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SYNTHESIS AND ANTI-BACTERIAL/CATALYTIC PROPERTIES OF SCHIFF BASES AND SCHIFF BASE METAL COMPLEXES DERIVED FROM 2,3-DIAMINOPYRIDINE

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ABSTRACT

Two new Schiff bases **(1a)-(2a)** derived from 2,3-diaminopyridine (DAPY) with pyrrole-2-carboxaldehyde (Pyrr) and 2-hydroxy-1-naphthaldehyde (NaphH), and new copper(II), iron(III), nickel(II), ruthenium(II) and zinc(II) complexes **(1b)-(1e)**, **(2b)-(2f)** and **(3b)-(3d)** derived from these two new Schiff bases, and the bis-condensed Schiff base of 2,3-diaminopyridine and salicylaldehyde (SalH) were synthesized. They were characterized by a combination of elemental analyses, magnetic susceptibility measurements, IR and NMR spectra. The two new Schiff bases and some of the metal complexes

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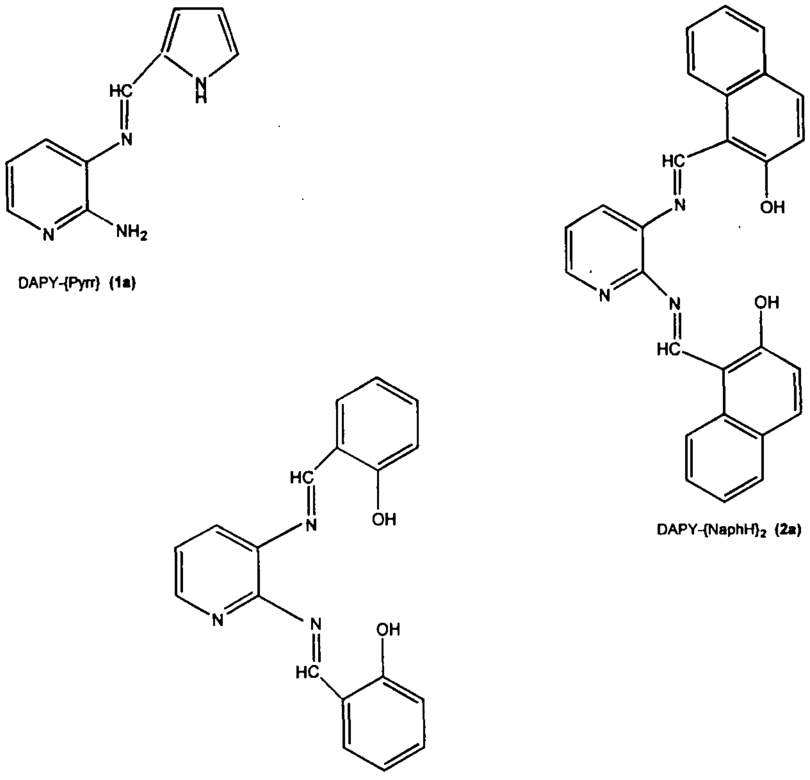
show antibacterial activity. The iron(III) and Ru(II) complexes display catalytic activity in the oxidation of alcohols in the presence of N-methylmorpholine-N-oxide as co-oxidant.

INTRODUCTION

Reactions of 2,3-diaminopyridine (DAPY) with carbonyl compounds often result in the formation of cyclized products such as imidazopyridines[1-3] or imidazolones[4]. The formation of Schiff bases and transition metal Schiff base complexes derived from DAPY and aldehydes was reported by Dubey and Ratnam[1], Cimerman *et al.*[5-6], and Jeewoth *et al.*[7] Of the Schiff bases synthesized, only two were bis-condensed Schiff bases. DAPY-$\{SalH\}_2$ and the mixed Schiff base DAPY-{4-OHBenz}{SalH} (where 4-OHBenz = 4-hydroxybenzaldehyde) were prepared by condensation of DAPY with 2 equivalents of salicylaldehyde (SalH), and by condensation of the mono-Schiff base derived from DAPY and 4-OHBenz (DAPY-{4-OHBenz}) with salicylaldehyde (SalH) respectively[5,7].

