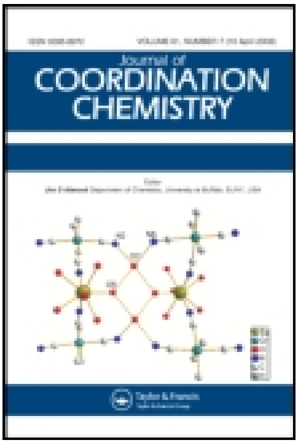

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Synthesis, spectroscopic (IR, electronic, FAB-mass, and PXRD), magnetic, and antimicrobial studies of new iron(III) complexes containing Schiff bases and substituted benzoxazole ligands

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Synthesis, spectroscopic (IR, electronic, FAB-mass, and PXRD), magnetic, and antimicrobial studies of new iron(III) complexes containing Schiff bases and substituted benzoxazole ligands

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Mixed ligand complexes of iron(III), $[Fe(sb)_2(py)Cl]\cdot 2H_2O$ (**1–9**) [where sb**H** = Schiff bases (derived from condensation of 2-aminopyridine (sap**H**), 2-aminophenol (saph**H**), *o*-toluidine (*o*-smab**H**), aminobenzene (sab**H**), *p*-toluidine (*p*-smab**H**), 3-nitroaniline (snab**H**), and anthranilic acid (saa**H**) with salicylaldehyde and substituted (mercapto-)benzimidazole (mbz**H**), {2-(*o*-hydroxyphenyl)}benzoxazole, (pbox**H**)], have been synthesized by the interactions of iron(III) chloride with corresponding ligands in 1 : 2 molar ratio in refluxing pyridine. These complexes have been characterized by elemental analyses, melting points, spectral, and magnetic studies. Powder X-ray diffraction studies of some representative complexes are also reported herein. The antibacterial and antifungal activities of the free ligands and their iron(III) complexes were found *in vitro*. The complexes showed good antibacterial and antifungal effect to some bacteria and fungi. Two standard antibiotics (chloromphenicol and terbinafine) were used for comparison with these complexes.

Keywords: Schiff bases; Iron(III) complexes; UV-Vis; IR; FAB-MS; Magnetic studies; PXRD; Biological activity

1. Introduction

Metal complexes of Schiff bases have been studied for the multidenticity of these ligands and their pharmacological and antitumor activities [1, 2]. Design, synthesis, and characterization of iron complexes with Schiff bases play a role in the coordination chemistry of iron due to their importance as synthetic models for iron-containing enzymes and oxidation catalysts [3]. Our recent investigations on Schiff base–mixed-ligand complexes of "3d" transition metals [4–13] prompted us to synthesize and characterize new mixed ligand complexes of iron(III) due to their biological activities [14, 15] and also in preparation of drugs [16]. Transition metal complexes of Schiff bases and substituted benzimidazole/benzoxazole have attracted attention due to their

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significant role in enhancing fungicidal and agrochemical activities [17]. A number of mononuclear iron(III) complexes of nitrogen, carboxylate, and phenolate donors have been synthesized as functional models to explore their dioxygenase activity [18]. Such mixed-ligand complexes have potential applications in photoluminescence, catalysis, magnetism, molecular architecture, materials chemistry, and therapeutic effects [19, 20].

In continuation to our interest on synthetic and structural characterization of some mixed ligand complexes of transition metals, we report herein the synthesis, characterization (IR, UV-Vis, FAB-mass), powder X-ray diffraction (PXRD), and magnetic values as well as biological studies of iron(III) complexes.

2. Experimental

All the chemicals and solvents used in all preparative and analytical works were of A.R. (BDH or Fluka) grade. Solvents were dried by standard procedures [21]. Iron was determined by atomic absorption spectroscopy, GBC-932 AA and chloride present in the complexes was estimated by Volhard's method [22]. Elemental analyses (C, H, and N) were carried out on a Heraceous Carlo Erba 1108. IR (4000–200 cm^{-1}) and electronic spectra were recorded on Perkin Elmer grating and Pye-Unicam model 557/SP 8-100 spectrophotometers. Magnetic susceptibilities were measured on a Guoy-balance using $Hg[Co(NCS)_4]$ as the standard. FAB-mass spectra of iron(III) complexes were recorded on JEOLSX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB-gas. PXRD of complexes were recorded on a Rigaku model D/Max-2200 PC using Cu-Kα_1 radiation ($\lambda = 1.5406$ Å).

