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Synthesis, Characterization and Antibacterial Activityof Schiff Bases Derived from 4-Dimethylaminobenzaldehyde with Some Amino Acids and 4-Aminoantipyrine toward Cu (II), Ni (II), Co (II), Cd (II) and Mn (II) Ions

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Abstract: *A new chain of Schiff base complexes made up of Cu (II), Co (II), Cd (II),Ni (II), and Mn (II) ions derivatives were obtained by the condensation of 4-dimethyl-aminobenzaldehyde, and 4-aminoantipyrin and some amino acids. The structures of all synthesized complexes were established on the basis of their elemental analysis (UV, FTIR, and [1]HNMR). The study of X-ray crystallographic shows that the compound (Z)-4-((4-(dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (**L_5**) crystallized in monoclinic system with space group of C2/c and the unit cell dimensions are a= 17.7916, b= 6.8610, c= 29.7199, α =90.000 β =101.326 γ = 90.000., Z = 8 and V = 3557.20 Å^3.The antibacterial activity of the complexes are tested against Bacillus subtilis, Bacillus cereus and Pseudomonas aeruginosa.*

Key Words*: Schiff base, 4-dimethyl-aminobenzaldehyde, 4-aminoantipyrin, Schiff base complexes, Bacillus cereus, Pseudomonas aeruginosa and Bacillus subtilis.*

I. Introduction

Schiff bases are an important class of ligands in management science and has a wide range of application in many fields [1]. Schiff bases obtained from the salicylaldehydes are popular polydentate ligands coordinated in neutral forms. Recently, metal complexes of Schiff bases are gaining popularity because of their antibacterial, antifungal and antitumor activities [2-3]. El-ajaily et al.(4) studied the antibacterial activities of the Schiff base derived from the salicylaldehyde and cysteine and its Mn (II), Co(II), Ni (II), Cu (II) and Cd (II) complexes on some pathogenic bacteria. The study intends to create Schiff base complexes of Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) ions which are obtained from the reaction of 4-dimethylaminobenzaldehyde, L-valine, L-tyrosine, L-glycine, L-asparagine or 4-aminoantipyrine). Their geometrical structures are verified using different methods.The antibacterial properties of the complexes have been tested against *Bacillus subtilis, Bacillus cereus and Pseudomonas aeruginosa.*

II. Experimental

2.1Chemicals and reagents

All chemicals and reagents utilised in this study were laboratory pure purchased from Aldrich or BDH which include4-dimethylaminobenzaldehyde, L-valine, L-tyrosine, L-glycine, L-asparagine, 4-aminoantipyrine, NaOH, C_2H_5OH, CH_3OH, $[Cd(C_2H_3O_2)_2.2H_2O]$, $[Co\ (C_2H_3O_2)_2.4H_2O]$, $NiCl_2.6H_2O$, Cu $(CH_3COO)_{2.}H_2O$, $(MnCl_2.4H_2O)$, $CHCl_3$ and dimethyl sulfoxide (DMSO).

2.2 Synthesis of Schiff bases

The amino acid Schiff bases were prepared according to the following procedure:- NaOH (10 mmol, 0.4g) is dissolved in methanol (30 cm^3) and the amino acids [L-valine, L-tyrosine, L-glycine, L-asparagine or 4-aminoantipyrine] (10 mmol) were added to it. The mixtures were stirred with a magnetic there at room temperature. When the mixtures turneds homogeneous, a solution of 4-dimethylaminobenzaldehyde (10 mmol, 1.49 g) in ethanol (20 ml) was added. After 2 minutes the solutions was evaporated to 20% of its original volume and 1ml of acetic acid was added immediately. After 2 hours yellow crystals formed. The crystals were then filtered and washed with ethanol and recrystallized from hot methanol to give yellow crystals with the yield of ca. 75-85 % [4]. The proposed structures for the synthesized Schiff bases are shown in Scheme1:

Scheme 1: Ligand structures

2.3 Synthesis of Schiff base complexes

The Schiff base complexes were produced by mixing 50 ml of methanol containing NaOH (20 mmol, 0.8 g) of the amino acids; [L-valine, L-tyrosine, L-glycine, L-asparagine or 4-aminoantipyrine] (20 mmol) with 50 ml of the methanol solvent in a flask and stirred at room temperature. A solution of 4-dimethylaminobenzaldehyde (20 mmol, 2.98 g) in (50 ml) of ethanol was then added into the solution. After 2 minutes, the metal ions (10 mmol) and the mixtures were stirred magnetically for 3 hours. The solution was evaporated to reduce 75% of the original volume and the residue was left to stand overnight. The products obtained were filtered and recrystallized from a methanol/ethanol (50%) mixture[4].

