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Synthesis, characterization and antimicrobial activity of some transition metal complexes of Schiff base and Neutral bidentate ligand

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ABSTRACT

The mixed ligand complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff bases, formed by condensation of 2-Hydroxy-1-naphthaldehyde/Salicylaldehyde and p-Anisidine with Neutral bidentate ligand 4-Hydroxybenzldehyde/3-Ethoxy-4-hydroxybenzaldehyde (Ethylevanilline) and o-Phenylinediamine have been synthesized and characterized. The complexes have been characterized with the help of elemental analysis (C, H and N), magnetic measurements, thermo gravimetric analysis and their structural configuration have been determined by various spectroscopic (electronic, IR, UV-visible) techniques. The elemental analysis data suggest that the stoichiometry- of the complexes to be 1 : 2 : 1 [M : L_1 : L_2] ratio. The infrared spectral data showed the coordination sites of the free ligand with the central metal ion. The electronic absorption spectral data revealed the existence of an octahedral geometry for Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes. Supported their geometrical structures which confirmed by the electronic absorption spectra. The thermo gravimetric analysis data of the complexes display the existence of hydrated water/crystal water molecules. All prepared compounds were also evaluated for their antibacterial and antifungal activities by the Agar well diffusion method. The antibacterial activity was tested against the bacteria *Bacillus subtilis* (Gram positive), *Escherichia coli* (Gram negative). The antifungal activity was tested against *Aspergillus niger*. The results obtained were evaluated with antibacterial and antifungal standard *Streptomycin*.

KEYWORDS

Schiff bases;
Complexes;
Characterization;
Antibacterial activity;
Antifungal activity.

INTRODUCTION

The chemistry of the carbon-nitrogen double bond plays a vital role in the progresses of chemistry science[1]. Organometallic chemistry has been developed, in the last four decades, to be the largest and important branch as a link connecting the fields of organic and inorganic chemistry[2]. Compounds containing an azomethine group (-CH=N-), known as Schiff bases are formed by the condensation of a primary amine with a carbonyl compound.

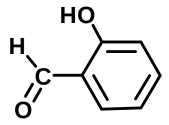
Schiff bases are generally bi- or tri- dentate ligands capable of forming very stable complexes with transition metals. Some are used as liquid crystals. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications[3,19]. Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases with donors (N, O) have structure similarities with natural biological systems and due to the presence of imines group (the -N=CH-), are utilized in elucidating the mechanism of transformation and rasemination reaction in biological systems[4]. Schiff base complexes have been used as drugs. Schiff bases and their complexes are well known for their pronounced biological activities[5-7]. They are actively associated with antibacterial[5], anti-fungal[8,9], herbicidal[10], antitubercular[11], anti-HIV[8] and anticancer activities[12]. Metal ions play an important role in bioinorganic chemistry and metals such as Mn, Fe, Co, Ni, Cu and Zn may exist in trace amounts in biological systems. Structural studies of the complexes of these metals with biological compounds are extremely important. Many metal ions are known to play very important roles in biological processes in the human body[13,14]. For example, zinc(II) and copper(II) ions are the second and third most abundant transition metals in humans. These metals and some of their complexes have been found to exhibit antimicrobial activities[15-17]. Schiff bases derived from the salicylaldehyde are well known as polydentate ligands coordinating in neutral forms[18]. Several research papers have been synthesized and characterized on transition metal complexes of Schiff base derived from salicylaldehyde[19].

In the present work we have described the synthesis, characterization and antibacterial property of transition metal complexes containing bidentate Schiff bases derived from 2-Hydroxy-1-naphthaldehyde/Salicylaldehyde and p-Anisidine. The synthesized complexes are characterized by elemental, TGA, IR and UV visible spectroscopic analyses. The structure of the similar complexes is reported to be octahedral[20].

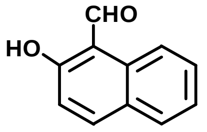
EXPERIMENTAL

Materials

2-Hydroxy-1-naphthaldehyde was purchased from National Chemicals Vadodara, INDIA, Salicylaldehyde and Metal salts were purchased from Chiti-Chem Corporation Baroda, INDIA. All the chemicals used were of A.R. grade. The solvents were dried and distilled before use according to standard procedures.