2.1. *Synthesis*

2.1.1. Preparation of ligands. The Schiff bases (sap**H**, *o*-smab**H**, *p*-smab**H**, sab**H**, saph**H**, snab**H**, and saa**H**) were synthesized by refluxing (~4–5 h) a mixture of an equimolar amount of salicylaldehyde with corresponding amines (such as 2-aminopyridine, *o*-toluidine, *p*-toluidine, aniline, 2-aminophenol, 3-nitroaniline, and anthranilic acid) in methanol on a water bath. The resulting products were recrystallized using THF–C_6H_6 mixture. 2-(*o*-hydroxyphenyl)-benzoxazole was prepared by standard literature procedure [23]. The general structures of the ligands are given in figure 1.

2.1.2. Preparation of $[Fe(sb)_2(py)(Cl)]\cdot 2H_2O$. The iron(III) complex $[Fe(sb)_2(py)(Cl)]\cdot 2H_2O$ has been prepared by the interaction of a mixture of iron(III) chloride hexahydrate (1.32 g, 4.9 mmol) with sap**H** (1.94 g, 9.8 mmol) in 1 : 2 molar ratio in freshly distilled boiling pyridine (~50 mL), immediately followed by the addition of zinc dust (~1 g). The mixture was refluxed for ~1 h and then filtered while hot and the filtrate was allowed to attain room temperature. The filtrate was treated with a few milliliters of water (5 mL), stirred thoroughly, and filtered to obtain $[Fe(sap)_2(py)Cl]\cdot 2H_2O$. Yield: 2.127 g, 72%.

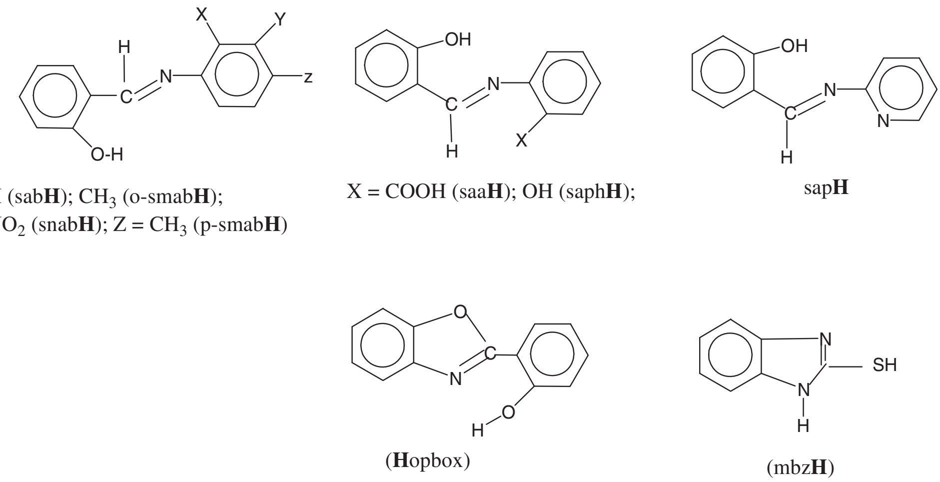


Figure 1. General structure of the ligands.