2.4 Determining antibacterial activities using the agar well diffusion method

Three pathogenic bacteria are exposed to Schiff bases complexes by utilising well diffusion technique [5]. Pathogenic bacteria namely *Bacillus subtilis*, *Bacillus cereus* and *Pseudomonas aeruginosa* are cultured on nutrient agar (NA) plates and incubated at 37 ºC for 24 hours to test for purity colonies. Next, they were inoculated into nutrient broth (NB) for overnight culture. One sterile swab was dipped into the suspension of bacteria 104 and rolled separately on the surface of plates which contains nutrient agar (Oxoid). The plates were then dried in a laminar hood at room temperature for duration of 15 minutes. Then, 6 mm holes are made with a cork borer and 20 µL of nutrient agar were pipetted to cover the base of the hole to prevent leakage Schiff bases and Schiff bases complexes. 150 µL Schiff bases and Schiff bases complexes were added to each hole and the plates were incubated at 37 ºC for 24 hours aerobically. Finally, after 24 hours the diameter of the growth inhibition area around each hole was measured using a ruler and recorded.

III. Results And Discussion

3.1Microanalysis

Table 1 shows the elemental analysis data of Schiff based complexes with the formation of 1:1 [M:L] ratio. The findings are in agreement with the theoretical values. Thin-layer chromatography (TLC) method and elemental analyses. (C, H and N) have been utilised to analyse the purity of the Schiff based complexes.

Table (1): Elemental analysis data of Schiff bases and their complexes

Schiff bases complexes	C%	H%	N%	Mwt	Yield%
L1	68.01	7.69	11.33	248	75%
($C_{14}H_{20}N_2O_2$)	**68.00**	**7.65**	**11.31**		
[$CuL_1(Cl)(H_2O)_3$]3H_2O	29.60	6.83	7.97	454	65%
	28.98	**5,83**	**7.51**		
[$CdL_1(OH)(H_2O)_3$]	39.07	6.05	6.51	430	68%
	39.00	**5.98**	**6.48**		
L2	69.27	6.41	8.97	312	78%
($C_{18}H_{20}N_2O_3$)	**69.26**	**6.40**	**8.91**		
[$MnL_2(OH)(H_2O)_3$]	47.26	5.69	10.50	457	56%
	47.12	**5.70**	**10.47**		
[$NiL_2(OH)(H_2O)_3$]	46.87	5.64	10.42	460.86	70%
	46.80	**5.65**	**10.39**		
L3	57.83	6.02	16.86	249	85%
($C_{12}H_{15}N_3O_3$)	**57.75**	**5.98**	**16.45**		
[$MnL_3(OH)(H_2O)_3$]3H_2O	33.64	6.31	9.81	428	75%
	33.60	**6.29**	**9.80**		
[$CdL_3(Cl)(H_2O)_3$]3H_2O	28.63	5.16	8.35	503	70%
	28.56	**5.10**	**8.33**		
L4	64.07	6.67	13,59	206	80%
($C_{11}H_{14}N_2O_2$)	**64.02**	**6.75**	**13.53**		
[$CuL_4(Cl)(H_2O)_3$]6H_2O	28.33	6.65	5.21	466	66%
	28.30	**6.63**	**5.20**		
[$CdL_4(Cl)(H_2O)_3$]3H_2O	31.13	4.95	6.60	424	60%
	31.00	**4.96**	**6.50**		
L5	71.83	6.63	16.75	334	79%
($C_{20}H_{22}N_4O$)	**71.83**	**6.63**	**16.75**		
[$CoL_5(Cl)_2(H_2O)_2$]	48.09	5.21	11.22	499	70%
	48.00	**5.20**	**11.20**		
[CuL_5(Cl)2] H_2O	49,33	4.93	11.51	486	65%
	50.13	**4.12**	**11.63**		

Bold =Experimental values.