Salicylaldehyde



2-Hydroxy-1-naphthaldehyde

Synthesis of Schiff base

An ethanolic solution of 2-Hydroxy-1-naphthaldehyde/Salicylaldehyde and p-Anisidine in equimolar ratio was mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained crystals ware collected and ware dried in air. Yield: 82-87%

Synthesis of Neutral bidentate ligand

The preparation of Neutral bidentate ligand was carried out by refluxing an alcoholic solution of 4-Hydroxybenzldehyde/3-Ethoxy-4-hydroxybenzaldehyde with o-Phenylinediamine for an hour. The solution was then concentrated, scratched and was cooled in air. The obtained crystals were collected and recrystallized crystals were dried in air.

Synthesis of mixed-ligand complexes

The preparation of mixed-ligand complexes of [M(II)bis(Nap-Anisi)/bis(Sal-Anisi).(Ben.H-Phdia)/(EtBen.H-Phdia)].H_2O [where M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)] was carried out by refluxing an alcoholic solution of diaqua bis(Nap - Anisi)M(II)/diaqua bis(Sal-Anisi)M(II) [where M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)] with (Ben.H-Phdia)/(EtBen.H-Phdia) for an hour. The solution was then concentrated, scratched and was cooled in refrigerator overnight. The obtained crystals were collected and recrystallized crystals were dried in air.

$$\mathbf{MCl_2 + 2(SB_1.H) \xrightarrow{H_2O} [M(SB_1)_2.(H_2O)_2] + 2HCl}$$

where, M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) & SB_1.H = Nap.H-Anisi, Sal.H-Anisi

$$\mathbf{[M(SB_1)_2.(H_2O)_2] + (SB_2.H) \xrightarrow{Reflux,\ 1hr} [M(SB_1)_2.(SB_2.H)].H_2O + H_2O}$$

where, M = [Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)], SB_1 = Nap-Anisi, Sal-Anisi and SB_2.H = Ben.H-Phdia, EtBen.H-Phdia

Biological screening

The metal complexes were screened against bacteria (*Bacillus subtilis* and *Escherichia coli*) and fungal strains (*Aspergillus niger*). Anti bacterial and fungal screening was done by the agar well diffusion method[21] at 200 μg/mL concentration in DMSO. Testing samples and Control samples were prepared in DMSO.

Anti-bacterial screening

These complexes ware screened for anti-bacterial activity against *Bacillus subtilis* (as gram positive bacteria) and *Escherichia coli* (as gram negativebacteria) organism using the agar well diffusion method[21] at 200 μg/mL concentration in DMSO. Nutrient agar was used as for the growth of bacterial. The results were compared with standard antibiotics of *Streptomycin* and dimethyle sulfoxide (DMSO) were used as control.

Anti-fungal screening

The antifungal activity of the complexes was carried out against *Aspergillus niger using* the agar well diffusion method[21] at 200 μg/mL concentration in DMSO. Potato dextrose agar was used as for the growth of fungus. The results were compared with standard antibiotics of Streptomycin and dimethyle sulfoxide (DMSO) were used as control.

Compounds containing promising antimicrobial activity were selected for minimum inhibitory concentration (MIC) studies. The minimum inhibitory concentration was determined using the agar well diffusion method[21]. Test extract loaded discs inoculated with microorganisms were incubated at 37 °C for 24 h for the bacteria and at 30 °C 72 h for fungi. During the incubation period, the test solution diffused and the growth of the inoculated microorganisms was affected. The concentration at which an inhibition zone developed was noted.

Physical measurements

Carbon, hydrogen and nitrogen analysis of the complexes were carried out on a CHN analyzer Parkin Elmer 2400 series II (USA). IR spectroscopy analyses were recorded on Spectrum GX FT-IR Perkin Elmer spectrophotometer (USA) in 4000–200 cm^{-1} range using solid samples as KBr pellets. Magnetic susceptibility measurements were carried out by the Gouy balance at room temperature. The electronic absorption spectrum was carried out by using a Perkin Elmer model Lambda 19 spectrophotometer (USA) in the wave length range 185-3200 nm using DMF as a solvent. Thermo gravimetric analyses data were measured from room temperature to 900 °C at a heating rate of 20 °C/min. The data were recorded on a Thermo Gravimetric Analyzer (TGA-1) Perkin Elmer (USA). All the complexes melting points were recorded in open capillaries in a capillary melting point apparatus.