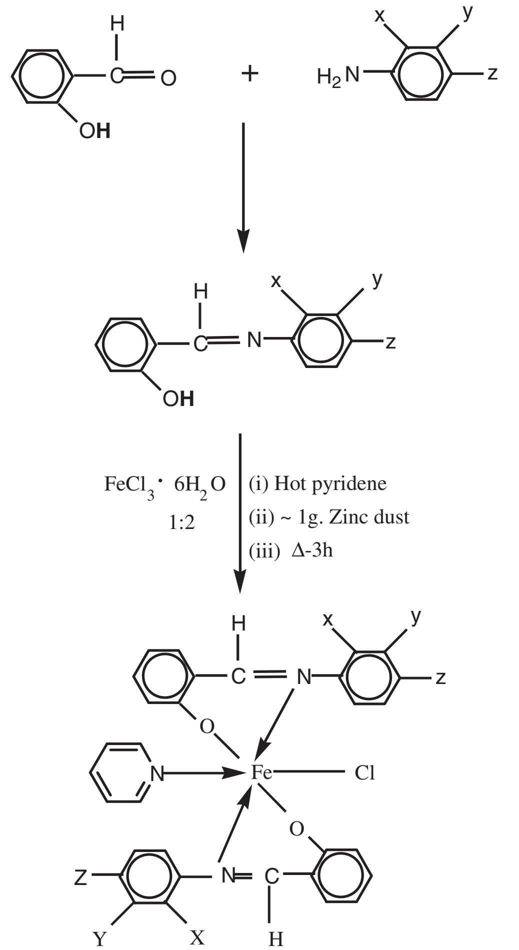
Table 1. Synthetic, analytical and magnetic data of iron(III) complexes containing Schiff bases and substituted benzoxazole.

S. No.	Reactants (g, mmol)		Product (g, % yield)	% Analysis found (Calcd) C	H	N	Fe	Cl	μ_{eff} (B.M.)
1	$FeCl_3 \cdot 6H_2O$ (1.32, 4.9)	+ sap**H** (1.94, 9.8)	$[Fe(sap)_2(py)Cl] \cdot 2H_2O$ (**1**) (2.127, 72)	57.25 (57.96)	4.26 (4.52)	11.40 (11.65)	9.01 (9.9)	5.60 (5.89)	5.81
2	$FeCl_3 \cdot 6H_2O$ (1.08, 4.0)	+ *o*-smab**H** (1.69, 8.0)	$[Fe(smab)_2(py)Cl] \cdot 2H_2O$ (**2**) (1.88, 75)	62.62 (63.21)	5.06 (5.30)	6.18 (6.70)	8.68 (8.90)	5.40 (5.65)	5.76
3	$FeCl_3 \cdot 6H_2O$ (1.107, 4.1)	+ *p*-smab**H** (1.732, 8.2)	$[Fe(smab)_2(py)Cl] \cdot 2H_2O$ (**3**) (1.8, 70)	62.95 (63.21)	5.21 (5.30)	6.29 (6.70)	9.75 (8.90)	5.42 (5.65)	5.80
4	$FeCl_3 \cdot 6H_2O$ (1.026, 3.8)	+ sab**H** (1.58, 7.6)	$[Fe(sab)_2(py)Cl] \cdot 2H_2O]$ (**4**) (1.547, 68)	61.80 (62.16)	4.36 (4.88)	6.80 (7.01)	9.16 (9.32)	5.95 (5.92)	5.79
5	$FeCl_3 \cdot 6H_2O$ (1.05, 3.9)	+ saph**H** (1.66, 7.8)	$[Fe(saph)_2(py)Cl] \cdot 2H_2O]$ (**5**) (1.74, 71)	59.15 (59.01)	4.27 (4.63)	6.31 (6.65)	8.98 (8.85)	5.45 (5.62)	5.70
6	$FeCl_3 \cdot 6H_2O$ (0.967, 3.58)	+ snab**H** (1.73, 7.16)	$[Fe(snab)_2(py)Cl] \cdot 2H_2O$ (**6**) (1.6, 65)	53.56 (54.04)	3.41 (3.95)	9.20 (10.16)	8.26 (8.10)	5.17 (5.14)	5.85
7	$FeCl_3 \cdot 6H_2O$ (0.864, 0.32)	+ saa**H** (1.54, 6.4)	$[Fe(Saa)(Py)Cl] \cdot 2H_2O$ (**7**) (1.71, 78)	58.07 (57.69)	4.08 (4.25)	6.25 (6.11)	8.02 (8.13)	5.25 (5.16)	5.75
8	$FeCl_3 \cdot 6H_2O$ (0.648, 2.4)	+ pbox**H** (1.01, 4.8)	$[Fe(Pbox)(Py)Cl] \cdot 2H_2O$ (**8**) (1.20, 20)	58.85 (59.43)	3.78 (4.02)	6.87 (6.70)	8.32 (8.91)	5.41 (5.66)	5.76
9	$FeCl_3 \cdot 6H_2O$ (1.297, 4.8)	+ mbz**H** (1.44, 9.6)	$[Fe(mbz)_2(py)Cl] \cdot 2H_2O$ (**9**) (1.98, 82)	45.56 (45.20)	3.22 (3.79)	13.34 (13.87)	10.06 (10.37)	6.92 (7.07)	5.80