3.2 Infrared spectra

The infrared bands analysis of L-valine, L-tyrosine, L-asparagine and L-glycine Schiff bases show a band at1506- 1630 cm^{-1} rang assignable to νC=N of the azomethine[6]. The infrared spectral data of the same Schiff bases shows a band at 1576 to 1670 cm^{-1}rang which proves the existence of CO groups of the L-glycine, L-valine, L-tyrosine, and L-asparagine[7]. The Schiff bases display a broad band at 3144-3397 cm^{-1} rang which is due to the presence of ν(OH)[8]. The infrared spectra of the present complexes are compared with the free Schiff bases to establish the changes that have taken place during the complexation. Infrared spectral values of complexes portrays bands in the range of 1515 to1602 cm^{-1} assignable to ν(C=N) of the azomethine[9]. A slight change is noticedat ν(C=N) band after complexation. The infrared spectral data of all metal complexes display a band a 1609 to 1631 cm^{-1}, which indicate the existence of C=O group of the carboxyl group. This band is present in the higher and lower frequencies compared to the original position in free ligand that is 1576 to 1670 cm^{-1}. The complexation process uses the oxygen of carboxylic groups of the, L-valine, L-tyrosine, L-asparagine and L-glycine and nitrogen atoms of azomethine groups, the ligands are bidentate. A broad band which ranging from 3091 to 3466 cm^{-1}verifies the existence of water molecules in the separated complexes. δOH disappears and new bands will appear in the spectra of complexes molecules around the range of 469 to 688 $cm^{-1}$and 528 to 660 cm^{-1} are assign to ν(M-O) and ν(M-N) bonding [10]. For the L_5 the infrared spectra of these complexes display a broadband at 3292-3466 cm^{-1} because of the presence of water molecules [11]. The absorption bands at 1610 , 1529 cm^{-1} are dedicate to the existence of ν(C=N) group of azomethine. The change to a lower frequency show how this group is effected by complexation [12]. Another, complexation site that takes part in coordination is the (C=O) group. The proved can be observed at 1613 cm^{-1} in the spectrum of free ligand which may be attributed to (C=O) of a carbonyl group. The shifting from a higher frequency and *vice versa* in the spectra of the complexes suggests the participation of (C=O) group in coordination with the metal ion through the oxygen atom of a carbonyl group of 4-aminoantipyrine [13] .New bands which are not observed in the free Schiff bases are observed at 464-632 and 628-522 cm^{-1} due to ν(M-O) and ν(M–N) vibrations. This provides a good proof for the sharing of the oxygen and nitrogen atoms during complexation [14].

3.3 Electronic spectra

The electronic spectrum of Cu (II)-L^1 complex show bands in the wavelength range of 265-340 nm (8833-11333 cm^{-1}) because of $^2E_g \rightarrow {}^2T_{2g}$ transition and an octahedral geometry is suggested. At the same time, the spectral data of Cu (II)-L^4 Schiff based complex show two bands at 295 and 650 nm (9833 and 21667cm^{-1}) which are accredited to charge transfer transitions. The intensity of these two bands supports the presence of an octahedral structure. For Cu (II)-L^5 complex, the spectrum displays bands in the range of 300 to 680 nm (10000-22667 cm^{-1}) because of charge transfer and $^2T_2g \rightarrow {}^2Eg$ transitions which propose a square planar geometry[15]. The electronic spectrum of Co (II)-L5 Schiff based complex of [Co L_5 $(H_2O)_2(Cl)_2$] illustrate two bands at 320 and 515nm (10667 and 17167cm-1). The first band happens because of ^4T_1g (F) $\rightarrow {}^4T_2g$ (F) transition and the second one occurs due to^4T_1g (F)$\rightarrow {}^4T_1g$ (P) transition. These data illustrate an octahedral geometry. The cadmium complexes display only the charge transfer transitions that can be associated with the charge transfer from ligand to metal and *vice versa*, no d-d transition are expected for d10 Cd(II) complexes [16]. In the electronic spectra of both complexes which are recorded in (DMSO) solution, an absorption band in the range of 270 to 420 nm is noticed and this may be linked with a $\pi \rightarrow \pi^*$ transition originating mostly in the azomethine chromophore (imine $\pi \rightarrow \pi^*$ transition). Cd (II) complexes are colourless and diamagnetic as expected for d10 system. For Ni (II)-L^2 Schiff based complex, the spectrum displays bands in the range of 299 to 560 nm (9967-18667 cm^{-1}) which are linked to$^3A_{2g}$ (F)$\rightarrow {}^3T_{2g}$ (F) and$^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) transitions. These data prove the presence of an octahedral geometry. The electronic spectra of the Mn(II)-L_2 complex illustrates absorption bands at 298nm (17819cm-1),575nm (19167cm^{-1}) which is a feature of octahedral geometry that correspond to $^6A_1g \rightarrow {}^4T_2g$ (G), $^6A_1g \rightarrow {}^4E_1g$, ^4A_1g (G) transitions. The electronic spectra of the Mn(II)-L_3 complex shows absorption bands at 295nm, 380nm (9833-12667 cm^{-1}) which is a feature of octahedral geometry that correspond to $^6A_1g \rightarrow {}^4T_2g$ (G), $^6A_1g \rightarrow {}^4E_1g$, ^4A_1g (G) transitions[17].

Table 2: Infrared assignments (cm^{-1}) and electronic absorption (nm, cm^{-1}) of Schiff bases complexes.

