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Spectral, Magnetic, Thermal and Antibacterial Properties of Some Metal (II) Complexes of Aminoindanyl Schiff Base

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Abstract: The Schiff base, 2-(Indan-4-yliminomethyl)-6-methoxy-phenol and its Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes were synthesized and characterized by microanalysis, magnetic susceptibility, conductance, thermal, infrared and electronic spectral measurements. The ligand was bidentate, coordinating through the phenolic *O* and imine *N* atoms. The Mn(II), Co(II) and Zn(II) complexes were formed as $[ML(NO_3)]$ while Ni(II), Cu(II) and Pd(II) complexes were isolated as $[ML_2]$. Spectroscopic and magnetic data were consistent with the adoption of tetrahedral/square planar geometry for the Cu(II), Zn(II), Ni(II) and Pd(II) complexes. The complexes were all magnetically diluted and monomeric with exceptions of the Mn(II) and Co(II) complexes which were magnetically concentrated. They were isolated as air-stable powdery solids with high melting points, which decomposed on programmed heating mostly to the metals. The antibacterial activities of the ligand and its complexes against five Gram negative (*Enterobacter cloacae, Salmonella arizonae, Serratia sp. Escherichia coli* and *Pseudomonas sp.*) and three Gram positive (*Staphylococcus aureus*, *Chromobacter violaceum* and *Bacillus sp.*) bacteria were reported. The Cu(II) and Co(II) complexes had broad-spectrum activity like gentamycin (17.0-50.0 mm), although much lower, with inhibitory zones range of 7.0-14.0 and 7.0-20.0 mm respectively.

Key words: Antibacterial Properties · Magnetically Dilute · Magnetically Concentrated · Schiff Base

INTRODUCTION

Amino indane and its derivatives are associated with lots of bioactivities such as analgesics, HIV protease inhibitors and anticonvulsants [1-4]. Moreover, Schiff bases derived from indane-1, 3-dione-2-imine-N-acetic acid and 2-imino-N-2-propionic acid and ninhydrin, glycine /L-alanine and their metal (II) chelates exhibit unique geometries and good antimicrobial activities against *E. coli, P. mirabilis, S. aureus* and *P. faecalis* [5-6]. A detailed literature search has shown that no work is reported on the Schiff base, 2-(Indan-4-yliminomethyl)-6-methoxy-phenol (derived from condensation of 4-aminoindane and o-vanillin) and its Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes [7-10]. Thus, our aim was to synthesize and characterize the above named Schiff base and its metal (II) complexes in order to investigate their magnetic, thermal and antibacterial properties for possible magnetic behaviors such as anti- and ferro-magnetisms, probable use as metal precursor in material science and broad-spectrum activities against pathogenic bacteria. Consequently, this research work is a continuation of our studies on the synthesis, characterization and bioactivities of some metal (II) complexes of various Schiff bases [11-16].

MATERIALS AND METHODS

Reagents and Solvents: Reagent grade 4-aminoindane and o-vanillin (Aldrich) and hydrated manganese(II) nitrate, cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate and palladium(II) chloride (BDH chemicals) were used as received. Solvents were purified by standard methods [17]. The elemental analyses for C, H and N were recorded on GmbH Vario El analyser. Manganese, cobalt, nickel, copper, zinc and palladium were determined titrimetrically [18].

Preparation of the Schiff Base: The ligand, 2-(Indan-4-yliminomethyl)-6-methoxy-phenol, HL, was prepared by refluxing a 50 mL ethanolic solutions of 9.85 mmol (1.50 g) of o-vanillin and 9.85 mmol (1.31 g) 4-amino indane to

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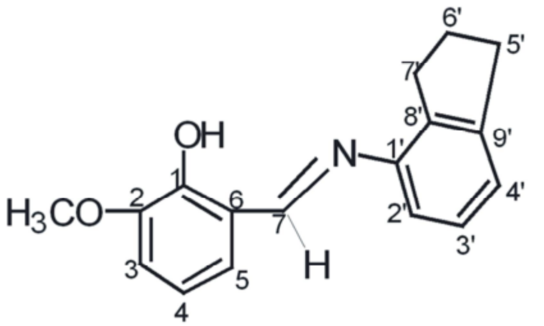

Fig. 1: Structural formula of 2-(Indan-4-yliminomethyl) -6-methoxy-phenol.