Similar procedure was adopted for the preparation of other iron(III) complexes. All the synthetic details are collected in table 1. The synthesis and structures of the representative complexes are given in scheme 1.

2.2. *Antimicrobial evaluation*

Most of the synthesized complexes and ligands were screened for their *in vitro* antimicrobial activities against three human pathogenic bacterial species



[X=H for (sab); CH_3 for (o-smab); Y=NO_2 for (snab); Z=CH_3 for (p-smab)]

Scheme 1. Synthesis and structure of iron(III) complexes with Schiff bases.

[*Staphylococcus aureus* (ATCC 9144) (G^+), *Bacillus subtilis* (ATCC 6051) (G^+), and *Escherichia coli* (ATCC 9037) (G^+) and two plant fungal species [*Aspergillus niger* (ATCC 9029) and *Penicillium chrysogenum* (ATCC 10106)] by using the well disc diffusion method [23]. Chloromphenicol and terbinafine were used as standard drugs for comparison. The compounds were dissolved in DMF to get 200 $\mu g\,mL^{-1}$ solutions. Further progressive double dilution was performed to obtain the required concentrations of 100 and 50 $\mu g\,mL^{-1}$. About 0.5 mL (containing 10^7 microorganisms per milliliter) of investigated microorganism was added to a sterile nutrient agar (for bacteria)/dextrose agar (for fungi) medium just before solidification, then poured onto sterile petri dishes (9 cm in diameter) and left to solidify. Using a sterile cork borer (6 mm in diameter), three holes (wells) were made in each disc and then 1 mL of tested compound dissolved in DMF (50, 100, and 200 $\mu g\,mL^{-1}$) was poured into these holes.

Table 2. Physical properties and electronic spectral data of iron(III) complexes.

Compound	Physical state	M.p. (°C)	Transition (cm^{-1}) $^6A_{1g} \to {}^4T_{1g}(G)$	$^6A_{1g} \to {}^4T_{2g}(G)$	$^6A_{1g} \to {}^4E_g(G)$	C.T. Bands	
1	Light brown solid	300[b]	12,360	19,986	25,560	30,550	34,560
2	Brown solid	240[a]	12,072	20,260	26,770	29,290	–
3	Brown solid	260[a]	12,796	20,520	25,240	29,450	34,056
4	Blackish brown	200[a]	12,836	20,775	25,768	30,560	–
5	Chocolaty solid	325[b]	12,332	20,230	25,950	30,772	34,210
6	Dark brown solid	290[a]	12,560	19,896	25,470	–	34,280
7	Brown solid	320[b]	12,140	20,350	25,650	30,320	34,427
8	Brown solid	300[b]	12,800	20,440	25,372	29,980	34,561
9	Pinkish brown solid	325[b]	12,230	20,760	25,452	29,210	–

[a]Decomposed.
[b]Neither melt nor decomposed to the measured temperature.

Finally the dishes were incubated at 37°C for 24 h for bacteria and at 30°C for 72 h for fungi, where clear inhibition zones were detected around each hole. Inhibitory activity was measured (in mm) as the diameter of the inhibition zones. A blank containing only DMF showed no inhibition on organisms in a preliminary test.