In continuation of our work on Schiff bases and transition metal Schiff base complexes derived from DAPY, we now report the preparation of two new Schiff bases derived from DAPY with pyrrole-2-carboxaldehyde (DAPY-{Pyrr}), and 2-hydroxy-1-naphthaldehyde (DAPY-$\{NaphH\}_2$) (Fig. 1), and new copper(II), iron(III), nickel(II), ruthenium(II) and zinc(II) complexes derived from these Schiff bases and the bis-condensed Schiff base DAPY-$\{SalH\}_2$. The antibacterial properties of the new products and the catalytic oxidation of alcohols by the iron(III) and ruthenium(II) complexes in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant are also reported.



DAPY-{Pyrr} **(1a)**

DAPY-{NaphH}$_2$ **(2a)**

DAPY-{SalH}$_2$ **(3a)**

Fig. 1. Structures of the Schiff Bases **(1a)-(3a)**.

RESULTS AND DISCUSSION

Synthesis

The analytical, physical and spectroscopic data of the Schiff bases **(1a)-(2a)** and Schiff base metal complexes **(1b)-(1e)**, **(2b)-(2f)** and **(3b)-(3d)** are given in Tables I and II.

Table I. Analytical and Physical Data of the Schiff Bases and Metal Schiff Base Complexes

Compound No.	Compound Molecular Formula	Mol. Weight	M.p. (°C)	Colour	Yield (%)	Elemental Analysis Found (calc.), %			
						C	H	N	M
(1a)	DAPY-{Pyrr} $C_{10}H_{10}N_4$	186.2	92	Brown	87	65.0 (64.5)	5.6 (5.4)	30.4 (30.1)	
(2a)	DAPY-{NaphH}$_2$ $C_{27}H_{19}N_3O_2$	417.5	243	Yellow	90	78.1 (77.7)	4.7 (4.6)	10.3 (10.1)	
(1b)	[Zn(DAPY-{Pyrr})Cl_2] $C_{10}H_{10}N_4Cl_2Zn$	322.5	>250	Yellow	56	37.4 (37.2)	3.3 (3.1)	17.5 (17.4)	20.2 (20.2)
(1c)	[Ni(DAPY-{Pyrr})(OAc)$_2$] $C_{14}H_{16}N_4O_4Ni$	363	>250	Black	60	46.8 (46.3)	4.7 (4.4)	15.7 (15.4)	16.8 (16.2)
(1d)	[Cu(DAPY-{Pyrr})Cl_2] $C_{10}H_{10}N_4Cl_2Cu$	320.7	>250	Brown	64	37.7 (37.5)	3.2 (3.1)	17.8 (17.5)	19.4 (19.8)
(1e)	[Ru(PPh_3)(DAPY-{Pyrr})Cl_2(H_2O)] $C_{28}H_{27}N_4OCl_2PRu$	638.5	>250	Black	40	53.0 (52.7)	4.5 (4.3)	8.6 (8.8)	
(2b)	[Zn(DAPY-{Naph}$_2$)] $C_{27}H_{17}N_3O_2Zn$	480.8	>250	Yellow	68	67.1 (67.4)	4.0 (3.6)	8.7 (8.7)	13.7 (13.6)
(2c)	[Ni(DAPY-{Naph}$_2$)] $C_{27}H_{17}N_3O_2Ni$	474.1	>250	Red	67	68.7 (68.4)	3.8 (3.6)	9.1 (8.9)	12.3 (12.4)
(2d)	[Cu(DAPY-{Naph}$_2$)] $C_{27}H_{17}N_3O_2Cu$	479	>250	Brown	54	67.8 (67.7)	3.5 (3.6)	8.7 (8.8)	13.5 (13.3)
(2e)	[Fe(DAPY-{Naph}$_2$)Cl] $C_{27}H_{17}N_3O_2ClFe$	506.8	>250	Reddish-brown	66	63.7 (64.0)	3.3 (3.4)	8.3 (8.3)	11.2 (11.0)
(2f)	[Ru(DAPY-{Naph}$_2$)(PPh_3)(H_2O)].3H_2O $C_{45}H_{40}N_3O_6PRu$	850.9	215	Black	57	63.0 (63.5)	4.7 (4.7)	5.0 (4.9)	
(3b)	[Cu(DAPY-{Sal}$_2$)] $C_{19}H_{13}N_3O_2Cu$	378.9	>250	Black	39	59.6 (60.2)	3.5 (3.5)	10.8 (11.1)	16.2 (16.8)
(3c)	[Fe(DAPY-{Sal}$_2$)Cl] $C_{19}H_{13}N_3O_2ClFe$	406.6	>250	Black	59	55.9 (56.1)	3.4 (3.2)	9.9 (10.3)	13.8 (13.7)
(3d)	[Ru(DAPY-{Sal}$_2$)(PPh_3)(H_2O)].2H_2O $C_{37}H_{34}N_3O_5PRu$	732.7	162	Black	55	60.5 (60.7)	5.0 (4.7)	5.6 (5.7)	