which 6 drops of acetic acid were added for 6 h. The orange product, formed on cooling in ice, was filtered and recrystallized from ethanol and dried *in vacuo* over anhydrous calcium chloride [12]. The yield of the resulting Schiff base (Figure 1) was 1.84 g (70%); ^{1}H nmr (ppm) δ 11.12(s, 1H, C^{1}OH), δ 9.92(s, 1H, HC^{7}N), δ 7.17-8.64 (m, 3H, C^3, C^4, C^5); δ 3.94 (s, 3H, C^{2}OCH$_3$). Indane ring: δ 7.00-7.06 (m, 3H, C$^{2'}$,C$^{3'}$, C$^{4'}$); δ 6.88-6.97 (t, 2H, C$^{7'}$); δ 2.96-3.04 (q, 2H, C$^{6'}$); δ 2.09-2.14 (t, 2H, C$^{5'}$).

Preparation of the Metal (II) Complexes: The various complexes were prepared by refluxing a homogeneous solution of 0.30 mmol (0.053-0.089 g) of hydrated M (II) nitrates (M = Mn, Co, Ni, Cu, Zn) and 0.60 mmol (0.16 g) of the ligand, to which 0.60 mmol (0.061 g) of triethylamine was added in 30 mL ethanol for 6 h. The products formed were filtered, washed with ethanol and dried *in vacuo* over anhydrous calcium chloride [13]. The same procedure was used for the preparation of the Pd (II) complex from its chloride. The yields were 0.08 g(70%), 0.08 g(70%), 0.13 g (70%), 0.09 g(50%), 0.08 g(70%) and 0.10 g(50%).

Proton nmr measurements were done only for the diamagnetic Zn(II) and Pd(II) complexes; Zn(II) complex: ^{1}H nmr (ppm) δ 8.95(s, 1H, HC^{7}N), δ 7.19-7.24 (m, 3H, C^3, C^4, C^5); δ 3.94 (s, 3H, C^{2}OCH$_3$) and indane ring: δ 7.13-7.17 (m, 3H, C$^{2'}$,C$^{3'}$, C$^{4'}$); δ 6.87-7.11 (t, 2H, C$^{7'}$); δ 2.90-2.95 (q, 2H, C$^{6'}$); δ 2.03-2.08 (t, 2H, C$^{5'}$).

Pd(II) complex was ^{1}H nmr (ppm) δ 8.52(s, 1H, HC^{7}N), δ 7.04-7.25 (m, 3H, C^3, C^4, C^5); δ 3.94 (s, 3H, C^{2}OCH$_3$) and indane ring: δ 6.54-6.77 (m, 3H, C$^{2'}$,C$^{3'}$, C$^{4'}$); δ 6.34-6.43 (t, 2H, C$^{7'}$); δ 2.86-3.02 (q, 2H, C$^{6'}$); δ 1.93-1.98 (t, 2H, C$^{5'}$).

Antibacterial Assay: The assay was carried out on the ligand and its metal (II) complexes. The bacteria used were identified laboratory strains of *E. cloacae, S. arizonae, Bacillus sp, S. aureus, Serratia sp. Pseudomonas sp. E. coli* and *C. violaceum*. The antibacterial susceptibility test was carried out using the agar well diffusion technique [5]. The surface of the agar plate (Muller Hinton) was uniformly inoculated with 0.3 mL of 18 h old test bacteria culture (10^6 CFU/ mL). Using a sterile cork borer, 6 mm wells were bored into the 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 minutes before incubation at 37°C for 24 h after which inhibitory zones (in mm) were taken as a measure of antibacterial activity. The experiments were conducted in duplicates and gentamycin was used as the reference drug.

Physical Measurements: 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 quoted in ppm. Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance at room temperature (26°C) and diamagnetic corrections were calculated using Pascal's constants [19]. The reflectance spectra were recorded on a Perkin-Elmer λ25 spectrophotometer equipped with an integrating sphere. The infrared spectra were measured as KBr discs on a Perkin-Elmer FTIR spectrum BX spectrophotometer in the range 4000-400 cm^{-1}. Electrolytic conductivities of the compounds in nitromethane were determined using a MC-1, Mark V conductivity meter with a cell constant of 1.0 and melting points (uncorrected) were recorded on a Stuart scientific melting point apparatus smp3.

