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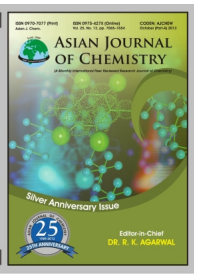

Synthesis and Antibacterial Activity of New Schiff Bases Derived from 2,3-Diaminopyridine and Their Copper(II), Iron(III), Nickel(II) and Zinc(II) Complexes

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Three new *bis*-condensed Schiff bases (**1**-**3**), one imidazo-pyridine (**4**) and twelve Schiff base metal complexes derived from 2,3-diaminopyridine (DAPY) have been synthesised. The mixed Schiff bases DAPY-{ValH}{SalH} (**1**) and DAPY-{ValH}($DhbH_2$) (**2**) were obtained by equimolar reaction of the mono-condensed Schiff base of DAPY and *o*-vanillin (ValH), DAPY-{ValH}with salicylaldehyde (SalH) and 2,3-dihydroxybenzaldehyde ($DhbH_2$), respectively. 1:2 Molar condensation of DAPY with $DhbH_2$ yielded the Schiff base (**3**), whereas reaction of the same reagents in a 1:0.8 mol ratio gave the imidazo-pyridine, 2-(2,3-dihydroxyphenyl)-1*H*-imidazo-(4,5-b)pyridine (**4**). The Schiff bases and Schiff base metal complexes (1600 µg cm^{-3}) were screened *in vitro* against three bacteria (*Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli*) using the diffusion method. Some of them were found to be more active than the control cetyl trimethyl ammonium bromide.

Key Words: Schiff bases, 2,3-Diaminopyridine, 2,3-Dihydroxybenzaldehyde, *o*-Vanillin, Salicylaldehyde, Antibacterial, Imidazo-pyridine.

INTRODUCTION

Various Schiff bases (mono-condensed and bis-condensed) and Schiff base metal complexes derived from the aromatic diamine, 2,3-diaminopyridine (DAPY) have been synthesised in the literature. Eight mono-condensed Schiff bases were reported by Dubey and Ratnam[1] using the following aldehydes (benzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-X-benzaldehyde {X = CH_3, Cl, OH, NO_2, OCH_3} and five others were prepared, respectively with salicylaldehyde (SalH)[2], *o*-vanillin (ValH)[3], pyrrole-2-carbaldehyde[4], 3-ethoxy-vinylidene-2,4-pentanedione[5] and 3-oxo-3-(4'-nitrophenyl)-propionaldehyde[5]. On the other hand, *bis*-condensed Schiff bases with SalH[2,6-8], ValH[3,9], 5-bromosalicylaldehyde[10], 2-hydroxy-1-naphthaldehyde[4,11], 3-methoxy-4-butoxybenzaldehyde[12], 3-methoxy-4-carboxymethylbenzaldehyde[12] and ethoxyvinylidene-2,4-pentanedione[5] and only one *bis*-condensed mixed Schiff base with 4-hydroxybenzaldehyde and SalH[6] have been reported. From the above Schiff bases, several copper, iron, nickel, ruthenium and zinc complexes were synthesized[3,4,6-8,10,13,14]. The structures of the copper(II) and nickel(II) Schiff base complexes derived from DAPY and SalH and that of zinc(II) complex derived from DAPY and 5-bromosalicylaldehyde have been determined by X-ray crystallography[8,10,13]. Some of the Schiff bases and/or their metal complexes were tested as catalytic oxidants[4], antimicrobial agents[3,4,6,12], analytical reagent[7] or electrochemical sensor[9].

In continuation of our work on Schiff bases derived from DAPY[3,4,6] we now report the synthesis of three new *bis*-condensed Schiff bases (**1-3**), of which two are mixed, one imidazo-pyridine (**4**) and twelve transition metal (copper, iron, nickel and zinc) Schiff base complexes (**1a**-**1d**), (**2a**-**2d**) and (**3a**-**3d**).