Table II. Spectroscopic Data and Magnetic Moments of the Schiff Bases and Metal Schiff Base Complexes

Compound No.	IR (cm^{-1})[a] ($\nu_{C=N}$)	^{1}H NMR[b,c] (ppm)	μ_{eff} (B.M.)
(1a)	1619	5.25 (NH_2, s, 2H), 6.30-7.93 (ring, m. 6H), 8.27 (CH=N, s, 1H), 10.71 (NH, s, 1H)[b]	
(2a)	1575 1623	6.92-8.40 (ring, m, 15H), 9.61 (CH=N, s, 1H), 9.97 (CH=N, s, 1H), 14.32 (OH, s, 1H), 15.36 (OH, s,1H)[b]	
(1b)	1616	6.27 (NH_2, s, 2H), 6.54-8.75 (ring, m, 6H), 8.47 (CH=N, s, 1H), 10.74 (NH, s, 1H)[c]	D
(1c)	1565		3.77
(1d)	1566		1.77
(1e)	1570	6.18-7.84 (ring and NH_2, m, 23 H), 8.35 (CH=N, s, 1H)[c]	D
(2b)	1552 1602	6.99-8.66 (ring, m, 15H), 9.85 (CH=N, s, 1H), 10.88 (CH=N, s, 1H)[c]	D
(2c)	1539 1616	7.15-8.96 (ring, m, 15H), 9.88 (CH=N, s, 1H), 10.67 (CH=N, s, 1H)[c]	D
(2d)	1544 1616		1.74
(2e)	1556 1612		5.87
(2f)	1543 1601	6.57-7.83 (ring, m, 30H), 8.12 (CH=N, s, 1H), 8.27 (CH=N, s, 1H)[c]	D
(3b)	1556 1604		1.78
(3c)	1543 1604		5.86
(3d)	1543 1601	6.59-7.87 (ring, m, 26H), 8.19 (CH=N, s, 1H), 8.28 (CH=N, s, 1H)[c]	D

[a] KBr pellets. [b] Solvent-$CDCl_3$. [c] Solvent-d_6-DMSO. D = Diamagnetic.

The two Schiff bases, (DAPY-{Pyrr}) **(1a)** and (DAPY-{NaphH}$_2$) **(2a)** were synthesized by mixing the diamine, DAPY, with stoichiometric amounts of pyrrole-2-carboxaldehyde (Pyrr) and 2-hydroxy-1-naphthaldehyde (NaphH), respectively, in ethanol. The structures of the two Schiff bases and of **(3a)** are shown in Fig. 1. **(1a)** is a mono-condensed Schiff base where condensation has occurred only at the 3-amino group which is less resonance stabilized than the 2-amino group. Attempted synthesis of the corresponding bis-condensed Schiff base was unsuccessful, even when reacting 1 equivalent of the diamine with up to 4 equivalents of the aldehyde. It is interesting to note that the Schiff base **(1a)** contains two nitrogen heterocycles, a six-membered and a five-membered ring.

