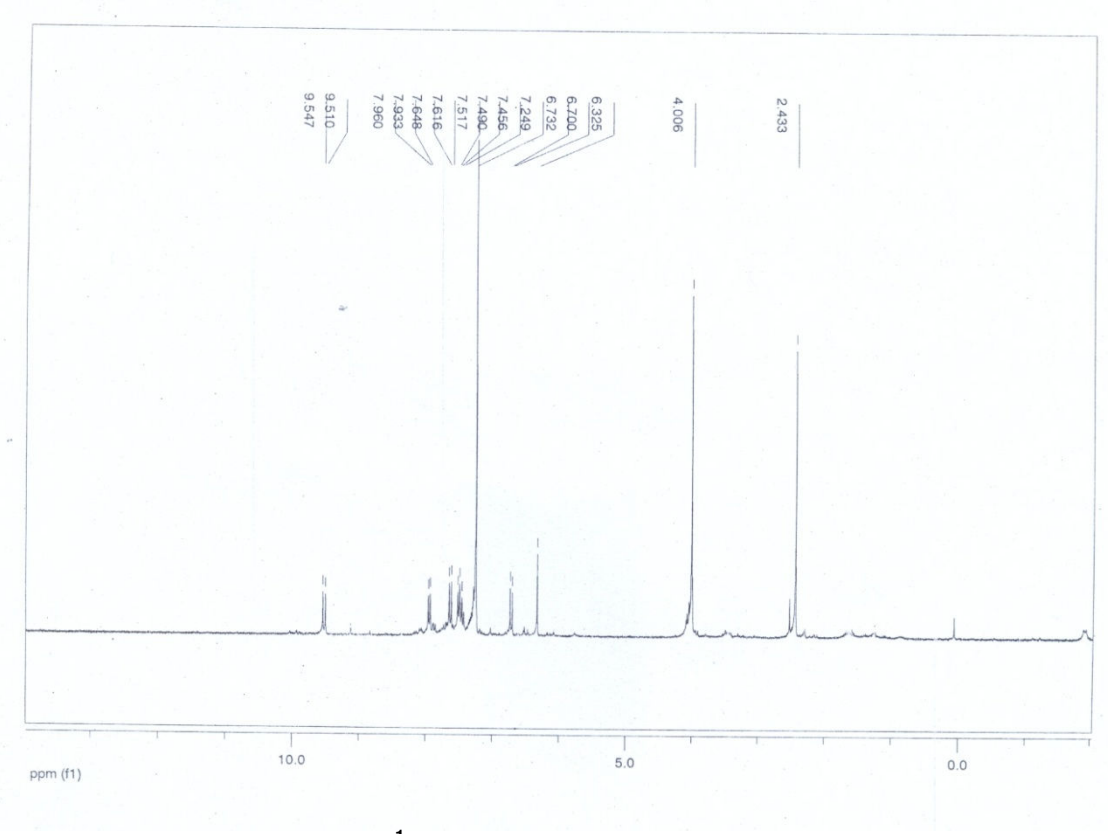
Appendix 4. Mass spectrum of the Cu (II) complex



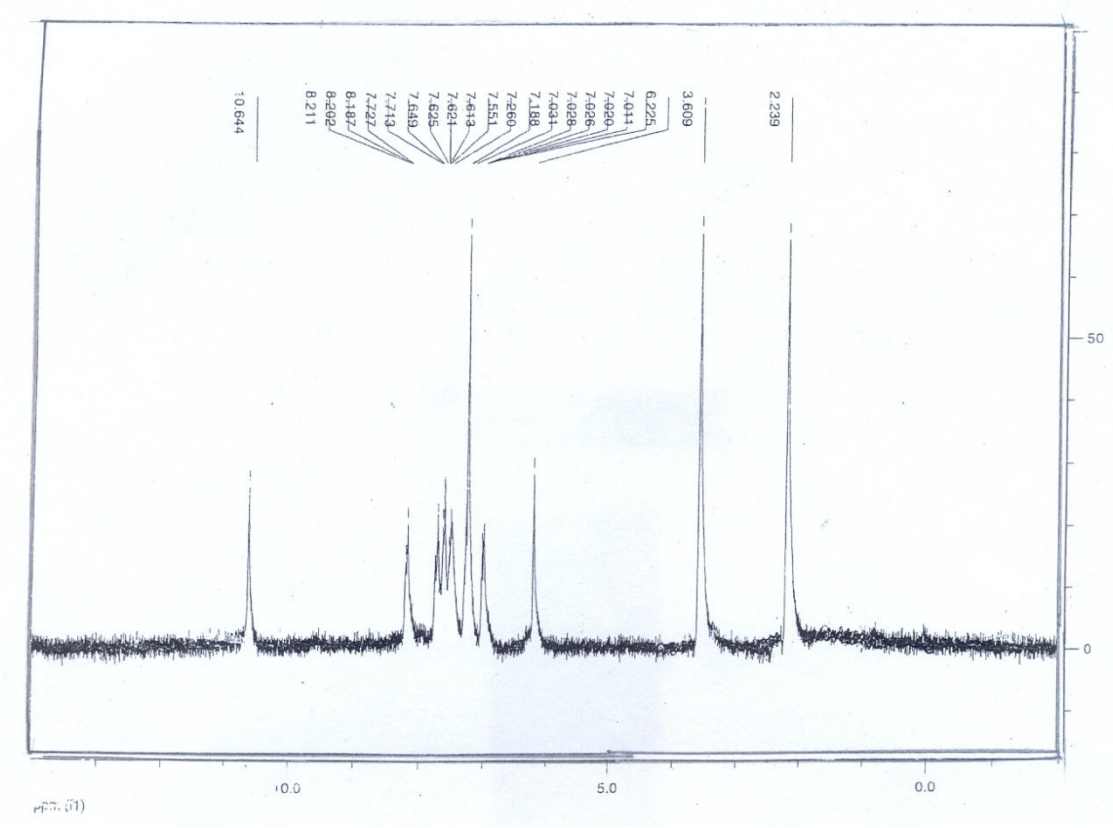
Appendix 5. Mass spectrum of the Co (II) complex



Appendix 6. ^{1}HNMR spectra of the ligand



Appendix 7. ^{1}HNMR spectra of the Pd (II) complex



Appendix 8. ^{1}HNMR spectra of the Zn(II) complex