Ligand/Complexes	ν(OH) (H_2O)	ν(COO^-)	ν(C=N)	ν(M-O)	ν(M-N)	υ(NH_2)	λ_{max} nm cm^{-1}	Expected geometry
L1	3395	1670	1583	-	-	-	**253** 8433	-
$[CuL_1(Cl)(H_2O)_3]3H_2O$	3387	1631	1553	653	550	-	**300** 10000 **340** 11333	octahedral
$[CdL_1(OH)(H_2O)_3]$	3289	1620	1594	469	629	-	**280** 9333 **305** 10167	octahedral
L2	3144	1605	1582	-	-	-	**249** 8300	-
$[MnL_2(OH)(H_2O)_3]$	3397	1609	1513	648	528	-	**325** 10833 **575** 19167	octahedral
$[NiL_2(OH)(H_2O)_3]$	3394	1603	1515	645	521	-	**320** 10667 **560** 18667	octahedral
L3	3197	1670	1630	-	-	3097	**285** 9500	-
$[CdL_3(Cl)(H_2O)_3]3H_2O$	3391	1658	1595	608	553	2914	**299** 9967 **385** 12833	octahedral
$[MnL_3(OH)(H_2O)_3]3H_2O$	3363	1641	1602	631	596	2914 ,2806	**299** 9967 **380** 12667	octahedral
L4	3397	1576	1506	-	-	-	**343** 11433	-
$[CuL_4(Cl)(H_2O)_3]6H_2O$	3369	1610	1515	688	545	-	**300** 10000 **650** 21667	octahedral
$[CdL_4(Cl)(H_2O)_3]3H_2O$	3581	1627	1550	681	660	-	**305** 10166 **370** 12333	octahedral
L5	3172	1613	1586	-	-	-	**343** 29155 **362** 27624	-
$[Cu\ L_5\ (Cl)_2]\ H_2O$	3466	1615	1610	464	628	-	**280** 33670 **517** 19342	square planar
$[Co\ L_5(H_2O)_2(Cl)_2]$	3292	1647	1529	632	522	-,	**320** 10667 **515** 17167	octahedral

3.4 ^{1}HNMR spectra

The 1HNMR spectra data of L_1 which is recorded in DMSO-d^6 shows signals at 0.833 , 3.044 and 2.083 ppm that is corresponding to $(CH_3)_2$,$(CH_3)_2N$ and CH groups. The multiplet signals at 6.782 to7.691 ppm are caused by aromatic protons. The -OH of carboxyl group emerged at 10.00 ppm. The data obtained proof the connection between these two groups. Nevertheless, the --NH_2, group vanishes when L_1 is formed, signifying the presence of azomethine group at 8.52 ppm. The ^{1}HNMR spectra data of L_2 which is recorded in DMSO-d^6 shows signals at 2.83 , 2.96 and 4.63 ppm that corresponds with -CH_2,$(CH_3)_2N$ and -CH groups. The signal at 5.91 ppm corresponds to OH Aromatic. The multiplet signals at 6.77 -7.68 ppm are caused by aromatic protons. The signal at 9.90 ppm corresponds with azomethine proton. ^{1}HNMR spectra data of the L_3which is recorded in DMSO-d^6 shows signals at 7.18, 3.075 and 3.36 ppm corresponding to NH_2, $(CH_3)_2N$ and CH groups. The multiplet signal at 6.69 to7.72 ppm are due to aromatic protons. The -OH of carboxyl group appears at 9.664 ppm. These data support the involvement of these two group. Nevertheless, the --NH_2, group will vanish when

L_3 is formed, indicating the presence of azomethine group at 8.03 ppm. The ^{1}H-NMR spectrum of L_4 is recorded in DMSO-d^6 at room temperature and it shows C_6H_5 multiplet at 6.75 to 7.68 ppm, -CH_2 at 3.89 ppm, N-$(CH_3)_2$ at 3.009 ppm and –OH proton appears at 9.996 ppm[18]. Similarly, the --NH_2, group vanishes with the formation of L_4 which indicates the presence of azomethine group at 9.996 ppm. ^{1}HNMR spectra data of L_5 which is recorded in DMSO shows signals at 3.101, 2.97 and 4.49 ppm corresponding to N-CH_3, $(CH_3)_2$N and CH_3 groups[19]. At the same time, the --NH_2, group vanishes with the formation of L_5which indicates the presence of azomethine group at 9.416 ppm. There is an absence of –OH proton due to complexation. A considerable change is observed in all other signals in this complexes[20].

3.5 X-ray crystallographic study of the compound L^5

The X-ray investigation of the compound showed that the compound L_5 crystallized in monoclinic system with space group of C2/c and the unit cell dimensions are a= 17.7916, b= 6.8610, c= 29.7199, α =90.000 β = 101.326 γ = 90.000., Z = 8 and V = 3557.20 Å3. Figure 1 shows the molecular structure with the numbering scheme of the compound, the molecule is discrete and the asymmetric unit consist two molecules. The phenyl rings in each molecule (C1—C6) and (C21—C26) make a dihedral angle of 56.4(7) and 56.4(8)° with the pyrazol heterocyclic ring, respectively. The bond lengths and angles are in normal ranges and comparable to those in N,N′-bis(2,3,4-trimethoxybenzaldiimine)-1,4-diaminocyclohexane[21] (Table 3) .