The complexes were analyzed for the metal contents by the EDTA titration[22]. After decomposing the Complexes with a mixture of conc. HCL- conc. HNO_3 (1:3 aquaregia media).

RESULTS AND DISCUSSION

The Schiff base and their mixed ligand complexes are found to be stable in air. All mixed ligand complexes are colored, non-hygroscopic, and thermally stable solids, signifying a possibility of presence of strong metal ligand bond. The ligand is soluble in common organic solvents but their complexes are insoluble in water and most organic solvents, but complexes are easily soluble in DMSO.

The color, melting point, elemental analysis, magnetic measurement and empirical formulae of the prepared complexes are listed in TABLE 1.

The condensation of 2-Hydroxy-1-naphthaldehyde/ Salicylaldehyde and p-Anisidine in ethanol gives single product according to the following reaction;

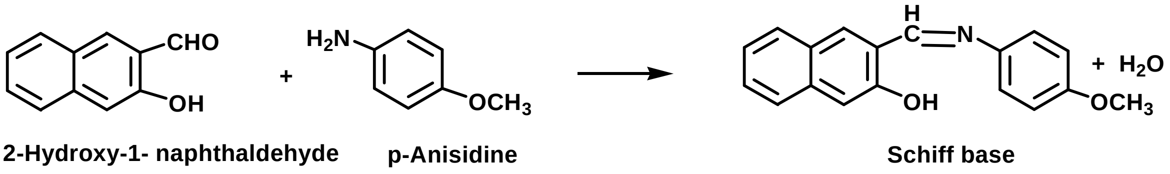
The results of the elemental analysis are in good agreement with the calculated values. The metal contents of the complexes were determined according to literature methods[23]. The infrared spectra of the complexes confirmed the coordination of metal ion with ligands.

Infrared spectra and mode of bonding

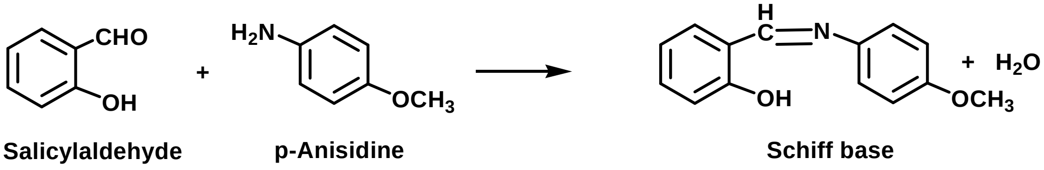
The important absorption frequencies of all metal complexes and their assignments are given in TABLE 2. The infrared spectrum of the free ligand is compared with that of the complexes to determine the coordination sites that may have involved in the chelation.

Electronic spectral analyses

The electronic spectrum gives information on the electronic environment of the metal. The splitting of d orbital and in turn the structure expected for the complexes.



(*Z*)-3-((4-Methoxyphenylimino)methyl)naphthalen-2-ol



(*Z*)-2-((4-Methoxyphenylimino)methyl)phenol

Thermal analyses

Thermo gravimetric analyses of the complex is used to get the;

(i) Information on water of hydration if present in the coordination sphere of the central metal ion.

(ii) Scheme of thermal decomposition of the complexes and

(iii) To find thermal stability of the complex.