EXPERIMENTAL

All chemicals (analar grade) were purchased from either Aldrich or BDH and used as received. IR spectra of the samples were recorded as KBr pellets on a FTIR Mattson 1000 spectrometer in the 4000-400 cm^{-1} region. ^1H and ^{13}C NMR spectra in DMSO-d_6 were obtained from a Bruker Spectrospin 250. Magnetic susceptibilities of metal complexes were determined using a Sherwood Scientific magnetic balance. Copper, iron, nickel and zinc content were found using a Unicam 929 atomic absorption spectrometer, whereas C, H and N analyses were obtained using a LECO 932 CHNS analyzer. Melting points were measured using a Stuart Scientific melting point apparatus and were uncorrected. Mass spectra were recorded on a Fissions VG Trio 2000 mass spectrometer, University of Manchester.

Preparation of Schiff bases: The mono-condensed Schiff base DAPY-{ValH} was synthesized using literature procedures[1,3].

Mixed Schiff base DAPY-{ValH}{SalH} (1): The mono-condensed Schiff base DAPY-{ValH} (0.49 g, 2 mmol) was dissolved in a 2:1 ethanol:chloroform mixture (10 mL) in a round bottom flask. Salicylaldehyde (0.25g, 2 mmol) was then added to the mono-condensed Schiff base solution. The reaction mixture was refluxed until a visible colour change was observed. The resulting solution was concentrated on a rotary evaporator to half its volume and then cooled in the refrigerator. The orange solid obtained was collected by filtration, washed with ethanol (2 mL) followed by diethyl ether (2 mL) and dried in a desiccator. Yield: 0.60 g, 87 %. m.p. 201 ºC. Anal. calcd. (%) for $C_{20}H_{17}N_3O_3$: C, 69.2; H, 4.9; N, 12.1. Found (%): C, 69.1; H, 4.9; N, 12.3.

Mixed Schiff base DAPY-{ValH}{DhbH$_2$} (2): The mono-condensed Schiff base DAPY-{ValH} (0.49 g, 2 mmol) was dissolved in a 2:1 ethanol:chloroform mixture (10 mL) in a round bottom flask. 2,3-Dihydroxybenzaldehyde (0.28 g, 2 mmol) was then added to the mono-condensed Schiff base solution. The reaction mixture was refluxed until a visible colour change was observed. The resulting solution was concentrated on a rotary evaporator to half its volume and then cooled in the refrigerator. The red solid obtained was collected by filtration, washed with ethanol (2 mL) followed by diethyl ether (2 mL) and dried in a desiccator. Yield: 0.67 g, 92 %. m.p. 213 ºC. Anal. calcd. (%) for $C_{20}H_{17}N_3O_4$: C, 66.1; H, 4.7; N, 11.6. Found (%): C, 66.0; H, 4.9; N, 11.8.

***Bis*-condensed Schiff base DAPY-{DhbH$_2$}$_2$ (3):** 2,3-Dihydroxybenzaldehyde (1.27 g, 9.2 mmol) was added to a clear ethanolic solution (20 mL) of DAPY (0.50 g, 4.6 mmol). The reaction mixture was stirred for 24 h. The red solid formed was removed by filtration, washed with cold ethanol (2 mL) followed by diethyl ether (2 mL) and finally dried in a vacuum desiccator. Yield: 0.95 g, 60 %. m.p. 200 ºC. Anal. calcd. (%) for $C_{19}H_{15}N_3O_4$: C, 65.3; H, 4.3; N, 12.0. Found (%): C, 65.3; H, 4.4; N, 12.1. MS (CI): *m/z* 350 $[M + H]^+$ (100 %).

2-(2,3-Dihydroxyphenyl)-1*H*-imidazo-(4,5-b) pyridine (4): 2,3-Dihydroxybenzaldehyde (0.51 g, 3.7 mmol) was added to a clear ethanolic solution (20 mL) of DAPY (0.50 g, 4.6 mmol). The reaction mixture was stirred for 24 h. The dark brown solid formed was removed by filtration, washed with cold ethanol (2 mL) followed by diethyl ether (2 mL) and finally dried in a vacuum desiccator. Yield: 0.50 g, 60 %. MS (CI): *m/z* 228 $[M + H]^+$ (100 %). Anal. calcd. (%) for $C_{12}H_9N_3O_2$: C, 63.4; H, 4.0; N, 18.5. Found (%): C, 63.3; H, 4.1; N, 18.4. ^{1}H NMR (DMSO-d_6): δ 6.72-8.32 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 113.1, 117.5, 118.9, 119.5, 119.7, 119.9, 145.2, 147.2, 148.3, 149.4, 154.6, 155.0. DEPT-135 NMR (DMSO-d_6): δ 117.5, 118.9, 119.5, 119.7, 119.9, 145.2.