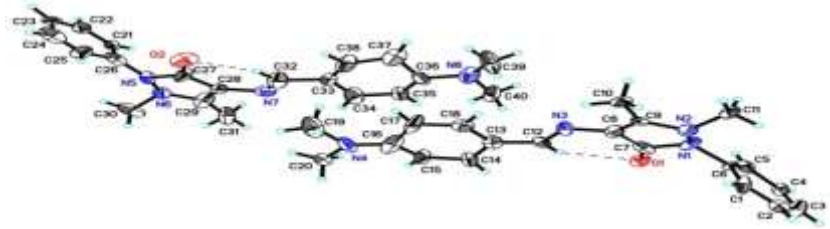

Fig.1. ORTEP diagram of the L5 drawn at 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for Compound L^5

Compound l5			
Bond	Dist.	Angle	(°)
O1-C7	1.237(17)	N2-N1-C7	112.1(9)
O2-C27	1.256(18)	N2-N1-C6	117.2(10)
N1-N2	1.415(17)	C7-N1-C6	121.9(12)
N1-C7	1.438(16)	C9-N2-N1	101.5(10)
N1-C6	1.488(11)	C9-N2-C11	127.5(10)
N2-C9	1.349(14)	N1-N2-C11	114.6(9)
N2-C11	1.431(18)	C12-N3-C8	123.4(12)
N3-C12	1.279(17)	C16-N4-C20	124.4(17)
N3-C8	1.389(13)	C16-N4-C19	121.4(17)
N4-C16	1.317(19)	C20-N4-C19	113.8(12)
N7-C32	1.19(2)	C27-N5-N6	107.3(10)

Both molecules showed the presence of C12—H12….O1 and C32—H32….O2 intramolecular hydrogen bond, as a result a pseudo-six membered O1….H12/C12/N3/C8/C7and O2….H32 /C32/N7/C28/C27 rings are formed (Table 4). In the crystal structure, the molecules are linked by C10—H10A···O1 and C32—H32···O2 intermolecular hydrogen bonds to form dimers. (Fig.2).

Table 4. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Compound L^5

Compound	D—H…..A	D—H	H…..A	D…..A	D—H…..A	Symmetry code
L_5	C12—H12….O1	0.93	2.38	3.059(15)	130	
	C32—H32···O2	0.93	2.25	2.97(2)	133	
	C10—H10A···O1	0.96	2.48	3.360(15)	153	x,-1+y,z
	C20—H20C···O1	0.96	2.56	3.491(19)	164	-1/2+x,1/2+y,z

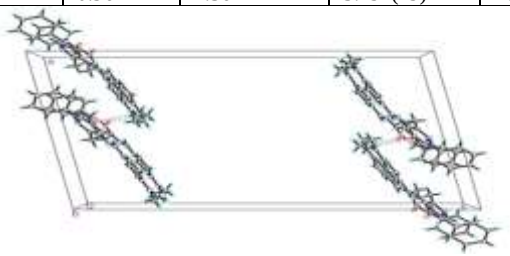

Fig. 2. Molecular packing of L_5 viewed down the b axis. Dashed lines denote C—H….O intermolecular hydrogen bonds.

3.6 Antibacterial Activity

The findings of the antibacterial activities are displayed in Tables 5-9. Schiff based complexes displayed good activities against three kinds of bacteria *namely Bacillus subtilis, Bacillus cereus and Pseudomonus aeruginosa.*

3.6.1 Antibacterial Activity of L^1,Cd (II) and Cu (II)-L^1complexes

The findings of antibacterial activities are displayed in Table 5. Schiff based complexes display good activity against three kinds of bacteria namely *Bacillus subtilis, Bacillus cereus* and *Pseudomonus aeruginosa.* Complexes which are obtained from L^1 show the highest inhibitory influence against the bacteria being tested. Basically, the inhibition area of the complexes increases along with their concentrations. The highest inhibition area is obtained by L^1.Cu against *Bacillus subtilis* whereas the minimum inhibition are is obtained by L^1 against *Bacillus cereus* and *Pseudomonus aeruginosa*. Hence complexation increases the antimicrobial activity. Such increased activity of the metal complexes can also be explained on the basis of chelation theory [4]. According to this, the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible π-electron delocalisation over the whole ring. This increases the lipophilic character of the metal chelate system which favours its permeation through lipid layer of the cell membranes.