RESULTS AND DISCUSSION

The Schiff base and its chelates were obtained in moderate-good yields (50-70%). All complexes isolated adopted [ML$_2$]xH$_2$O stoichiometry, except for the Mn(II), Co(II) and Zn(II) complexes that were formed as [ML(NO$_3$)]. Evidence for the formation of the ligand (Figure 1) in pure form was from microanalyses and ^{1}H nmr. The generalized equations for the formation of the complexes are:

$M(NO_3)_2{\bullet}2H_2O + 2HL \rightarrow [ML_2]0.3H_2O + 2HNO_3 + 1.7H_2O$
{Where M = Ni(II), Cu(II)} (1)
$M(NO_3)_2{\bullet}6H_2O + HL \rightarrow [ML(NO_3)] + HNO_3 + 6H_2O$ (2)
{Where M = Mn(II), Co(II), Zn(II)}

Table 1: Analytical data for the compounds

Compound	Formula			%		M.pt	Analysis (Calculated)			
(Empirical formula)	mass	Color	μeff	Yield	$\Lambda_m{}^*$	(°C)	%C	%H	%N	% M
HL	267.32	Orange	-	70	-	84-85	76.20	6.34	5.20	
($C_{17}H_{17}NO_2$)							(76.38)	(6.41)	(5.24)	-
$[MnL(NO_3)]_2$	383.27	Orange	4.24	70	18.0	245-246	53.25	4.43	7.51	14.35
($Mn_2C_{34}H_{32}N_4O_{10}$)							(53.27)	(4.21)	(7.31)	(14.33)
$[CoL(NO_3)]_2$	387.26	Yellow	3.26	70	22.0	236-237	52.79	4.20	7.37	15.20
($Co_2C_{34}H_{32}N_4O_{10}$)							(52.73)	(4.17)	(7.23)	(15.22)
$[NiL_2]0.3H_2O$	596.76	Olive	0.30	70	15.0	230-231	68.35	5.46	4.58	9.78
($NiC_{34}H_{32.6}N_2O_{4.3}$)		Green					(68.43)	(5.51)	(4.69)	(9.84)
$[CuL_2]0.3\ H_2O$	601.60	Dark	1.75	50	20.0	181-182	68.02	5.42	4.54	10.54
($CuC_{34}H_{32.6}N_2O_{4.3}$)		Purple					(67.88)	(5.46)	(4.66)	(10.56)
$[ZnL(NO_3)]$	393.33	Orange	D	70	16.0	239-240	52.19	4.24	7.19	16.48
($CuC_{17}H_{16}N_2O_5$)		Yellow					(51.91)	(4.10)	(7.12)	16.53)
$[PdL_2]2.5H_2O$	684.09	Green	0.30	50	13.0	170-171	59.63	5.45	4.15	16.55
($PdC_{34}H_{37}N_2O_{6.5}$)							(59.70)	(5.45)	(4.10)	(15.55)

D= diamagnetic

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

Compound	νOH	ν(C=N)	νPh/C¯O	δC¯H	ν(M¯N)	ν(M¯O)	Electronic transitions (kK)
[HL]	3440b	1612s 1569s	1465s 1361s	970s	-	-	33.50, 36.25, 40.20
$[MnL(NO_3)]$	-	1637s 1504s	1233s 1171s	881s 749s	524m 502s	451m 433s	14.30, 19.60, 31.60, 38.20, 40.80
$[CoL(NO_3)]$	-	1639s 1501s	1214m 1174m	864s 789m	551s 528m	487m 446m	12.50, 17.20, 30.09, 35.20, 41.24
$[Ni(L)_2]0.3H_2O$	3500b	1604s 1581s	1258s 1210s	868s 744m	560s 549s	499m 462s	18.0, 27.0, 32.70, 39.50, 42.10
$[Cu(L)_2]0.3H_2O$	3500b	1588s 1514s	1288m 1181m	859s 749s	524s 517s	481s 429s	15.20, 23.80, 30.71, 33.26, 41.30
$[ZnL(NO_3)]$	-	1639s 1502s	1213m 1173m	864s 788m	528s 516m	481m 429m	28.40, 34.00, 45.00
$[Pd(L)_2]2.5H_2O$	3500b	1603s 1541s	1244s 1168s	864m 795m	544m 528m	480m 432m	17.24, 29,0, 34.26, 45.00