General preparation of the transition metal Schiff base complexes (1a-1d), (2a-2d) and (3a-3d): An ethanolic solution (5 mL) of lithium hydroxide monohydrate (1.5 or 3.0 mmol) followed by an ethanolic solution (10 mL) of the appropriate metal salt (zinc(II) chloride, nickel(II) chloride, copper(II) chloride or iron(III) chloride) (1.5 mmol), was added to a solution of the Schiff base (1.5 mmol) in tetrahydrofuran (10 mL). The resulting solution was refluxed until a change in colour was observed. The reaction mixture was then concentrated on a rotary evaporator and left in the refrigerator overnight. The solid formed was filtered, washed with a little ethanol (2 mL) followed by diethyl ether (2 mL) and finally dried in a desiccator. Yield 57-70 %.

Antibacterial tests: The bacterial subcultures for *Escherichia coli, Bacillus subtilis* and *Staphylococcus aureus* were obtained from Victoria Hospital, Mauritius. About 1 mL of a 24 h broth culture containing 10^6 CFU/mL was placed in sterile petri-dishes. Molten nutrient agar (10 mL) kept at 45 ºC was then poured in the petri-dishes and allowed to solidify. Afterwards, 2 holes of 6 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions (1600 μg cm^{-3} in DMSO). The plates were incubated for 24 h at 37 ºC. The mean value obtained for the two holes was used to calculate the zone of growth inhibition of each sample. The same procedure was repeated using a positive control, namely cetyl trimethyl ammonium bromide (CTAB), a chemical possessing anti-bacterial properties.

RESULTS AND DISCUSSION

The equimolar reaction of the mono-condensed Schiff base of DAPY and *o*-vanillin, DAPY-{ValH}, with SalH and DhbH$_2$ gives new mixed Schiff bases, DAPY-{ValH}{SalH} (**1**) and DAPY-{ValH}{DhbH$_2$} (**2**), respectively. The reaction of DAPY with DhbH$_2$ in a 1:2 molar ratio in ethanol gives DAPY-{DhbH$_2$}$_2$ (**3**) as a red powder. On the other hand, condensation of DAPY with DhbH$_2$ in a 1:0.8 mol ratio gives a dark brown compound (**4**). The proposed structures of Schiff bases (**1-3**) and the imidazo-pyridine (**4**) are shown in Fig. 1 and their spectroscopic data summarized in Table-1.

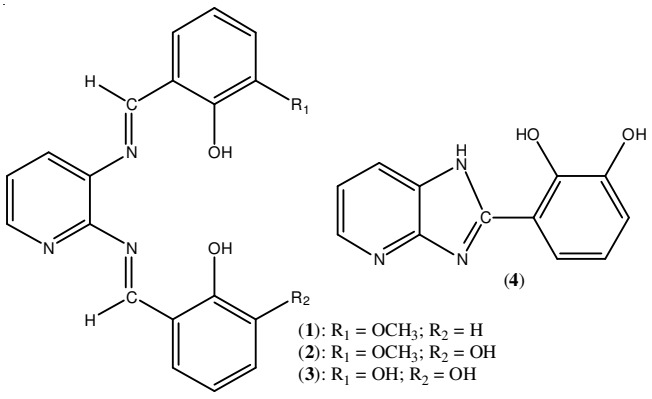

Fig. 1. Proposed structures of Schiff bases (**1-3**) and of imidazo-pyridine (**4**)

Refluxing the mixed Schiff bases (**1**) and (**2**) with ethanolic solutions of the appropriate metal chloride and lithium hydroxide monohydrate in a 1:1:1 molar ratio gives the respective mono-nuclear copper(II), iron(III), nickel(II) and zinc(II) complexes (**1a-1d**) and (**2a-2d**) whereas metal Schiff base complexes (**3a-3d**) result on refluxing the *bis*-condensed Schiff base (**3**) with the metal chloride and lithium hydroxide monohydrate in a 1:1:2 molar ratio.

The Schiff base metal complexes (**1a-1d**), (**2a-2d**) and (**3a-3d**) were characterized by a combination of elemental analysis, magnetic susceptibility and IR spectroscopy. Their proposed structures and their analytical and spectroscopic data are shown in Fig. 2 and Table-2, respectively.