On the other hand, **(2a)** is a doubly-condensed Schiff base obtained easily after a few hours of stirring at room temperature. Though 2,3-diaminopyridine is reluctant to have both of its amino groups condensed, this Schiff base, as in the case of the bis-condensed Schiff base with salicylaldehyde (DAPY-{SalH}$_2$)[5] **(3a)**, is formed very rapidly. This can be explained by the fact that, as in salicylaldehyde, 2-hydroxy-1-naphthaldehyde is also a stable aromatic system with an *ortho* hydroxyl proton that can be stabilized by the azomethine nitrogen by hydrogen bonding. However, stirring equimolar ratios of the aldehyde and the diamine did not give the expected mono-condensed Schiff base but the bis derivative **(2a)**. Starting with even lower amounts of the aldehyde resulted in a mixture of bis- and mono-condensed Schiff bases which proved very difficult to separate. This unprecedented behavior of 2,3-diaminopyridine in forming preferentially the bis-condensed Schiff base rather than the mono-condensed one is very unexpected since many mono-condensed Schiff bases but only two bis-Schiff bases have been described in the literature[5,7].

The interaction of Schiff base **(1a)** with zinc(II) chloride, nickel(II) acetate, copper(II) chloride and $RuCl_2(PPh_3)_3$ yielded the mono-condensed complexes **(1b)-(1e)**, respectively, where the metal is bound to the ligand through the azomethine and the amino nitrogen atoms.

Complexation of the Schiff base **(2a)** with zinc(II) chloride, nickel(II) acetate, copper(II) chloride, iron(III) chloride and $RuCl_2(PPh_3)_3$ resulted in the bis condensed complexes **(2b)-(2f)**, in which the metal is coordinated through both azomethine nitrogen and oxygen atoms formed after deprotonation of both *ortho* hydroxyl groups.

Three new copper(II), iron(III) and ruthenium(II) complexes **(3b)-(3d)** derived from the bis-condensed Schiff base of salicylaldehyde, (DAPY-$\{SalH\}_2$) **(3a)**, have also been synthesized. The salient feature to note here is the successful formation of the bis-condensed copper(II) complex **(3b)** from copper(II) acetate. We have already reported[7] the synthesis of the mono-condensed copper(II) complex starting with the same bis-condensed Schiff base but using copper(II) chloride. We attributed the formation of the mono-condensed complex to metal-induced partial hydrolysis of the doubly-condensed ligand.

All the metal complexes synthesized were found to be soluble in DMSO but not in common organic solvents.

Infrared Spectra

The infrared spectra (KBr pellets) of the Schiff bases **(1a)-(2a)** showed strong stretching bands in the 1575-1623 cm^{-1} region confirming the formation of azomethine linkage(s).

The infrared spectra of all the metal complexes showed a shift to lower frequency in their azomethine stretching bands (1539-1616 cm^{-1}) as compared to their respective free Schiff base, indicating coordination of metal through the azomethine nitrogen(s). In the case of the mono-condensed complexes of pyrrole-2-carboxaldehyde **(1b)-(1e)**, a shift to lower frequency was also observed in the N-H stretching bands of the NH_2 group from 3380-3350 to 3250-3210 cm^{-1}, substantiating coordination through this group also. Sharp peaks are also observed at 509, 694 and 740 cm^{-1} in the spectra of the ruthenium(II) complexes **(1e)**, **(2f)** and **(3d)** confirming the presence of a triphenylphosphine group.