TABLE 1 : Physical properties and analytical data for the complexes

Complexes	Empirical Formulae	Formula Weight	Colour	Yield (%)	M.P (^{o}C)	Found (Calculated) (%)				μ_{eff} (B.M)
						C	H	N	Metal	
[Mn(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}MnO_7N_4$	940.94	Brown	82.15	200	71.45 (71.41)	4.93 (4.89)	5.99 (5.95)	5.86 (5.84)	5.79
[Fe(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}FeO_7N_4$	941.85	Yellowish Green	59.46	298	71.42 (71.35)	4.89 (4.88)	6.01 (5.95)	5.98 (5.93)	4.78
[Co(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}CoO_7N_4$	944.93	Greenish Yellow	74.84	186	71.15 (71.12)	4.91 (4.87)	5.99 (5.93)	6.29 (6.24)	4.82
[Ni(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}NiO_7N_4$	944.69	Dark Green	78.28	190	71.19 (71.13)	4.96 (4.87)	5.89 (5.93)	6.22 (6.12)	2.95
[Cu(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}CuO_7N_4$	949.55	Dark Blue	66.82	256	70.86 (70.77)	4.88 (4.84)	5.96 (5.89)	6.74 (6.69)	1.92
[Zn(Nap -Anisi)$_2$.(Ben.H-Phdia)].H_2O	$C_{56}H_{46}ZnO_7N_4$	951.39	Light Yellow	79.42	215	70.61 (70.63)	4.81 (4.84)	5.92 (5.89)	6.91 (6.87)	–
[Mn(Sal-Anisi)$_2$.(EtBen.H-Phdia).H_2O	$C_{52}H_{50}MnO_9N_4$	928.94	Brown	72.35	164	67.24 (67.17)	5.49 (5.38)	6.08 (6.03)	6.99 (5.91)	5.91
[Fe(Sal-Anisi)$_2$.(EtBen.H-Phdia).H_2O	$C_{52}H_{50}FeO_9N_4$	929.85	Brown	52.84	186	67.18 (67.11)	5.41 (5.38)	6.05 (6.02)	6.07 (6.00)	4.92
[Co(Sal-Anisi)$_2$.(EtBen.H-Phdia).H_2O	$C_{52}H_{50}CoO_9N_4$	932.93	Dark Brown	75.82	226	66.99 (66.89)	5.38 (5.36)	6.01 (6.00)	6.39 (6.31)	4.89
[Ni(Sal-Anisi)$_2$.(EtBen.H-Phdia .H_2O	$C_{52}H_{50}NiO_9N_4$	932.69	Yellowish Green	81.62	172	66.87 (66.90)	5.45 (5.36)	6.09 (6.00)	6.27 (6.29)	2.96
[Cu(Sal-Anisi)$_2$.(EtBen.H-Phdia).H_2O	$C_{52}H_{50}CuO_9N_4$	937.55	Dark Blue	68.31	178	66.61 (66.56)	5.39 (5.33)	5.99 (5.97)	6.81 (6.78)	1.90
[Zn(Sal-Anisi)$_2$.(EtBen.H-Phdia).H_2O	$C_{52}H_{50}ZnO_9N_4$	939.39	Greenish Yellow	74.15	208	66.57 (66.43)	5.41 (5.32)	5.97 (5.96)	7.02 (6.96)	–

Magnetic moments

The magnetic moment values are useful in the evaluation of results provided by the other techniques of the structural investigation. The geometry assessment of the complexes around the Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) ions was supported further from the results of the magnetic moments.

The magnetic moment μ_{eff} of the Mn(II) (d5) complex is 5.78-5.96 B.M which suggests octahedral geometry around the metal ion[24]. The magnetic moment μ_{eff} for the complex of Fe(II) (d6) were found to be 4.78-4.92 B.M respectively[25]. The magnetic moment

μ_{eff} Of the Co(II) (d7) complex is 4.82-4.89 B.M which suggests the high spin six-coordinated octahedral arrangement[26,27] of ligand molecules around the metal ion. The Ni(II) (d8) complex has magnetic moment value of 2.95-3.06 B.M indicating a spin-free octahedral[28,29] configuration. The magnetic moment μ_{eff} value of the Cu(II) (d9) complex is 1.92-1.90 B.M which suggests a distorted octahedral geometry[30,31] around the metal ion. The Zn(II) complex is found to be diamagnetic as expected for d10 configuration and is found to be octahedral geometry[32].

Electronic spectral analyses

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereo chemistries of metal ions in the complexes based on the positions and number of d–d transition peaks. The electronic absorption spectra of the complexes were recorded at room temperature. The bands observed in λmax(ε): 240 to 260 nm are due to $\pi\rightarrow\pi^*$ transition of benzene ring and azomethine group[33]. The bands were shifted to higher range, which is due nitrogen and oxygen that involved in coordination with metal ion. The absorption bands are observed in the range of λmax(ε): 320 to 370 nm due to $n\rightarrow\pi^*$ transition from imine group corresponding to the ligand or metal complexes.