TABLE-1
SPECTROSCOPIC DATA OF THE SCHIFF BASES (**1-3**)

Schiff base {Formula}	IR[a] (cm^{-1}) ν(C=N)	^{1}H NMR chemical shifts (δ, ppm)[b]	^{13}C NMR chemical shifts (δ, ppm)[b]
DAPY-{ValH}{SalH} (**1**) {$C_{20}H_{17}N_3O_3$}	1619 1553	13.55 (OH, s, 1H), 12.65 (OH, s, 1H), 9.43 (CH=N, s, 1H), 8.56 (CH=N, s, 1H), 8.34-6.81 (ring, m, 10H), 3.83 (OCH_3, s, 3H)	165.9 and 165.0 (HC=N), 161.5-115.4 (ring C), 56.1 (OCH_3)
DAPY-{ValH}{$DhbH_2$} (**2**) {$C_{20}H_{17}N_3O_4$}	1615 1556	12.56 (OH, s, 1H), 9.54 (CH=N, s, 1H), 9.44 (OH, s, 1H), 9.39 (OH, s, 1H), 8.97 (CH=N, s, 1H), 8.49-6.80 (ring, m, 9H), 3.40 (OCH_3, s, 3H)	167.2 and 165.0 (HC=N), 152.6-116.8 (ring C), 56.5 (OCH_3)
DAPY-{$DhbH_2$}$_2$ (**3**) {$C_{19}H_{15}N_3O_4$}	1614 1561	12.99 (OH, s, 1H), 12.42 (OH, s, 1H), 9.41 (CH=N, s, 1H), 9.29 (OH, s, 1H), 9.24 (OH, s, 1H), 8.85 (CH=N, s, 1H), 8.38-6.69 (ring, m, 9H)	167.2 and 165.5 (HC=N), 151.6-119.8 (ring C)

[a]KBr pellets. [b]Solvent is DMSO-d_6.

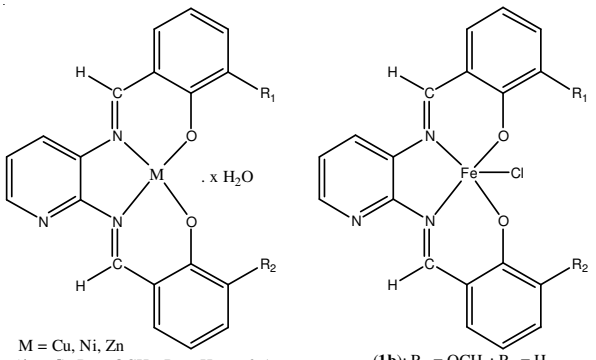

Fig. 2. Proposed structures of the Schiff base complexes

Elemental analysis and mass spectra: Elemental analytical data of the Schiff bases (**1-3**), imidazo-pyridine (**4**) and Schiff base metal complexes (**1a-1d**), (**2a-2d**) and (**3a-3d**) are in close agreement with the theoretical values of the proposed chemical formulae of the compounds. The structure of (**3**) is corroborated by its CI mass spectrum indicating its $[M + H]^+$ ion, $[C_{19}H_{16}N_3O_4]^+$ at *m/z* 350 and the major molecular fragment $[C_{12}H_{12}N_3O_2]^+$ at *m/z* 230. Similarly the CI mass spectrum of (**4**) confirms the formation of a compound having molecular mass 227 consistent with the formation of the imidazo-pyridine.

Infrared spectra: The IR spectra (KBr pellets) of the Schiff bases (**1-3**) indicate two ν(C=N) frequencies at 1619, 1553; 1619, 1556 and 1614, 1561 cm^{-1}, respectively confirming the condensation of both amino groups of the pyridine moiety[7]. A broad band at 3467-3445 cm^{-1} region due to stretching frequency of O-H is also observed.