Table 5. Diameter of inhibition zone for antibacterial screening of L^1,Cd(II) and Cu(II)-L^1complexes. Inhibition zone diameter in mm

Ligand/Complexes	*Concentration*	*Paeruginosa*	*Bacillus subtilis*	*Bacillus cereus*
L^1	5mg/ml	0	4	0
	10mg/ml	0	6	0
	20mg/ml	0	8	0
$[CdL_1(OH)(H_2O)_3]$	5mg/ml	4	16	4
	10mg/ml	10	19	10
	20mg/ml	19	24	18
$[CuL_1(Cl)(H_2O)_3]3H_2O$	5mg/ml	8	16	6
	10mg/ml	14	19	9
	20mg/ml	22	25	16

Notes: SD inhibition zone = ± 1 mm (biological replicates, 3).

3.6.2 Antibacterial of L^2,Ni(II) and Mn(II)-L^2complexes

In order to test the antibacterial activity of L^2, Ni (II) and Mn (II)-L^2 complexes, more than one test organism is utilised to increase the probability of detecting the antibiotic potential of the tested materials. The sensitivity of a microorganism to antibiotics and other antimicrobial agents are determined by the assay plates which are incubated at 37 ◦C for a day (for bacteria).The compounds which are tested display biological activities against different kinds of Gram-positive and Gram-negative bacteria. The findings are displayed in Table 6. When the biological activity of the Schiff bases and their metal complexes are compared the findings show that the biological activity of Ni (II) and Mn (II) complexes is higher than Ligand. The biological activity of the complexes are Ni (II) > Mn (II).

Table 6. Diameter of inhibition zone for antibacterial screening of L^2,Ni(II) and Mn(II)-L^2complexes. Inhibition zone diameter in mm

Ligand/Complexes	*Concentration*	*Paeruginosa*	*Bacillus subtilis*	*Bacillus cereus*
L^2	5mg/ml	10	11	9
	10mg/ml	13	15	12
	20mg/ml	15	16	14
$[NiL_2(OH)(H_2O)_3]$	5mg/ml	10	13	12
	10mg/ml	14	16	15
	20mg/ml	17	25	18
$[MnL_2(OH)(H_2O)_3]$	5mg/ml	20	10	9
	10mg/ml	20	12	11
	20mg/ml	22	13	12

Notes: SD inhibition zone = ± 1 mm (biological replicates, 3).

3.6.3 Antibacterial Activity of L^3, Cd (II) and Mn (II)-L^3complexes

The antibacterial features of L^3, Cd (II) and Mn (II)-L_3 on test bacteria (two Gram-positive and one Gram-negative) is displayed in Table 7. The findings show that the compounds display antibacterial features against two Gram-positive and one Gram-negative namely *Bacillus cereus*, *Bacillus subtilis* and *Paeruginosa*. Nevertheless, the antibacterial features of Cd(II) and Mn(II) complexes is higher than Ligand. Hence complexation increases the antimicrobial activity. Such increased activity of the metal complexes can also be explained on the basis of chelation theory [10]. According to this, the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible π-electron delocalisation over the whole ring. This increases the lipophilic character of the metal chelate system which favours its permeation through lipid layer of the cell membranes.

Table 7. Diameter of inhibition zone for antibacterial screening of L^3,Cd(II) and Mn(II)-L^3complexes. Inhibition zone diameter in mm

Ligand/Complexes	*Concentration*	*Paeruginosa*	*Bacillus subtilis*	*Bacillus cereus*
L^3	5mg/ml	4	4	4
	10mg/ml	7	8	6
	20mg/ml	9	18	13
$[CdL_3(Cl)(H_2O)_3]3H_2O$	5mg/ml	4	17	14
	10mg/ml	8	19	17
	20mg/ml	19	29	24
$[MnL_3(OH)(H_2O)_3]3H_2O$	5mg/ml	4	4	4
	10mg/ml	6	5	7
	20mg/ml	10	8	13

Notes: SD inhibition zone = ± 1 mm (biological replicates, 3).

3.6.4 Antibacterial Activity of Cd (II), $L^4$and Cu (II)-L^4complexes

The antibacterial features of Cd (II), L^4 and Cu (II) - L^4on three bacteria (two Gram-positive and one Gram-negative) is displayed in Table 8. The findings show that compounds portray antibacterial features against two Gram-positive and one Gram-negative which are notably *Bacillus cereus, Bacillus subtilis,* and *Paeruginosa*. Nevertheless, the antibacterial features of Cd (II) and Cu (II) complexes are higher than ligand.