Electronic spectrum of Mn(II) Complex exhibits three bands at λ max(ε) : ~301 nm, ~365 nm and ~515 nm which may be assigned to transitions ${}^6A_{1g}\rightarrow{}^4T_{1g}(P)$, ${}^6A_{1g}\rightarrow{}^4T_{2g}(D)$ and ${}^6A_{1g}\rightarrow{}^4T_{1g}(G)$ respectively. These values are in good agreement with the reported octahedral geometry 0f Mn(II) complex[34]. The electronic spectra of the Ni(II) complex displayed three bands in the range at λmax(ε) : ~375 nm, ~515 nm and ~1101 nm assignable to ${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$, ${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$, ${}^3A_{2g}\rightarrow{}^3T_{2g}(F)$ transitions respectively. This confirms the presence of an octahedral geometry for the Nickel complex[35,36]. The electronic spectrum of the Cobalt complexes exhibited three bands at λmax(ε): ~505 nm, ~560 nm and ~1120 nm, which may reasonably be assigned to ${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$, ${}^4T_{1g}\rightarrow{}^4A_{2g}$, ${}^4T_{1g}\rightarrow{}^4T_{2g}$ transitions, respectively, suggesting an octahedral geometry around Co(II) ion[37]. The electronic spectrum of the Fe(II) complex exhibit a band at λmax(ε): ~891 nm, assigned to the ${}^5T_{2g}\rightarrow{}^5E_g$ transition. A strong charge transfer band is observed at λmax(ε): ~380 nm. These data suggest an octahedral geometry[39]. Cu(II) complexes displayed a broad band in the range at λmax(ε): ~851 nm that can be assigned to ${}^2E_g\rightarrow{}^2T_{2g}$ transition, indicating the Cu(II) complexes have octahedral geometry[38]. Zn(II) complex does not exhibit any characteristic d-d transitions. The Zn(II) complexes have been found to be diamagnetic in nature[40].

Thus based on the UV-Visible spectroscopy it is found that metals form complexes with the prepared Schiff base ligand with octahedral geometry.

Infrared spectra and mode of bonding

IR spectra have proven to be the most suitable technique to give enough information to elucidate the mode of bonding of the ligands to the metal ions[41-43]. The various criteria proposed for determining the mode of bonding have been discussed by Nakamoto[44]. In general, the bonding depends on (a) the nature of central atom, (b) the nature of other ligands in the coordination sphere and (c) environmental controls and kinetic (mechanistic) controls.

The infrared spectral data of complexes reveal broad band in the range of 3306-3400 cm^{-1} attributed to the existence of crystallized water molecules[45]. The infrared spectra of complexes register the ν(C=C) band at about 1535 cm^{-1}[46]. The frequencies in the range 1150-1165 cm^{-1} attributed to ν(C-N) stretching[47].

The shift of the characteristic ν(C=N) (azomethine) band from 1590-1620 to 1578-1605 cm^{-1} indicated coordination of the azomethine nitrogen's to the metal atom[48]. Further coordination of azomethine is confirmed with the presence of new bands at 490-515 cm^{-1} region assignable to ν(M-N) for these complexes. Also the absorption band at 1262-1299 cm^{-1} due to ν(C-O) vibration of the ligand is shifted to higher frequency indicating its involvement in coordination with the metal ions through the oxygen atom[49,50]. A new band in the 440-460 cm^{-1} region in the spectra of the complexes is assignable to ν(M-O)[51]. Thus it is concluded from the IR spectrum for metals, that the metal is participating in the bond formation through the azomethine C=N group and the C=O carbonyl group[52]. The infrared spectrum of the complex under investigation displays a band at 953 cm^{-1} which is due to the presence of a coordinate OH group of salicylaldehyde to M(II) ion[53]. The band at 3306 cm^{-1} is due to the presence of OH group in the complex (from it's the chemical structure). The infrared spectra show more bands which were found in range of 783-800 cm^{-1} can be assigned as M-N=C stretching respectively[54].

The appearance of this vibration supports the involvement of –OH, –CHO and –N = N– group in chelation[55].