^{1}H NMR Spectra

The ^{1}H NMR spectra of **(1a)** and **(2a)** in $CDCl_3$ provided compelling evidence for their respective mono and bis-condensed nature. For Schiff base **(1a)**, only one signal attributed to an azomethine proton was observed at δ 8.27 ppm, and the signal for the amino protons appeared at δ 5.25 ppm. On the other hand, the NMR spectrum of **(2a)** showed two signals due to the presence of two azomethine protons at 9.61 and 9.97 ppm and absence of peaks due to free amino protons. Furthermore, two peaks attributed to hydroxyl protons were observed at high frequencies (14.32 and 15.36 ppm) due to intra-molecular hydrogen bonding as was the case found for the Schiff base (DAPY-{SalH}$_2$)[5] **(3a)**.

Comparison of the ^{1}H NMR spectrum of **(1a)** with that of Zn(DAPY-{Pyrr})Cl_2 **(1b)** indicates a downfield shift in the signals of the azomethine proton and amino protons, confirming the coordination of metal to these groups while a negligible shift was observed for the N-H peak of the pyrrole ring. Similarly, a downfield shift in the signals of both azomethine protons in the spectra of **(2b)** and **(2c)** as compared to the spectrum of the precursor ligand **(2a)** reveals coordination through both azomethine groups. On the other hand, the peak(s) due to azomethine proton(s) in the ^{1}H NMR spectra of the ruthenium(II) Schiff base complexes showed an upfield shift compared to their respective Schiff base as has been observed in the literature[8]. The NMR spectra of **(2b)**, **(2c)**, **(2f)** and **(3d)** also confirm the formation of 2 metal-oxygen bonds as no signals were recorded for the hydroxyl protons.

Magnetic Measurements

Magnetic measurements were recorded at room temperature and the effective magnetic moment (μ_{eff}) values of the complexes are presented in Table II.

The magnetic moment of the copper(II) complexes **(1d)**, **(2d)** and **(3b)** was observed in the range of 1.74-1.78 B.M. which corresponds to a single unpaired electron with a very slight orbital contribution.

The effective magnetic moment value of 3.77 B.M. for the nickel(II) complex **(1c)** suggested the presence of two unpaired electrons with significant orbital contribution and a tetrahedral geometry around Ni(II). On the other hand, the nickel(II) complex **(2c)** was found to be diamagnetic indicating most probably a square-planar structure.

The iron(III) complexes **(2e)** and **(3c)** displayed magnetic moments in the range of 5.86-5.87 B.M. indicating the presence of five unpaired electrons and high-spin five-coordinate stereochemistry.

All of the ruthenium(II) and zinc(II) complexes were diamagnetic, in accord with their t_{2g}^6 low spin and d^{10} electronic configuration, respectively.

The proposed structures of all the metal complexes are shown in Fig. 2.

Antibacterial Screening

The results of the antibacterial screening of the two Schiff bases **(1a)-(2a)** and some of the metal complexes at a concentration of 5000 μg/mL against two bacteria, namely *Pseudomonas aeruginosa* and *Salmonella typhi*, are given in Table III.