Key: s = strong, m = medium, b = broad, 1 kK = $1000cm^{-1}$

Table 3: Thermal data for the studied complexes

		TG weight loss (%)		
Compound	Temperature range (°C)	Calc.	Found	Assignments
HL	30-100	5.99	5.98	½O_2
($C_{17}H_{17}NO_2$)	100-180	11.97	11.86	$C_2H_6 + H_2$
	180-700	82.02	82.16	$C_{15}H_9NO$
$[MnLNO_3]$ ($MnC_{17}H_{16}N_2O_5$)	30-210	7.83	10.91	$N_2 + H_2$
	210-320	24.02	26.52	C_6H_4O
	320-700	53.75	56.89	$C_{11}H_{10}O_4$
				Mn(residue)
$[CoLNO_3]$($CoC_{17}H_{16}N_2O_5$)	30-180	3.62	4.04	½N_2
	180-310	23.76	26.89	C_6H_6N
	310-700	57.33	58.57	$C_{11}H_{10}O_5$
				Co (residue)
$[NiL_2]0.3\ H_2O$	30-210	3.25	2.70	$0.3H_2O$ + ½N_2
($NiC_{34}H_{32.6}N_2O_{4.3}$)	210-360	21.78	22.12	C_9H_8N
	360-700	59.05	59.85	$C_{22}H_{24}O_4$
				NiO(residue)
$[CuL_2]0.3H_2O$	30-230	13.86	14.05	$0.3H_2O + C_6H_6$
($CuC_{34}H_{32.6}N_2O_{4.3}$)	230-400	46.21	46.34	$C_{19}H_{18}O_2$
	400-700	29.32	30.0	$C_9H_8N_2O_2$
				Cu(residue)
$[ZnLNO_3]$	30-170	7.63	9.84	$N_2 + H_2$
($ZnC_{17}H_{16}N_2O_5$)	170-320	23.90	25.65	C_6H_6O
	320-700	51.87	53.91	$C_{11}H_8O_4$
				Zn(residue)
$[PdL_2]2.5H_2O$	30-220	6.60	6.61	$2.5H_2O$
($PdC_{34}H_{37}N_2O_{6.5}$)	220-320	33.48	33.64	$C_{11}H_{21}N_2O_3$
	320-700	39.03	39.21	$C_{20}H_{11}O$
				PdO(residue)

Table 4: Zones of inhibition (in mm) of the compounds against various bacterial isolates.

Complexes	E. cloacae	S. arizonae	Bacillus sp	S. aureus	Serratia sp	P. Fluorescence	E. Coli	C. violaceum
HL	7.0±0.1	25.0±0.1	11.0±0.1	12.0±0.1	7.0±0	R	13.0±0.1	7.0±0.1
[MnL(NO$_3$)]	9.0±0.1	R	7.0±0.1	7.0±0.01	11.0±0	9.0±0.2	8.0±0.25	7.0±0.1
[CoL(NO$_3$)]	15.0±0.1	9.0±0.02	20.0±0.02	13.0±0.3	14.0±0.2	7.0±0.2	13.0±0	8.0±0.1
[Ni(L)$_2$]0.3H$_2$O	R	8.0± 0.1	25.0±0.5	8.0±0.1	9.0±0	7.0±0.1	8.0±0.1	R
[Cu(L)$_2$]0.3H$_2$O	7.0±0.2	10.0±0	14.0±0.3	10.0±0	13.0±0.1	7.0±0.2	10.0±0	9.0±0
[ZnL(NO$_3$)]	7.0±0.35	20.0±0.3	10.0±0	7.0±0.35	9.0±0	7.0±0.2	R	8.0±0.2
[PdL$_2$]2.5H$_2$O	7.0±0.2	10.0±0.01	13.0±0	7.0±0.1	12.0±0.02	7.0±0.01	7.0±0.3	R
Gentamycin$^+$	40.0±0	36.0±0.2	50.0±0.2	35.0±0.1	30.0±0	17.0±0.03	30.0±0.12	40.0±0.1

R= resistant, $^+$ = Positive standard, *E. cloacae = Enterococcus cloacae*; *S. arizonae = Salmonella arizonae*; *S. aureus = Staphylococcus aureus*; *E. Coli = Escherichia coli*; *C. violaceum = Chromobacter violaceum*; *P. fluorescence = Pseudomonas fluorescence*