TABLE 2 : IR absorption frequencies of complexes (cm^{-1})

Complexes	ν (C=N)	ν (C-N)	ν (C=C)	ν (C-O)	ν (M-O)	ν (M-N)
[Mn(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	1625	1152	1528	1299	447	515
[Fe(Nap -Anisi)$_2$.(Ben.H-Phdia)].H$_2$O	1615	1162	1530	1280	450	495
[Co(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	1620	1160	1535	1287	460	510
[Ni(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	1630	1150	1532	1289	455	515
[Cu(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	1606	1174	1536	1286	457	505
[Zn(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	1610	1169	1530	1288	450	510
[Mn(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1615	1165	1525	1296	455	515
[Fe(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1602	1150	1517	1286	453	514
[Co(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1630	1152	1530	1285	455	510
[Ni(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1615	1160	1535	1290	460	495
[Cu(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1610	1155	1532	1298	450	505
[Zn(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	1625	1162	1528	1296	455	515

Thermal analyses

The thermal properties of the prepared complexes were examined by thermal gravimetric analysis (TGA). Thermal analysis by the TG techniques has proved to be very useful in determining the crystal water content in complexes and their thermal stability and decomposition mode under a controlled heating rate. The thermal behavior of the complexes depended on the nature and the environment around the metal ion. The simultaneous TG curves of metal complexes were recorded in the nitrogen atmosphere at a heating rate 20 °C/min, and the weight loss was measured from the ambient temperature up to 900 °C. The TG curves of the complexes elucidate that as temperature increases the decomposition of complexes takes place due to fragmentation and show considerable loss in weight. The TGA of the complexes shows that they are thermally quite stable to a varying degree. The TGA results show good agreement with the formula suggested from the analytical data. The dynamic TGA with the percentage mass loss at different steps have been recorded. The TGA curves of all metal complexes show that the initial mass loss occurring within 100-120 °C range is interpreted as loss of moisture and hydrated water molecules during the chelate drying process.

In the first step, weight loss observed in the temperature range of 35-120 °C may be due to loss of water molecule. The second step, weight loss observed in the temperature range of 120-450 °C, which may be due to decomposition of Schiff base. The final step, weight loss observed in the temperature range of 450-650 °C, which may be due to decomposition of Neutral bidentate ligand. Above 650 °C a constant plateau is observed which explicate complete decomposition of the complex. Thus, the TG curve indicates that the final decomposed product is MO$_2$ (metal oxide)[56,57].

Antimicrobial activity

The antibacterial and antifungal activities of the complexes were assayed against some of the bacteria and fungi. In the present study, all chemically synthesized compounds were evaluated against one Gram- positive, one Gram-negative bacterium and one fungi. The antibacterial activity was determined with the agar well diffusion method[31]. Stock solutions were prepared by dissolving the compound in DMSO[58,59], and the sample concentration was 200 micro/ml. The metal complexes were screened separately for their antibacterial activity against the bacteria *Bacillus subtilis* (as gram positive bacteria), *Escherichia coli* (as gram negative bacteria). The results were compared against the controls, which were screened simultaneously. The activity was measuring the diameter of the inhibited zone in millimeters (mm). The agar well diffusion method[31] was used to assay antifungal activity against *Aspergillus niger*. Stock solutions were prepared by dissolving the compound in DMSO[58,59] and the sample concentration was 200 micro/ml. Both the complexes show antifungal activity to a moderate extent against the fungi. Nutrient agar was used as bacterial growth medium while Potato dextrose Agar was used as for the growth of fungus. Standard antibiotics and standard antifungal drug namely *streptomycin* were used for comparison with antibacterial and antifungal activities shown by these compounds and dimethyle sulfoxide (DMSO) were used as control, respectively. Test extract loaded discs inoculated with microorganisms were incubated at 37 °C for 24 h for the bacteria and 30 °C for 72 h for fungi. During the incubation period, the test solution diffused and the growth of the inoculated microorganisms was affected. The concentration at which an inhibition zone developed was noted. The minimum inhibitory concentration (MIC) values of the investigated compounds are summarized. Such increased activity of the complexes can be explained based on the Overtone's concept and the Tweedy chelation theory[60].

The results reported in TABLE 3 reveal that all the complexes are particularly active against bacteria *Bacillus subtilis, Escherichia coli* and against fungi, namely, *Aspergillus niger*.