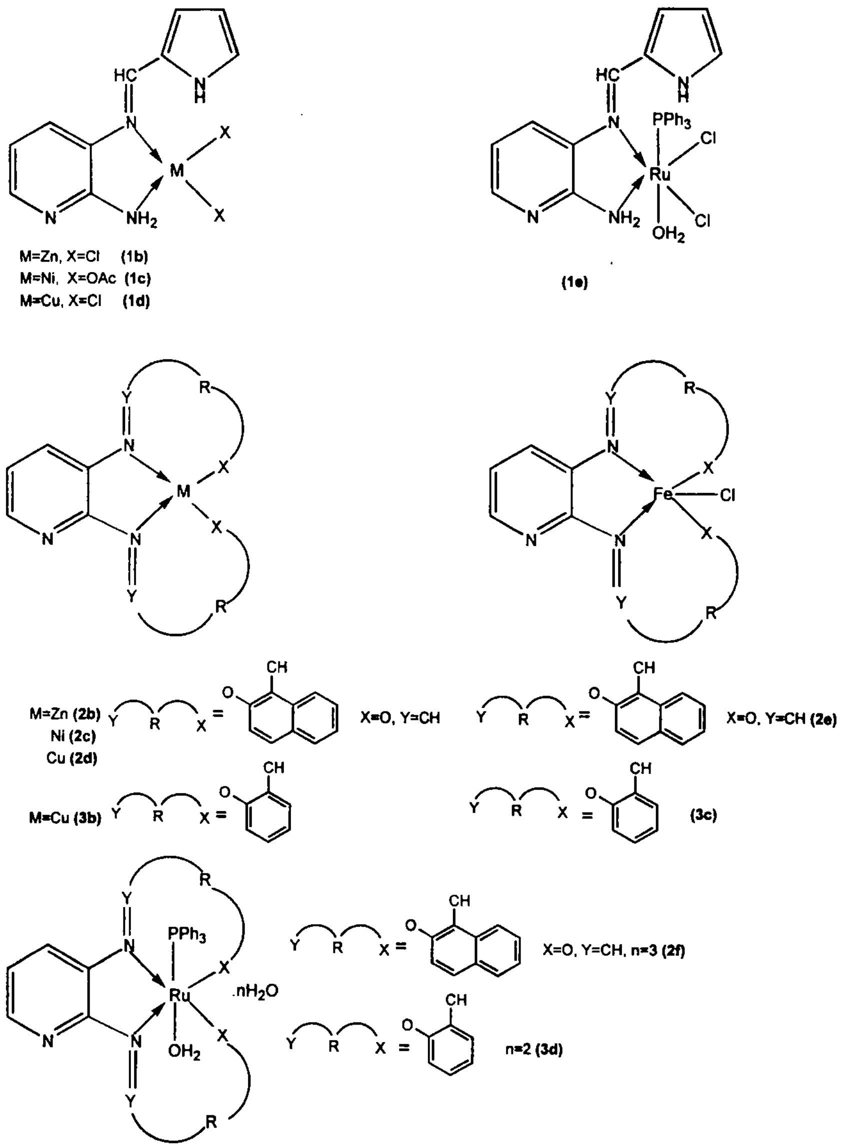


Fig. 2. Proposed Structures of the Transition Metal Schiff Base Complexes.

Table III. Antibacterial Screening Results

Compound[a]	Zone of inhibition (mm)	
	P. aeruginosa	*S. typhi*
DAPY	-	-
DAPY-{Pyrr} **(1a)**	12.18	13.45
DAPY-{NaphH}$_2$ **(2a)**	13.84	12.04
[Zn(DAPY-{Pyrr})Cl$_2$] **(1b)**	-	-
[Ni(DAPY-{Pyrr})(OAc)$_2$] **(1c)**	-	-
[Cu(DAPY-{Pyrr})Cl$_2$] **(1d)**	-	-
[Ru(PPh$_3$)(DAPY-{Pyrr})Cl$_2$(H$_2$O)] **(1e)**	8.52	-
[Zn(DAPY-{Naph}$_2$)] **(2b)**	8.22	13.14
[Ni(DAPY-{Naph}$_2$)] **(2c)**	7.94	8.25
[Cu(DAPY-{Naph}$_2$)] **(2d)**	-	-
[Fe(DAPY-{Naph}$_2$)Cl] **(2e)**	14.11	16.84
[Ru(DAPY-{Naph}$_2$)(PPh$_3$)(H$_2$O)].3H$_2$O **(2f)**	10.55	8.53

[a]Concentration used: 5000 μg/mL in DMSO. - = inactive.