3. Results and discussion

The new complexes have been synthesized by the interactions of $FeCl_3 \cdot 6H_2O$ with salicylidene-2-aminopyridine (sap**H**), salicylidene-2-methyl-1-aminobenzene (*o*-smab**H**), salicylidene-4-methyl-1-amino-benzene (*p*-smab**H**), salicylidene-1-aminobenzene (sab**H**), salicylidene-2-aminophenol (saph**H**), salicylidene-3-nitroaniline (snab**H**), salicylidene-anthranilic acid (saa**H**), 2-(*o*-hydroxyphenyl)-benzoxazole (pbox**H**), and 2-mercaptobenzimidazole (mbz**H**) in pyridine. The structures of the iron(III) complexes are given in scheme 1; the syntheses are represented by the following general equation:

$$FeCl_3 \cdot 6H_2O + sb\mathbf{H} \xrightarrow[\sim 1\text{ g zinc dust}]{\text{hot pyridine}} [Fe(sb)_2(py)Cl] \cdot 2H_2O.$$

All these complexes are colored solids (table 2), purified by washing with ethanol and drying over fused $CaCl_2$. The complexes were soluble in hot pyridine, DMSO, and DMF but insoluble in water, carbon tetrachloride, and benzene; purity of the complexes was checked by TLC. The complexes are thermally stable and do not melt or decompose up to 240°C. The synthetic and analytical data of these complexes are collected in table 1. Elemental analyses are in agreement with the values calculated for molecular formulae assigned to these complexes; suggested structures of the complexes are shown in figure 2.

3.1. *IR spectral studies*

IR absorption bands (table 3) due to $\nu_{C=N}$ at 1655–1618 cm^{-1} in the Schiff bases and substituted benzimidazole/benzoxazole [6] shifted to lower frequency, 1686–1595 cm^{-1}.

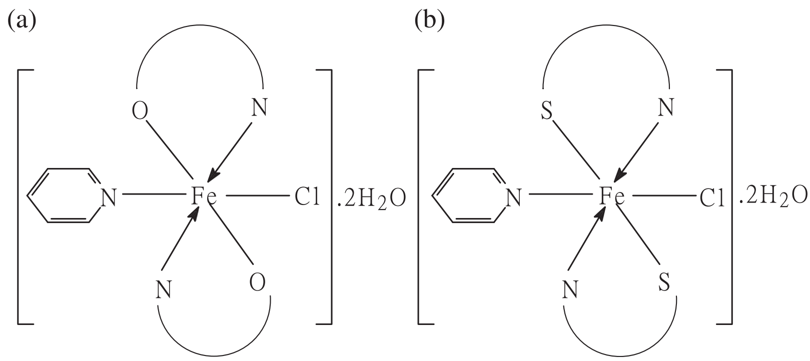


Figure 2. Proposed structures of $[Fe(sb)_2(py)Cl]\cdot 2H_2O$ (a) (**1–8**) and (b) (**9**) complexes.

Table 3. Characteristic IR frequencies (cm^{-1}) of **1–9**.

Complexes	$\nu_{Fe–N}$	$\nu_{Fe–O}$	$\nu_{Fe–S}$	$\nu_{(C–O)}$ Phenolic	$\nu_{C=N}$	ν_{COO^-}	$\nu_{C=N}$ Pyridine	νNO_2	ν_{OH}
1	560	442	–	1276	1602	–	$1449_{(S)}$ $1067_{(M)}$	–	3400 858
2	558	463	–	1278	1597	–	$1479_{(S)}$ $1040_{(M)}$	–	3443 838
3	552	460	–	1281	1608	–	$1468_{(S)}$ $1065_{(M)}$	–	3428 820
4	545	458	–	1280	1596	–	$1450_{(S)}$ $1034_{(M)}$	–	3422 827
5	539	445	–	1289	1595	–	$1472_{(S)}$ $1040_{(M)}$	–	3430 820
6	577	456	–	1275	1617	–	$1465_{(S)}$ $1047_{(M)}$	$1330_{(S)}$	3447 827
7	542	459	–	–	1686	1396	$1452_{(S)}$ $1034_{(M)}$	–	3424 836
8	558	453	–	1279	1605	–	$1480_{(S)}$ $1040_{(M)}$	–	3445 816
9	585	–	402	–	1599	–	$1400_{(S)}$ $1075_{(M)}$	–	3445 841