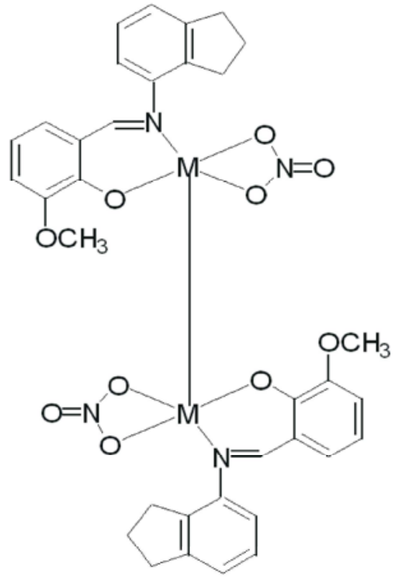

Fig. 2: The proposed structure for the Mn(II) and Co(II) complexes.

Single x-ray diffraction measurements could not be done due to the formation of non-suitable crystals. The molar conductivities of the complexes in nitromethane were in the range 13-22 ohm^{-1} cm^2 mol^{-1}, showing that they were non-electrolytes in the solvent. A value of 90-115 ohm^{-1} cm^2 mol^{-1} was expected for a 1:1 electrolyte [20].

^{1}Hnmr Spectra: The phenolic proton was observed at δ 11.12 ppm, while the imine proton was seen as a singlet at δ 9.92 ppm. The proton on C^3, C^4 and C^5 resonated as a multiplet at δ 7.17-8.64 ppm and 3H of the methoxy group was seen as a singlet at δ 3.94 ppm. The protons at C$^{2'}$, C$^{3'}$and C$^{4'}$ in indane ring were observed as a multiplet at δ 7.00-7.06 ppm. The 2H at C$^{5'}$ came up as a triplet at δ 2.09-2.14 ppm while those at C$^{6'}$ resonated as quintet between δ 2.96-3.04 ppm. Finally, the 2H at C$^{7'}$ resonated as a triplet between δ 6.88-6.97 ppm.

In the spectra of the Zn(II) complex, the phenolic proton at δ 11.12 ppm was absent. This confirmed coordination through the phenol O atom. The imine proton was seen as a singlet at δ 8.95 ppm while 3H of the methoxy group appeared as a singlet at δ 3.94 ppm. The proton at C^3, C^4, C^5 resonated as a multiplet at δ 7.19-7.24 ppm, while those of C$^{2'}$, C$^{3'}$ and C$^{4'}$ in indane ring resonated as a multiplet and were up shifted to δ 7.13-7.17 ppm. The 2H at C$^{5'}$ were seen as a triplet and were down shifted to δ 2.03-2.08 ppm while those at C$^{6'}$ resonated as quintet and were also down shifted to δ 2.90-2.95 ppm. The 2H protons at C$^{7'}$ resonated as a triplet between δ 6.87-7.11 ppm and were up shifted. These shifts are indicative of coordination through the imine N atom [10].

Similarly, the spectrum of the Pd complex showed the absence of the phenolic proton at δ 11.12 ppm, which confirmed coordination through the phenol O atom. The imine proton was seen as a singlet at δ 8.52 ppm while the 3H of the methoxy group was observed as a singlet at δ 3.94 ppm and the proton at C^3, C^4 and C5 resonated as a multiplet at δ 7.04-7.25 ppm and were down shifted. All the protons in the indane ring were downshifted related to that of the ligand as follows, the proton at C$^{2'}$, C$^{3'}$ and C$^{4'}$ were observed as a multiplet at δ 6.54-6.77 ppm. The 2H at C$^{5'}$ was seen as a triplet at δ 1.93-1.98 ppm, while those at C$^{6'}$ resonated as quintet between δ 2.86-3.02 ppm and the 2H at C$^{7'}$ resonated as a triplet between δ 6.37-6.43 ppm. These shifts are indicative of coordination through the imine N atom [21].