Table 8. Diameter of inhibition zone for antibacterial screening of L^4, Cu (II) and Cd (II)-L^4complexes. Inhibition zone diameter in mm

Ligand/Complexes	*Concentration*	*Paeruginosa*	*Bacillus subtilis*	*Bacillus cereus*
L^4	5mg/ml	4	4	4
	10mg/ml	5	8	12
	20mg/ml	9	12	14
$[CuL_4(Cl)(H_2O)_3]6H_2O$	5mg/ml	13	19	6
	10mg/ml	18	24	12
	20mg/ml	24	29	14
$[CdL_4(Cl)(H_2O)_3]3H_2O$	5mg/ml	14	16	6
	10mg/ml	19	28	10
	20mg/ml	29	31	20

Notes: SD inhibition zone = ± 1 mm (biological replicates, 3).

3.6.5 Antibacterial Activity of L^5,Co (II) and Cu (II)-L^5complexes

Table 9 displays the findings obtained for antibacterial activities. The Schiff base complexes which are being examined show good response towards three kinds of bacteria namely *Bacillus cereus, Pseudomonus aeruginosa* and *Bacillus subtilis*. Complexes which are obtained from L^5 show the highest inhibitory influence towards the bacteria which are being investigated. Basically, the inhibition area of the complexes increases as their concentration increase. The highest inhibited area is obtained by L^5.Co against *Bacillus subtilis* whereas the least inhibited area is obtained by L^5against Bacillus cereus. Therefore, complexation enhances the anti-microbial activity. This increased activity of metal complexes may also be explained on the basis of the chelation theory [22]. The study chelation reduces the polarity of the metal atom mainly due to the sharing of its partial positive charge with the group of donors and can tc electronic delocalization throughout the cycle. This increases the lipophilicity of the metal chelate system that facilitates its permeation through the lipid bilayer of cell membranes.

Table 9. Diameter of inhibition zone for antibacterial screening of L^5,Cu(II) and Co(II)-L^5complexes. Inhibition zone diameter in mm

Ligand/Complexes	*Concentration*	*Paeruginosa*	*Bacillus subtilis*	*Bacillus cereus*
L^5	5mg/ml	10	11	8
	10mg/ml	13	13	10
	20mg/ml	15	15	12
$[Cu\ L_5\ (Cl)_2]\ H_2O$	5mg/ml	10	8	8
	10mg/ml	24	23	23
	20mg/ml	29	27	26
$[Co\ L_5(H_2O)_2(Cl)_2]$	5mg/ml	20	16	13
	10mg/ml	24	20	18
	20mg/ml	25	22	20

Notes: SD inhibition zone = ± 1 mm (biological replicates, 3).

IV. Conclusion

Schiff base amino acid and 4-Aminoantipyrine complexes were prepared and characterized by based on the elementary analysis. X-ray, infrared, electronic absorption and ^{1}H NMR. An in vitro investigation carried out on the synthesized complexes showed that all the complexes displayed very good results against antibacterial activityof the selected microorganisms which are being examined.

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References

[1] Şakıyan, İ., Gündüz, N. & Gündüz, T. Synthesis and Characterization of Manganese (III) Complexes of Schiff Bases Derived From Amino Acids and 2-Hydroxy-1-naphthaldehyde. Synth. React. Inorg. Met.-Org. Chem, **2001**, 31 (7): 1175-1187.

[2] El-Tajoury, A. N., El-Ajaily, M. M., Maihub, AN A. & Ben Geweirif. N-Salicylideneaminoacidato Complexes of Divalent Transition Metal Ions from the Cysteine Pure and Applied Journal, Sebha University, **2006**,5(1):108-123.

[3] Sarkar S& Dey K. Synthesis and spectroscopic characterization of some transition metal complexes of a New Hexadentate $N_2S_2O_2$ Schiff Base ligand. Spectrochimica Acta Part A **2005**, 62 383-393.

[4] El-Ajaily, M. M., Abdlseed, F. A. & Ben-Gweirif, S. Preparation, Characterization and Antibacterial Activity of Some Metal ion Complexes. E-Journal of Chemistry.**2007**, 4, No. 4, pp. 461-466.

[5] 'Bauer A W, Kirby W M M, Sherris J C & Turck M. Antibiotic susceptibility testing by a standardized single disk method. Amer. I. C/in. Pathol. **1966**, 45:493-6.

[6] Raman,N., . Raja, Y.P . & Kulandaisary, A. Synthesis and characterisation of Cu (II), Ni (II), Mn (II), Zn (II) and VO (II) Schiff base complexes derived fromo-phenylenediamine and acetoacetanilide, Indian Academy of Science. **2001**, 113, 183-185.

[7] Sato,Y., Miyasaka, H., Matsumoto, N. & Okawa H. Synthese, Structures and Magnetic Properties of the Tricyanoethenolate Adducts of Quadridentate Schiff Base Manganese(III) Complexes, Inorg. Chim. Acta 1996, 247, 57-63.