Such a shift on complexation suggests coordination *via* azomethine [24]. The characteristic $\nu_{(C–O)}$ (phenolic) stretching frequencies, at 1275–1265 cm^{-1} in all the free ligands, shifted to higher frequency at 1289–1275 cm^{-1}, showing chelation of ligands with the metal through the phenolic oxygen [9]. The free COOH group of saa**H** at ~1675 cm^{-1} is shifted to ~1577 cm^{-1} being consistent with unidentate carboxylate coordination [21].

In free mbz**H**, IR peak at ~3300 cm^{-1} (–NH of the imidazole group) remains unchanged in the complex [17], indicating that –NH of the imidazole ring does not coordinate to metal. However, $\nu_{(C=N)}$ (imidazole-tertiary nitrogen) occurring at ~1615 cm^{-1} in the complexes indicated coordination of ligand to iron *via* imidazole tertiary nitrogen [25]. Pyridine ring vibrations were observed at 1460 and 1065 cm^{-1} in the iron(III) complexes, supporting coordination of pyridine [26]. A broad band in all the complexes at ~3400 cm^{-1} is due to ν_{OH} of lattice water. Absence of δH_2O and

γH_2O, for coordinated water, confirms the presence of lattice water [27]. Beside these frequencies, all the iron(III) complexes showed characteristic IR bands at 480–450, 580–530, and 404 cm^{-1}, which can be attributed to $\nu_{(Fe–O)}$, $\nu_{(Fe–N)}$, and $\nu_{(Fe–S)}$ bands, respectively [28, 29]. The band at 360 cm^{-1} has been assigned for terminal $\nu_{(Fe–Cl)}$ [5].

3.2. *Electronic spectral studies*

The electronic spectra of iron(III) complexes (table 2) were measured in DMSO. The complexes exhibit three bands in the regions 12,475 ± 360, 20,325 ± 450, and 25,693 ± 260 cm^{-1}, assigned as $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, and $^6A_{1g} \rightarrow {}^4E_g(G)$ transitions expected for an octahedral iron(III) complexes [30–32].

3.3. *Magnetic studies*

The magnetic moments of iron(III) complexes (**1–9**) containing Schiff bases and substituted benzimidazole/benzoxazole (table 1) at room temperature were in the range $\mu_{eff} = 5.75$–5.88 B.M., indicating high-spin paramagnetic iron(III) in "Oh" geometry [33–35].

3.4. *FAB-mass spectral studies*

The FAB-mass spectrum [5, 8] of $[Fe(saph)_2(py)Cl] \cdot 2H_2O$ (**5**) and $[Fe(mbz)_2(py)Cl] \cdot 2H_2O$ (**9**) showed molecular ion peaks at $m/z = 594$ and 468 (figures 3 and 4, Supplementary material), respectively, which correspond to the molecular mass of **5** and **9** without $2H_2O$ molecules, support for their monomeric nature. Besides these peaks other important fragmentation ion peaks were observed, which are indicative for the fragmentation of ligand from the complexes by the formation of radical cations. The fragmentation patterns showing structural information are represented in schemes 2 and 3 (Supplementary material).

3.5. *PXRD studies*

XRD studies of $[Fe(smab)_2(py)Cl] \cdot 2H_2O$ (**2**), $[Fe(saph)_2(py)Cl] \cdot 2H_2O$ (**5**), and $[Fe(mbz)_2(py)Cl] \cdot 2H_2O$ (**9**) were made with the powder pattern method using Cu-Kα radiation with $\lambda = 1.5406$ Å. The PXRD pattern was recorded in the 2θ range between 15.239 and 81.554 with a step size of 0.0167. The PXRD diffractograms of iron(III) complexes exhibit almost similar, amorphous nature. The PXRD of these complexes are given in figures 5, 6, and 7 (Supplementary material).