Infrared Spectra: The relevant infrared data are presented in Table 2. The assignments of the infrared bands were made by comparing the spectra of the compounds with reported literature on similar systems [5-6, 11-16]. The broad band at 3440 cm^{-1} in the ligand was assigned as νOH. Its broadness is attributed to intramolecular hydrogen bonding [5]. The disappearance of this band in the complexes indicated the involvement of the phenolic *O* in bonding to the metal ions. The new broad band at

3500 cm^{-1} in the hydrated complexes was assigned to ν(OH) of crystallization water. The uncoordinated C=N stretching vibrations in the ligand were seen in the range 1612-1569 cm^{-1} [14-15]. These bands were bathochromic/hypsochromic shifted to 1639-1501 cm^{-1} in the metal complexes, confirming the involvement of the imine *N* atom in coordination to metal (II) ion. The δC¯H vibration of the ligand was observed at 970 cm^{-1} and it suffered a bathochromic shift to 868-744 cm^{-1} in the complexes due to the pseudo-aromatic nature of the chelates [14]. Further, evidence of coordination was the appearance of bands due to ν(M¯O) and ν(M¯N) in the complexes at 498-429 and 598-502 cm^{-1} respectively.

Electronic Spectra and Magnetic Moments: The electronic spectra are presented in Table 2. The spectra of Mn(II) complexes are usually characterized by forbidden transitions from the $^6A_1$ to higher quartet states for all geometries. The Mn(II) complex had two weak bands at 14.30 and 19.60 kK, typical of a tetrahedral geometry and were assigned to the forbidden transitions $^6A_1 \rightarrow {}^4E_1$ (ν_1) and $^6A_1 \rightarrow {}^4A_1$ (ν_2) [22]. A moment of 5.92 B.M is usually observed for the Mn(II) compounds, regardless of stereochemistry because the ground term is an A, with no higher T term of the same multiplicity and thus, orbital contribution is nil. The Mn(II) complex studied in this work had a moment of 4.24 B.M. indicative of the presence of some anti-ferromagnetism [25].

The Co(II) complex had absorption bands at 12.50 and 17.20 kK typical of a 4-coordinate, tetrahedral geometry and were assigned to $^4A_{2\,?}\,{}^4T_1(P)$, (ν_2) and $^4A_{2\,?}$ $^4T_1(P)$, (ν_3) transitions [5, 6]. Tetrahedral cobalt(II) complexes were expected to have magnetic moments in the range 4.20-4.60 B.M. However, the cobalt(II) complex studied had a moment of 3.26 B.M. which was lower than expected due to anti-ferromagnetism [19].

The reflectance spectra of the Ni(II) complex showed absorptions typical of a square-planar geometry at 18.00 and 27.00 kK assigned to $^1A_{1g}$? $^1B_{1g}$ and A^1_{1g} ? A^1_{2g} transitions [8,23] and its expectedly diamagnetic with a moment of 0.3 B.M [13].

Copper(II) complexes are often subjected to Jahn-Teller distortions, resulting in unsymmetrical bands and/or occurrence of multiple bands. Regular tetrahedral complexes should have a single broad band below 10.0 kK, while square-planar complexes absorb in the region 10.0-20.0 kK [6, 8]. The observance of two bands at 15.20 and 23.80 kK supports the assignment of the bands to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions in a square planar environment and an observed moment of 1.75 B.M. is indicative of its monomeric nature.

The Zn(II) complex was expectedly diamagnetic with only CT transitions from M?L at 28.40 kK in the visible region [10].

The spectrum of the Pd(II) complex showed typical square-planar, absorptions at 17.24 and 29.00 kK, which were assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$ transitions. The diamagnetic nature of the complex corroborated the assigned geometry [24].

The lower room temperature magnetic moments observed for Mn(II) and Co(II) complexes in this work is attributed to some anti-ferromagnetic interactions, operating through M-M interactions (Figure 2) which couldn't be probed further due to lack of facilities for variable temperature magnetic measurements and non suitable crystal for single x-ray diffraction measurement.

Thermal Studies: The decomposition stages, temperature ranges, percentage losses in mass and assignment of decomposition moieties are given in Table 3. The ligand, HL, decomposed in three stages as follows; stage one corresponded to the loss of half mole of oxygen within the temperature range of 30-100°C, with mass losses of (obs. = 5.98%, calc. = 5.99%). The second stage involved the loss of a mole hydrogen and ethane, with mass losses of (obs. = 11.86%, calc. = 11.97%) within a temperature range of 100-180°C and the final stage was the loss of the organic moiety, $C_{15}H_9O$ within a temperature range of 180-700°C, with mass losses of (obs. = 82.16%, calc. = 82.02%).