Bacillus subtilis

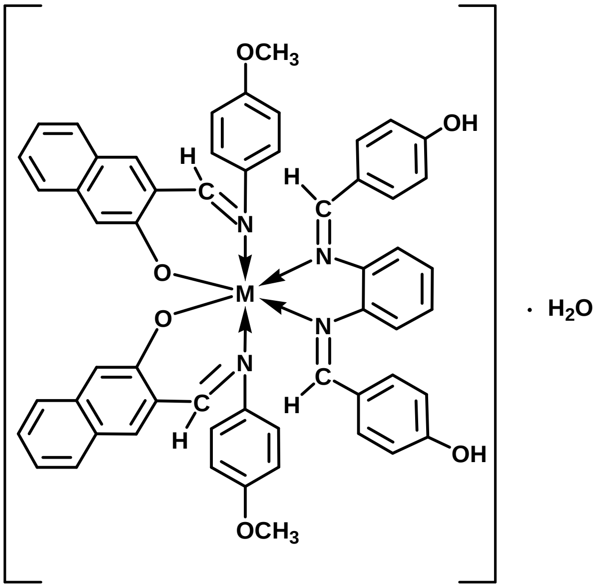
Escherichia coli

1 - [Mn(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O
2 - [Co(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O
3 - [Zn(Nap -Anisi)$_2$.(Ben.H-Phdia)].H$_2$O
4 - [Mn(Nap -Anisi)$_2$.(Ben.H-Phdia)].H$_2$O
S - Streptomycin (standard drug)
C - Dimethyle sulfoxide (DMSO) were used as control

TABLE 3 : Antimicrobial activities of metal complexes

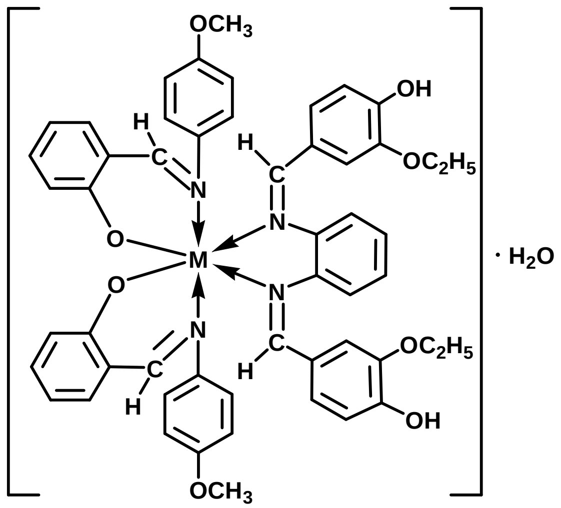
Complexes	Antibacterial activity		Antifungal activity
	Bacillus subtilis	*Escherichia coli*	*Aspergillus niger*
	Zone of inhibition in mm		
[Mn(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	18	24	16
[Fe(Nap -Anisi)$_2$.(Ben.H-Phdia)].H$_2$O	-	16	-
[Co(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	20	-	22
[Ni(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	-	18	20
[Cu(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	22	12	-
[Zn(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O	22	18	14
[Mn(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	22	16	-
[Fe(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	18	-	18
[Co(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	29	19	22
[Ni(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	12	14	-
[Cu(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	27	17	15
[Zn(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O	22	15	-

On the basis of results of the physicochemical studies, the bonding and structure for the metal complexes may be represented as show in figure.



[M(Nap -Anisi)$_2$.(Ben.H- Phdia)].H$_2$O

where, M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)



[M(Sal-Anisi)$_2$.(EtBen.H-Phdia)].H$_2$O

where, M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)

CONCLUSION

In this paper we have reported the co-ordination chemistry of complexes derived Schiff base ligand, obtained from the reaction of 2-Hydroxy-1-naphthaldehyde/Salicylaldehyde and p-Anisidine with Neutral bidentate ligand 4-Hydroxybenzldehyde/3-Ethoxy-4-hydroxybenzaldehyde and o-Phenylinediamine with metals such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Fe(II). The structures of the ligand[61] the structures of the complexes were confirmed by elemental analyses, magnetic measurement, IR spectroscopy, thermo gravimetric analyses and UV-Visible spectroscopic analyses. All these complexes are assigned to be in octahedral geometry and exhibit co-ordination number six. The spectral study of the complexes shows that metal ion is bonded through the N- and O- donor atoms of the ligands. In this work, the antibacterial and antifungal activities of the few mixed ligand metal(II) complexes have been done. Biological studies of these complexes reveal that these complexes show better activity.

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