3.6. *Antimicrobial activity*

The antimicrobial activities of some of the complexes have been carried out at 50, 100, and 200 µg mL^{-1} against three bacteria and two fungi. The inhibitory effects of these complexes are given in table 4. A chloromphenicol (antibacterial drug) and terbinafine (antifungal drug) were used as standard drugs for comparison. The results obtained by

Table 4. Antibacterial and antifungal activity of free ligands and their complexes with iron(III).

	Bacteria (concentration in $\mu g\,mL^{-1}$)									Fungi (concentration in $\mu g\,mL^{-1}$)					
	S. aureus (G^+)			*B. subtilis* (G^+)			*E. coli* (G^+)			*A. niger*			*P. chrysogenum*		
Compounds	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
pbox**H**	++	+++	+++	++	++	+++	+	++	++	++	+++	+++	++	++	+++
mbz**H**	++	+++	+++	++	++	+++	+	++	+++	++	+++	+++	++	++	+++
saph**H**	+	++	++	+	+	++	+	+	+	+	+	++	+	++	++
sab**H**	+	+	+	+	+	+	+	+	+	+	+	++	+	+	+
4	++	+++	++++	++	+++	++++	++	+++	++++	+	++	+++	++	+++	++++
5	++	+++	++++	++	+++	++++	++	+++	++++	+	++	+++	++	+++	++++
9	+	++	+++	+	++	+++	++	++	+++	+	++	–	–	–	–
A	+	+	++	+	+	++	+	++	+++	–	–	–	–	–	–
B	–	–	–	–	–	–	–	–	–	+	++	++	+	++	++

Well diameter = 6 mm, inhibition zone beyond the holes are + = 1–5 mm, ++ = 6–10 mm, +++ = 11–15 mm, ++++ = >16 mm, and – = not determined. A = chloromphenicol and B = terbinafine; pbox**H** = 2-(*o*-hydroxyphenyl)benzoxazole, mbz**H** = mercaptobenzimidazole, saph**H** = salicylidene-2-aminophenol, sab**H** = salicylidene-1-aminobenzene.

disc diffusion indicate that coordination compounds containing Schiff bases, substituted benzoxazole/mercaptoimidazole as well as coordinated pyridine have enhanced activity compared to the ligands (Schiff bases/imidazole). Comparing with chloromphenicol (standard antibacterial drug) and terbinafine (standard antifungal drug) the following results can be obtained: (i) all the complexes have higher or equal activity against all organisms than free ligands. (ii) All Schiff bases possess pronounced antimicrobial effect against all tested fungi and Gram-positive bacteria in comparison to antibiotics (terbinafine and chloromphenicol) used. (iii) The tested complexes have greater activity than standard antibiotics (terbinafine and chloromphenicol) against tested fungi and Gram-positive bacteria except **9**. (iv) Complexes **4** and **5** are better antimicrobial agents than chloromphenicol and terbinafine against all tested organisms.

4. Conclusions

$[Fe(sb)_2(py)(Cl)] \cdot 2H_2O$ (**1–8**) have been synthesized using bidentate Schiff bases and substituted benzoxazole having "O" and "N" donors, whereas **9** bears "S" instead of "O". The geometry is octahedral in all the iron(III) complexes. $[Fe(saph)_2(py)(Cl)] \cdot 2H_2O$ (**5**) and $[Fe(mbz)_2(py)(Cl)] \cdot 2H_2O$ (**9**) show molecular ion peaks corresponding to their formulation and other important peaks due to successive degradation of the monomer. Formulae of the prepared complexes have also been suggested by elemental analysis, electronic, IR, NMR (^1H, ^{13}C) spectral studies as well as magnetic values. PXRD patterns reveal that the complexes are amorphous. Antimicrobial studies indicate that **4** and **5** are more potent against three Gram-positive bacteria and two fungi, compared with literature values [31].

Acknowledgments

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