The Schiff bases **(1a)**-**(2a)** exhibited anti-bacterial properties against both bacteria as has been found for other Schiff bases of 2,3-diaminopyridine[7]. No real trend can be deduced for the metal complexes. Both copper(II) complexes **(1d)** and **(2d)** were inactive. On the other hand, the iron(III) complex **(2e)** was the most active one and it was found to be more potent bactericidally than its precursor Schiff base **(2a)**[9,10].

Catalytic Activity

The synthesized iron(III) and ruthenium(II) Schiff base complexes **(1e)**, **(2e)**-**(2f)** and **(3c)**-**(3d)** were used to catalyze the oxidation of *p*-methoxybenzyl, cinnamyl and piperonyl alcohols in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant in acetonitrile or dichloromethane at room temperature. Molecular sieves have been used to

Table IV. Catalytic Oxidation of Alcohols by Iron(III) and Ruthenium(II) Complexes in the presence of N-Methylmorpholine-N-Oxide[a]

Metal complex	Substrate	Product	Yield[b], %	Turnover[c]
(1e)	cinnamyl alcohol	A	98.8	51.2
	p-methoxybenzyl alcohol	A	99.0	52.2
	piperonyl alcohol	A	97.8	48.9
(2e)	cinnamyl alcohol	A	25.6	12.8
	p-methoxybenzyl alcohol	A	46.8	23.4
	Piperonyl alcohol	A	4.1	2.1
(2f)	Cinnamyl alcohol	A	96.5	53.7
	p-methoxybenzyl alcohol	A	99.9	52.3
	Piperonyl alcohol	A	98.1	53.5
(3c)	Cinnamyl alcohol	A	52.0	26.0
	p-methoxybenzyl alcohol	A	45.2	22.6
	Piperonyl alcohol	A	4.4	2.2
(3d)	Cinnamyl alcohol	A	98.2	56.5
	p-methoxybenzyl alcohol	A	99.9	51.2
	Piperonyl alcohol	A	98.5	50.1

A = corresponding aldehyde.

[a] Conditions: Catalyst = 0.019-0.020 mmol; alcohol = 1 mmol; NMO = 3 mmol; Solvent = CH_3CN or CH_2Cl_2

[b] Yield based on substrate

[c] Moles of product per mole of catalyst

remove water. The aldehydes formed after three hours of reaction were quantified as their 2,4-dinitrophenylhydrazone derivatives. It is noteworthy that the oxidation of alcohols by many ruthenium Schiff base complexes has been reported in the literature[8,11-13]. However, no oxidation of alcohols by iron(III) Schiff base complexes in the presence of NMO as co-oxidant has been reported to our knowledge. Table IV summarises the results obtained for the catalytic oxidation of the alcohols by the metal complexes **(1e)**, **(2e)**-**(2f)** and **(3c)**-**(3d)**.

In no case was there any detectable oxidation of alcohols in the presence of NMO alone in the absence of metal complex. All the metal complexes used were found to catalyze the oxidation of alcohols to aldehydes and secondary alcohols to ketones but the yields and the turnovers were found to vary with the different catalysts. The first salient feature is that the ruthenium(II) complexes were found to be much more effective than the iron(III) complexes in the oxidation of alcohols, presumably due to their easier formation of an oxo group. The ruthenium(II) Schiff base complexes were found to exhibit yields and turnovers comparable to those observed in the literature[8,11-13]. Another important point to note is that in the case of the ruthenium(II) complexes, the yields of the aldehyde did not seem to depend on the nature of the alcohol used while for the iron(III) complexes, the yields were found to be very low for piperonyl alcohol.

EXPERIMENTAL

General

All chemicals (analar grade) were purchased from either Aldrich or BDH Chemicals. Infrared spectra (KBr pellets) were recorded on a Mattson 1000 FT IR spectrometer in the range 4000-400 cm^{-1}. The ^{1}H NMR spectra were recorded at 25 °C using an FT Bruker 250 MHz spectrometer. Magnetic susceptibilities of the metal samples were carried out on a Sherwood Scientific magnetic balance. Copper(II), nickel(II), iron(III) and zinc(II) contents were determined using a Unicam 929 atomic absorption spectrometer and carbon, hydrogen and nitrogen analyses were obtained using a LECO 932 CHNS instrument. Melting points were measured using a Stuart Scientific melting point apparatus. The Schiff base (DAPY-{SalH}$_2$) **(3a)** was prepared according to the literature procedure[5].