[8] Heinert, D & Martell, A. E. Pyridoxine and Pyridoxal Analogs. V. Syntheses and Infrared Spectra of Schiff Bases. J. Am. Chem. Soc. **1962**, 84, 3257-3263.

[9] Keypour H., Shayesteh M., Sharifi-Rad A., Salehzadeh S., Khavasi H. & Valencia L. Synthesis and characterization of copper(II) and cobalt (II) complexes with two new potentially hexadentate Schiff base ligands. X-ray crystal structure determination of one copper(II) complex. Journal of Organomettalic Chemistry. **2008**, 693, 3179-3187.

[10] Parekh J, Inamdhar P., Nair R., BalujaS. & Chanda S. Synthesis and antibacterial activity of some Schiff bases derived from 4-aminobenzoicacid, J.Serb Chem. Soc. **2005**, 70 (10), 1155-1161.

[11] Abd-Elzaher,M. M. Spectroscopic characterization of some tetradentate Schiff bases and their complexes with nickel, copper and zinc Journal of the Chinese Chemical Society. **2001**, 48, 153-158.

[12] Islam ,M. S & Masiruddin, M. Preparation and characterization of some complexes of chromium (III), cobalt (III) and rhodium (III) ions containing 1, 4, 8, 12-tetra- azacyclopentadecane J. Bangladesh Chem. Soc. **1993**,6 (1): 25.

[13] Prasanna, S.M., Kumar, V., M.L., Hullatti ., K.K. & Manohara, Y.N. Antimicrobial activity of Cissampelos pareira, Cyclea peltata and Stephania japonica methanolic root extracts Journal of Pharmacy and Chemistry. **2007**, 1(1):15-17.

[14] Issa, Y. M., El-Ansary, A. L., Sharif ,O.E. & El-Ajaily, M. M. Separation and spectroscopic characterization of new metal chelates of 8-arylazo-6-formyl-7-hydroxy-5-methoxy- 2-methyl chromones , Transition Met. Chem. **1997**, 22, 441-449.

[15] Celina, M., Fernandez ,M.M & EPaniago, B. S. Synthesis of the Novel 4,4'- and 6,6'- Dihydroxamic - 2,2'-Bipyridines Carvalho, and Improved Routes to 4,4'- and 6,6'- Substituted 2,2'-Bipyridines and Mono-N-Oxide-2,2'-Bipyridine, Journal of the Brazil Chemical Society. **1998**, 5, 537-548.

[16] Maihub, A.A., El-Ajaily M.M., Abuzweda ,M. A., Al-Amari H. F & Ahmed, E.S.Experimental studies on Cobalt, Nickel and Copper ions–octahedral complexes with mixed ligand from Phthalic acid and Benzion,Journal of Basic and Applied Sciences. **2005**, 15(1): 41-49.

[17] Sanchez, M. & Aracona, J. R.T. Mixed-Ligand Chelate Formation of Co (II), Ni (II), Cu (II) and Zn (II) Ions with Schiff base as main ligand and amino acid as Co-Ligan. Journal of the Chilean Chemical Society. **2005**, 50(1): 15.

[18] Şakıyan, İ.; Gündüz, N & Gündüz, T. Synthesis and Characterization of Manganese (III) Complexes of Schiff Bases Derived From Amino Acids and 2-Hydroxy-1-naphthaldehyde. Synth. React. Inorg. Met.-Org.Chem. **2001**, *31* (7), 1175-1187.

[19] Guseva, E., . Morozov, V.T., Zinkicheva, A. Voloshina & E. Grishin. Complexes of rhodium (III) with N-functionalized calix [4] resorcinolol. Russian Journal of General Chemistry. **2012**, 82(8): 1323-1333.

[20] Sakıyan, I., E. Logoglu, S. Arslan, N. Sari & N. Şakiyan. "Antimicrobial activities of N-(2-hydroxy-1-naphthalidene)-amino acid (glycine, alanine, phenylalanine, histidine, tryptophane) Schiff bases and their manganese (III) complexes. Biometals. **2004**, 17(2): 115-120

[21] Ceyhan,G. , Köse,M. , Tümer, M., Demirtaş, Ş., Yağlioğlu, İ. , A., & McKee, V. Structural characterization of some Schiff base compounds: Investigation of their electrochemical, photoluminescence, thermal and anticancer activity properties thermal and anticancer activity properties. Journal of Luminescence. **2013**,143, 623-634.

[22] Singh, R. V., Dwivedi, R. & Joshi, S. C. Synthetic, magnetic, spectral, antimicrobial and antifertility studies of dioxomolybdenum(VI) unsymmetrical imine complexes having a N∩N donor system,"Transition Metal Chemistry. **2004**, 29, no. 1, pp. 70–74, 2004.