The IR spectra of the Schiff base metal complexes (**1a-1d**), (**2a-2d**) and (**3a-3d**) indicate a decrease in the ν(C=N) frequencies with respect to the free Schiff bases suggesting coordination of the azomethine nitrogens to the metal ion[15]. For example, the IR spectra of complexes (**1a-1d**) show ν(C=N) frequencies at 1612-1596 and 1542-1530 cm^{-1} compared to 1619 and 1553 cm^{-1} in the free Schiff base (**1**). For the metal complexes still possessing an OH group or having

TABLE-2
ANALYTICAL AND SPECTROSCOPIC DATA OF THE METAL COMPOUNDS

Compound {Formula}	m.p. (ºC) Colour	Found (Calcd.) (%)				IR[a] (cm^{-1}) ν(C=N)	$\mu_{eff.}$ (BM)
		C	H	N	M		
[Cu(DAPY-{Val}{Sal})] (**1a**)	200	58.5	3.8	10.5	15.3	1607	1.8
{Cu($C_{20}H_{15}N_3O_3$)}	Brown	(58.7)	(3.7)	(10.3)	(15.5)	1542	
[Fe(DAPY-{Val}{Sal})Cl] (**1b**)	280	54.8	3.4	9.4	13.0	1596	6.0
{Fe($C_{20}H_{15}N_3O_3$)Cl}	Green	(55.0)	(3.5)	(9.6)	(12.8)	1538	
[Ni(DAPY-{Val}{Sal})] (**1c**)	290	59.2	3.8	10.2	14.6	1603	D
{Ni($C_{20}H_{15}N_3O_3$)}	Red	(59.4)	(3.7)	(10.4)	(14.5)	1540	
[Zn(DAPY-{Val}{Sal})]·H_2O (**1d**)	215	55.8	3.8	9.6	15.4	1612	D
{Zn($C_{20}H_{15}N_3O_3$).H_2O}	Yellow	(56.0)	(4.0)	(9.8)	(15.3)	1530	
[Cu(DAPY-{Val}{DhbH})] (**2a**)	> 400	56.5	3.7	9.8	15.1	1601	1.8
{Cu($C_{20}H_{15}N_3O_4$)}	Brown	(56.5)	(3.6)	(9.9)	(15.0)	1535	
[Fe(DAPY-{Val}{DhbH})Cl] (**2b**)	> 400	52.9	3.4	9.5	12.5	1593	5.9
{Fe($C_{20}H_{15}N_3O_4$)Cl}	Green	(53.1)	(3.7)	(9.3)	(12.3)	1540	
[Ni(DAPY-{Val}{DhbH})].H_2O (**2c**)	> 400	55.0	3.9	9.5	13.6	1597	D
{Ni($C_{20}H_{15}N_3O_4$).H_2O}	Red	(54.8)	(3.9)	(9.6)	(13.4)	1542	
[Zn(DAPY-{Val}{DhbH})].2H_2O (**2d**)	> 400	52.0	3.9	8.9	14.2	1600	D
{Zn($C_{20}H_{15}N_3O_4$).2H_2O}	Yellow	(51.9)	(4.1)	(9.1)	(14.1)	1541	
[Cu(DAPY-{$DhbH_2$})] (**3a**)	320	55.7	3.4	10.0	15.5	1603	1.7
{Cu($C_{19}H_{13}N_3O_4$)}	Brown	(55.5)	(3.2)	(10.2)	(15.5)	1535	
[Fe(DAPY-{$DhbH_2$})Cl] (**3b**)	350	52.0	3.2	9.4	12.6	1594	5.8
{Fe($C_{19}H_{13}N_3O_4$)Cl}	Green	(52.0)	(3.0)	(9.6)	(12.7)	1547	
[Ni(DAPY-{$DhbH_2$})].2H_2O (**3c**)	310	51.4	3.9	9.3	13.4	1601	D
{Ni($C_{19}H_{13}N_3O_4$).2H_2O}	Red	(51.6)	(3.9)	(9.5)	(13.3)	1541	
[Zn(DAPY-{$DhbH_2$})].2H_2O (**3d**)	248	51.0	3.6	9.6	14.5	1604	D
{Zn($C_{19}H_{13}N_3O_4$).2H_2O}	Yellow	(50.9)	(3.8)	(9.4)	(14.6)	1534	

[a]KBr pellets. D = Diamagnetic.

water molecules, a broad band is also observed in the 3500-3400 cm^{-1} region.