Synthesis of Schiff Base (DAPY-{Pyrr}) (1a)

An ethanolic solution (30 mL) of 2,3-diaminopyridine (0.501 g, 4.6 mmol) and pyrrole-2-carboxaldehyde (0.437 g, 4.6 mmol) was stirred under reflux for five hours. The brown solution thus formed was then reduced to dryness and diethylether was added. The brown crystals which separated were washed with diethylether, filtered and vacuum dried. They were then recrystallized from a 1:2 solution of chloroform/diethylether; yield, 0.745 g.

Synthesis of Schiff Base (DAPY-{NaphH}$_2$) (2a)

An ethanolic solution (30 mL) of 2,3-diaminopyridine (0.501 g, 4.6 mmol) and 2-hydroxy-1-naphthaldehyde (1.584 g, 9.2 mmol) was stirred at room temperature for 2 hours. The pale brown precipitate formed was filtered, washed with ethanol and recrystallized from chloroform; yield, 1.728 g.

Synthesis of Copper(II), Iron(III), Nickel(II) and Zinc(II) Complexes (1b)-(1d), (2b)-(2e) and (3b)-(3c)

An ethanolic solution (30 mL) of the metal chloride (2 mmol) was added to an ethanolic solution of **(1a)** or **(3a)** (2 mmol), or a chloroform solution (30 mL) of **(2a)** (2 mmol). For the synthesis of nickel complexes **(1c)** and **(2c)** and of the copper complex **(3b)**, metal acetate (2 mmol) was used instead of chloride. The reaction mixture was stirred at room temperature for several hours. The solid obtained was then washed with the solvent(s) in which the reaction was performed, filtered and dried in a vacuum desiccator.

Synthesis of Ruthenium(II) Complexes (1e), (2f) and (3d)

$RuCl_2(PPh_3)_3$ (0.9623 g, 1 mmol) was added to a solution of Schiff base **(1a)-(3a)** (1 mmol) and triethylamine (0.3004 g, 3 mmol) in THF (20 mL). When the Schiff base **(1a)** was used, no triethylamine was added. The red solution obtained after stirring at room temperature was filtered to remove the white precipitate of $NEt_3.HCl$. The remaining solution was concentrated under vacuum. Addition of diethylether produced a black solid which was recrystallised in THF.

Antibacterial Testing

The bacterial subcultures for *Pseudomonas aeruginosa* and *Salmonella typhi* were obtained from Victoria Hospital, Mauritius.

About 1 mL of a 24-hour broth culture containing approximately 10^6 CFU/mL was placed in sterile petri-dishes. Molten nutrient agar (15 mL) kept at *ca.* 45 °C was then poured in the petri dishes and allowed to solidify. Then 2 holes of 6 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions (5000 µg/mL in DMSO). The plates were incubated for 24 hours at 37 °C. The mean value obtained for the two holes was used to calculate the zone of growth inhibition of each sample.

Catalytic Oxidation of Alcohols

To a solution of the alcohol (cinnamyl, *p*-methoxybenzyl or piperonyl) (1 mmol) in acetonitrile or dichloromethane, NMO (0.351 g, 3 mmol) was added followed by the iron(III) or ruthenium(II) complex (0.019-0.020 mmol). The solution was stirred for 3 hours in the presence of 4 Å molecular sieves ($\approx$ 0.5 g). The mixture was filtered, evaporated to dryness and extracted with diethyl ether (2x25 mL). The combined ether extracts were then filtered and evaporated to give the aldehyde which was then quantified as the 2,4-dinitrophenylhydrazone.

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