The Mn(II) complex decomposed in three steps. The first involved the loss of a mole of nitrogen and a mole of hydrogen, with mass losses of (obs. = 10.91%, calc. = 7.83%) within a temperature range of 30-210°C. The second step involved the loss of the fragment C_6H_4O, with mass losses of (obs. = 26.52%, calc. = 24.02%) between 210-320 °C. The final step was the loss of the organic moiety $C_{11}H_{10}O_4$ at a temperature range of 320-700°C, with mass losses of (obs. = 56.87 %, calc. = 53.75%), leaving behind Mn as the residue.

The thermal degradation of the Co(II) complex occurred in three steps. The first step was within the temperature range of 30-180°C and corresponds to the loss of half mole of nitrogen, with mass losses of (obs. = 4.04%, calc. = 3.62%). The second phase was within the temperature range of 180-310°C, characterized by loss of the fragment, C_6H_6N, with mass losses of (obs. = 26.89%, calc. = 23.76%). The final phase occurred within a temperature range of 310-700°C and equals the loss of the organic moiety $C_{11}H_{10}O_5$, with mass losses of (obs. = 58.57 %, calc. = 57.33%). The final product was cobalt.

The Ni(II) complex decomposed in three steps. The first, was the loss of 0.3 mole of water and half mole of nitrogen within a temperature range of 30-210°C, with mass losses of (obs. = 2.70%, calc. = 3.25%). The second step involved the loss of the organic fragment, C_9H_8N in the temperature range 210-360°C, with mass losses of (obs. = 22.12%, calc. = 21.78%). The last step was the loss of the organic fragment $C_{22}H_{24}O_4$ within the temperature range 360-700°C, with mass losses of (obs. = 59.85%, calc. = 59.05%). The remaining residue was NiO and the C_3 fragment was lost as carbon (IV) oxide.

The Cu(II) complex decomposed in three ways. The first involved the loss of 0.3 mole of water and a mole of C_6H_6 within a temperature range of 30-230°C, with mass losses of (obs. = 14.05%, calc. = 13.86 %). The second was within a temperature range of 230-400°C, which equals the loss of the fragment $C_{19}H_{18}O_2$ (obs. = 46.34%, calc. = 46.21%) and the final stage was within the temperature range 400-700°C and corresponds to the loss of the organic moiety $C_9H_8O_2N_2$ (obs. = 30.00%, calc. = 29.32%). The remaining fraction was copper.

The Zn(II) complex decomposed in three stages. The stage one was within the temperature range 30-170°C, which indicates the loss of a mole of nitrogen and hydrogen, with mass losses of (obs. = 9.84%, calc. = 7.63%). The second stage was in the temperature range 170-320°C, which corresponds to the loss of the fragment, C_6H_6O, with mass losses of (obs. = 25.65 %, calc. = 23.90%). The final stage involved the loss the organic fragment $C_{11}H_8O_4$, within the temperature range 320-700°C, with mass losses of (obs. = 53.91%, calc. = 51.87%). The remaining residue was Zn.

The Pd(II) complex decomposed also in three ways. The first, was the loss of 2.5 mole of water within a temperature range of 30-220°C, with mass losses of (obs. = 6.60%, calc. = 6.61 %). The second, involved the loss of the fragment, $C_{11}H_{21}N_2O_3$ within a temperature range of 220-320°C with mass losses of (obs. = 33.64%, calc. = 33.48%) and the final stage was within a temperature range of 320-700°C, corresponding to the loss of the organic moiety $C_{20}H_{11}O$, with mass losses of (obs.= 39.21%, calc.= 39.03%).The remaining fraction was PdO and the C_3 fragment was lost as carbon(IV) oxide thus, these metal complexes could be used as metal precursors in MOCVD (metal organic chemical vapor deposition) technique in materials science with exceptions of the Ni(II) and Pd(II) complexes [26-27].