NMR spectra: The ^1H NMR spectra of the mixed Schiff bases (**1**) and (**2**) in DMSO-d_6 provide evidence for the condensation of the amino group by the absence of signal corresponding to the amino protons in the range δ 5-6 ppm. Furthermore, an additional azomethine proton signal in the ^1H NMR spectra of (**1**) and (**2**) compared to the mono-condensed Schiff base, DAPY-{ValH} confirms the condensation of the amino group[6]. It is noteworthy that the signal(s) due to OH groups found *ortho* to the azomethine carbon occur(s) at high value(s) due to intra-molecular hydrogen bonding[6,7].

The ^{13}C NMR spectra of the mixed Schiff bases (**1**) and (**2**) show 20 peaks as expected from their proposed formulae. The two azomethine carbons are observed at δ 165.9 and 165.0 ppm for (**1**) and at 167.2 and 165.0 ppm for (**2**) while the peak at δ 56.1 and 56.5 ppm is attributed, respectively to the carbon of the OCH_3 group of (**1**) and (**2**). The remaining 17 peaks (δ 161.5-115.4 ppm for (**1**) and 152.6-116.8 ppm for (**2**)) are due to the other aromatic carbons. The DEPT-135 NMR spectrum of (**1**) confirms the presence of seven quaternary carbons as only 13 peaks are observed. They are the two carbon atoms of the pyridine moiety bound to the azomethine nitrogens, two carbon atoms of the salicylaldehyde moiety bound to the azomethine carbon and to the hydroxyl group and three carbon atoms of the *o*-vanillin moiety bound to the azomethine carbon, to the hydroxyl group and to the OCH_3 group. On the other hand, the DEPT-135 NMR spectrum of the mixed Schiff base (**2**) exhibits only 12 peaks consistent with the presence of eight quaternary carbon atoms.

The ^1H NMR spectrum of (**3**) provides evidence for the formation of a *bis*-condensed Schiff base by the presence of two singlets at δ 9.41 and 8.85 ppm attributable to two azomethine protons. The signals due to OH groups are observed at δ 9.24, 9.29, 12.42 and 12.99 ppm. Its ^{13}C NMR spectrum shows 19 peaks. The most downfield peaks are found at δ 167.2 and 165.5 ppm attributable to the azomethine carbons. The other peaks are attributed to the remaining aromatic carbons. Its DEPT-135 NMR spectrum confirms the presence of eight quaternary carbons as their signals are not observed. They are the four hydroxyl carbons, two aromatic carbons of the pyridine moiety bound to the azomethine nitrogens and two carbons observed at δ 146.5 and 146.6 ppm of the $DhbH_2$ moiety bound to the azomethine carbons.

NMR data of (**4**) are in accord with the formation of 2-(2,3-dihydroxyphenyl)-1*H*-imidazo-[4,5-*b*]pyridine instead of the expected mono-condensed Schiff base. The formation of imidazo-pyridines derived from 2,3-diaminopyridine has been reported in the literature[1]. The ^1H NMR spectrum of (**4**) in DMSO-d_6 indicates signals due to six aromatic protons in the range δ 6.72-8.32 ppm. Its ^{13}C NMR spectrum shows twelve peaks. The most downfield peaks are observed at δ 155.0 and 154.6 ppm assigned to azomethine carbons. The remaining ten peaks at δ 149.4-113.1 ppm are due to the other aromatic carbons. The DEPT-135 NMR spectrum of (**4**) shows the disappearance of six peaks with respect to its ^{13}C NMR spectrum indicating the presence of six quaternary carbons. If the mono-condensed Schiff base was formed, there would be disappearance of only five peaks. In addition, no signals are found in the δ 146-155 ppm region suggesting absence of an azomethine carbon bearing a proton. The NMR data thus point to the formation of an imidazole-type compound formed by attack of the amino group on the azomethine carbon followed by dehydration. It is noteworthy that (**4**) is a stable compound having three aromatic rings out of which two are benzene rings and one is a five-membered ring.

Magnetic susceptibilities: Magnetic susceptibility measurements show that the red nickel(II) complexes (**1c-3c**) are diamagnetic, in accord with a square planar geometry. The magnetic moments of the copper(II) complexes (**1a**-**3a**) are found in the range 1.7-1.8 BM, consistent with the presence of one unpaired electron in a d^9 system[16,17], whereas the magnetic moments of the iron(III) complexes are observed in the range of 5.8-6.0 BM corresponding to the presence of five unpaired electrons in a high spin d^5 system[18,19].