Antimicrobial Activity: The results of the antibacterial activities of the compounds are presented in Table 4. Seven organisms; *E. cloacae, S. arizonae, Serratia sp. E. coli, S. aureus, Bacillus sp.* and *C. violaceum* were sensitive to the ligand with inhibitory zones range of 7.0-25.0 mm while *P. fluorescence* was resistant. The metal complexes were mostly more active than the ligand against *Serratia sp. P. fluorescence and Bacillus sp.* .e.g. all the complexes exhibited higher antibacterial activity of 13.0-25.0 mm towards *Bacillus sp.* than the ligand (11.0 mm), with exceptions of Mn(II) and Zn(II) complexes with lower activities of 7.0 and 10.0 mm respectively. Furthermore, all the metal complexes had higher activities than the ligand (7.0 mm) with inhibitory zones range of 9.0-14.0 mm against *Serratia sp*. Similarly, all the complexes were more active against *P. fluorescence* with inhibitory zones range of 7.0-9.0 mm than the ligand, which wasn't inhibitory. Improved activities of the complexes are attributed to chelation, which reduces the polarity of the metal atom, mainly because of partial sharing of its positive charge with donor groups of the ligand and possible ð-electron delocalisation on the aromatic rings. This increases the lipophilic character, favouring its permeation into the bacterial membrane, causing the death of the organisms [28].

On the contrary, the ligand mostly exhibited higher activity than the metal complexes against *S. arizonae, S. aureus* and *E. coli* as follows; the ligand had a higher activity range of 12.0-25.0 mm than the metal complexes, whose inhibitory zones ranged between 8.0-20.0 mm with the exception of the Mn(II) complex which had no activity.

Similarly, the ligand's activity of 12.0 mm against *S. aureus* is higher than that of the complexes, with inhibitory zones range of 7-10 mm, with exception of the Co(II) complex whose activity is 13.0 mm. Furthermore, the sensitivity of *E. coli* to the ligand was 13.0 mm which was the same as that of Co(II) complex. However, with Mn(II), Ni(II), Cu(II) and Pd(II) complexes, the sensitivity was reduced to 7.0-10.0 mm, while the organism was resistant to the Zn(II) complex. The variation in the effectiveness of different complexes against different organisms depends either on the impermeability of the cells of the microbes or the difference in the ribosome of microbial cells [29].

Additionally, the ligand, Pd(II), Cu(II) and Zn(II) complexes all had the same activity of 7.0 mm against *E. cloacae* while Mn(II) and Co(II) complexes had higher activities of 9.0 and 15.0 mm respectively and the Ni(II) complex had no activity. Similarly, *C. violaceum* had a sensitivity of 7.0 mm to the ligand, which was the same as that of the Mn(II) complex, while Co(II), Zn(II) and Cu(II) complexes exhibited higher activity with inhibitory zone range of 8.0-9.0 mm and Ni(II) and Pd(II) complexes had no activity. The Cu(II) and Co(II) complexes were active against the eight bacteria used, thus proving their potential usefulness as a broad-spectrum antimicrobial agent with inhibitory zones range of 7.0-14.0 and 7.0-20.0 mm respectively.

A look at the antibiotic gentamycin whose antibacterial activities (17-50 mm) against the various bacterial isolates relative to the metal complexes (7-25 mm) showed that the activities of the latter were much lower, with the optimum activities being about half that of gentamycin, as seen in $[Ni(L)_2]$, $[CoL(NO_3)]$, $[ZnL(NO_3)]$ and $[MnL(NO_3)]$ against *Bacillus sp*, *Serratia sp*, *S. arizonae* and *P. fluorescence* respectively. Thus, we concluded from the optimum activities, that the organisms were more sensitive to the nitrate complexes, due to the formation of hydrogen bonds through the oxygen atom (of the nitrate group) with the active centers of the cell constituents resulting in interference with the normal cell process [30].

The ligand coordinates to the Ni(II), Cu(II) and Pd(II) ions in the ratio 2L:1M using the azomethine N and phenol O atoms, while it coordinates to the Mn(II), Co(II) and Zn(II) ions in the ratio 1L:1M using the azomethine N, phenol O and nitrate O atoms. The assignment of a monomeric, 4-coordinate, tetrahedral/square-planar geometry for the Zn(II), Ni(II), Cu(II) and Pd(II) complexes is corroborated by elemental analysis, magnetic, thermal, infrared and electronic spectral measurements. The observance of low room temperature magnetic moments in the Mn(II) and Co(II) complexes suggests the existence of some anti-ferromagnetism operating through a dimeric structure. The metal complexes with exceptions of the Ni(II) and Pd(II) complexes could be used as metal precursor in MOCVD (metal organic chemical vapor deposition) technique in material science. The Cu(II) and Co(II) complexes have broad-spectrum activity like gentamycin, although much lower, against the various bacteria isolates used.

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