Antibacterial screening: The synthesized products, dissolved in DMSO at a concentration of 1600 μg cm^{-3}, have been screened *in vitro* for antibacterial properties against two gram positive bacteria *Staphylococcus aureus* and *Bacillus subtilis* and one gram negative bacterium namely *Escherichia coli* using the diffusion method. The parameter used for the antibacterial activity is the diameter of the zone of inhibition. The results are shown in Table-3. Blank tests show that the solvent DMSO used in the preparation of the test solutions does not affect the growth of the microorganisms. CTAB is used as control. The copper(II) complex (**2a**) was found to be inactive at the concentration of 1600 μg cm^{-3} against all the three bacteria. The iron(III) and zinc(II) complexes are generally more active than the nickel(II) or copper(II) complexes as exemplified by the activity shown by (**2b**), (**2d**), (**3b**) and (**3d**). Three Schiff base metal complexes, namely (**2d**), (**3b**) and (**3d**), are found to be more active than the control CTAB against all the three bacteria. It is noteworthy that the diameters

TABLE-3
ANTI-BACTERIAL SCREENING RESULTS OF SCHIFF BASES AND THEIR METAL COMPLEXES

Compound[a]	Zone of inhibition (average diameter/mm)		
	E. coli	*B. subtilis*	*S. aureus*
DMSO	–	–	–
CTAB	12	11	12
DAPY-{ValH}{SalH} (**1**)	10	10	16
DAPY-{ValH}{$DhbH_2$} (**2**)	11	12	11
DAPY-{$DhbH_2$}$_2$ (**3**)	12	10	14
[Cu(DAPY-{Val}{Sal})] (**1a**)	11	11	11
[Fe(DAPY-{Val}{Sal})Cl] (**1b**)	11	10	9
[Ni(DAPY-{Val}{Sal})] (**1c**)	10	12	10
[Zn(DAPY-{Val}{Sal})].H_2O (**1d**)	11	–	12
[Cu(DAPY-{Val}{DhbH})] (**2a**)	–	–	–
[Fe(DAPY-{Val}{DhbH})Cl] (**2b**)	15	15	11
[Ni(DAPY-{Val}{DhbH})].H_2O (**2c**)	–	–	13
[Zn(DAPY-{Val}{DhbH})].$2H_2O$ (**2d**)	20	19	13
[Cu(DAPY-{$DhbH_2$}$_2$)] (**3a**)	10	–	–
[Fe(DAPY-{$DhbH_2$}$_2$)Cl] (**3b**)	13	16	20
[Ni(DAPY-{$DhbH_2$}$_2$)]·$2H_2O$ (**3c**)	–	10	10
[Zn(DAPY-{$DhbH_2$}$_2$)]·$2H_2O$ (**3d**)	17	18	15

[a]Concentration used: 1600 μg cm^{-3} in DMSO; – = inactive.

of zone of inhibition (9-20 mm) obtained for the samples tested at the concentration of 1600 μg cm^{-3} are comparable to those obtained by Adimado *et al.*[20] when the Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from 2,6-diaminopyridine, acetylacetone and benzoylacetone were screened against *E. coli* and *S. aureus* at concentrations 1000 μg cm^{-3} (8-18 mm) and 2000 μg cm^{-3} (10-21 mm).

Conclusion

In summary, sixteen new compounds derived from DAPY have been prepared and successfully characterised, namely three *bis*-condensed Schiff bases (**1-3**), out of which (**1**) and (**2**) are mixed, one imidazo-pyridine (**4**) and twelve transition metal (copper, iron, nickel and zinc) Schiff base complexes (**1a**-**1d**), (**2a**-**2d**) and (**3a**-**3d**). When screened *in vitro* against three bacteria (*S. aureus*, *B. subtilis* and *E. coli*) at a concentration of 1600 μg cm^{-3} using the diffusion method, three of them, namely (**2d**), (**3b**) and (**3d**), were found to be more active than the control CTAB against all the three bacteria. The *bis*-condensed Schiff base (**3**) is an example of a compartmental ligand, having two different adjacent coordination sites, an inner N_2O_2 and an outer O_2O_2 one[21]. Studies are underway in our laboratory to prepare hetero-dinuclear Schiff base metal complexes from (**3**).

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