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Spectral Characterization and Antimicrobial Studies of Synthesized Fe (III) and Mn (II) Mixed Ligand Complexes of Methionine-Phenylhydrazone with Thiophene

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Abstract

The synthesized ligand, methionine-phenylhydrazone was reacted with Fe (III) salt and thiophene or Mn(II) salt and thiophene. Two mixed ligand complexes were obtained. The ligand and its mixed ligand complexes were characterized on the basis of their colour, physical nature, solubility, melting points, molar conductivities, elemental analysis, and spectroscopic studies using infrared and visible spectra. The melting points were high in the range of 268-289°C inferring strong bonding network within the molecules. The low conductivities ($0.72-0.93 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicated the non-electrolytic nature of the compounds. The infrared spectral analysis revealed that the methionine-phenylhydrazone acted as bidentate and coordinated to the metal ions through the nitrogen atom of the azomethine group and the oxygen atom of the carbonyl group. The octahedral configuration of the molecules is as a result of the incorporation of the monodentate secondary ligand-thiophene. The antimicrobial studies were carried out by the paper disc diffusion method. The pure isolates used were *Staphylococcus aureus*, *Escherichia coli* as bacteria and fungi such as *Candida albicans* and *Aspergillus niger*. The results of zones of inhibition were compared with those produced by ampiclox and fluconazole. The results showed that both the ligand and its mixed ligand complexes had better antibacterial properties than antifungal properties. The complexes gave better inhibition zones compared to the free ligand but in all, less effective when compared to those caused by ampiclox and fluconazole.

Keywords: synthesis, characterization, antimicrobial, ligand, complexes

1. Introduction

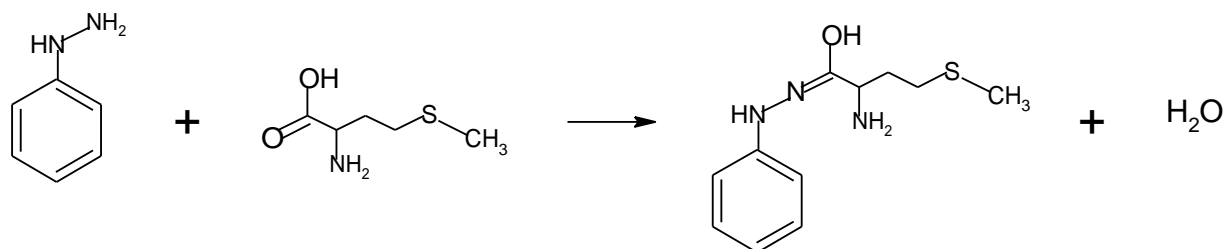
Recently many research works in bioinorganic chemistry and pharmaceutical fields have been focused on development of new drugs due to preponderant of infectious diseases [1, 2]. Antimicrobial agents are chemicals or mixtures which are used to inhibit the growth of micro-organisms or eliminate them totally and thereby stopping their proliferation [3]. Hydrazones and their derivatives are known to be biologically active in a wide variety of ways, such as serving as nematocides, rodenticides and even plant growth regulators. Some derivatives show spasmolytic activity against sarcoma and malignant neoplasm [4]. Some are used as plasticizers and stabilizers for polymers, polymerization initiators and antioxidants. While some used in preparative organic chemistry act as intermediates in synthesis of new products or in detection and determination of carbonyl groups and metals. In all, the existence of multidentate nature promotes the versatility of their coordination modes, thereby making modifications possible and hence enhancing wider application due to their inherent structure-activity potentialities [5]. This development stem from numerous binding sites in the ligand moiety which are listed to include (i) hydrophobic aryl ring (ii) hydrogen bonding domain (iii) an electron donor-acceptor system and (iv) another hydrophobic aryl ring responsible for metabolism [6,7]. The electronic configuration of transition metals allows chelation with polydentate molecule such as methionine-phenylhydrazone to produce highly organised supramolecular metal complexes with enhanced antimicrobial properties [8]. This present study focused on the synthesis characterization and antimicrobial studies of Fe (III)

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And Mn (II) mixed ligand complexes of methionine-phenylhydrazone with thiophene.

2. Experimental

All chemicals used for this research were of analytical grade purchased from Sigma Aldrich and were used without further purification. Shimadzu FTIR-8400S, Perkin- Elmer model 240 automatic elemental analyzer, double beam PC scanning spectrophotometer (UVD2960), Jenway 4510 conductivity bridge with conventional dip-type black electrode, Gallenkemp melting point apparatus, Uniscope SM 9053 Laboratory oven, nutrient agar, potato dextrose agar, autoclave, petri dishes, wire loop and paper disc.



4. Synthesis of Metal(II) mixed ligand complex

A solution of Fe(III) chloride (0.001mol, 0.162g) in 20ml ethanol was added to the synthesized methionine-phenylhydrazone (0.001mol, 0.239g) and stirred for 15 minutes, 20ml of thiophene was added and stirred for 2hours. The brown precipitate formed was filtered, washed

3. Synthesis of methionine-phenylhydrazone (primary ligand)

Phenylhydrazine (0.001mol, 0.108g) in 20ml ethanol was mixed with methionine solution (0.001 mol, 0.149g in 20ml ethanol) and stirred vigorously for 2 minutes using a magnetic stirrer. Five drops of glacial acetic acid was added as stirring continued for 2 hours. The solution was allowed to stand undisturbed over night. The white precipitate formed was filtered, washed with ethanol, recrystallized with hot methanol and dried over fused calcium chloride in desiccators. The equation for the reaction is:

with ethanol, recrystallized with hot methanol and dried over fused calcium chloride in a desiccators. The procedure was repeated with Mn(II) chloride. Percentage yield was calculated

5. Results

Table 1: Physical properties of the synthesized compounds

Compounds	Found(Calcd)% M C H N S	Colour	Physical nature	% yield	Melting points	Conductivity Ω^{-1} $\text{cm}^2 \text{mol}^{-1}$
MPH $\text{C}_{11}\text{H}_{16}\text{N}_3\text{S O}$	55.5 6.7 17.6 13.4 (55.4)(6.7) (17.3)(13.6)	White	Crystalline	48	268	0.72
$\text{Fe}(\text{MPH})_2\text{T}_2$ $\text{Fe}[\text{C}_{30}\text{H}_{40}\text{N}_6\text{S}_4\text{O}_2]$	8.0 51.4 5.7 12.0 18.3 (8.1) (50.9)(5.7)(12.4)(18.2)	Brown	Powdery	67	289	0.93
$\text{Mn}(\text{MPH})_2\text{T}_2$ $\text{Mn}[\text{C}_{30}\text{H}_{40}\text{N}_6\text{S}_4\text{O}_2]$	8.0 51.5 5.7 12.0 18.3 (8.1) (51.4)(5.7)(12.2)(18.2)	Pink	Powdery	56	272	0.75

Table 2: Infrared spectra of the ligand and metal complexes using KBr (cm^{-1})

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{S})$
MPH	3322	1599	910			
$\text{Fe}(\text{MPH})_2\text{T}_2$	3285	1536	844	509	435	391
$\text{Mn}(\text{MPH})_2\text{T}_2$	3330	1535	844	421	429	383

Table 3: Results of antimicrobial studies

Compounds	<i>S. aureus</i>	<i>E.coli</i>	<i>C. albicans</i>	<i>A. niger</i>
MPH	8	8	8	7
$\text{Mn-MPH})_2\text{T}_2$	12	11	11	9
$\text{Fe-MPH})_2\text{T}_2$	15	12	10	10
Ampiclox/ Fluconazole	25	22	22	23

Chart Title

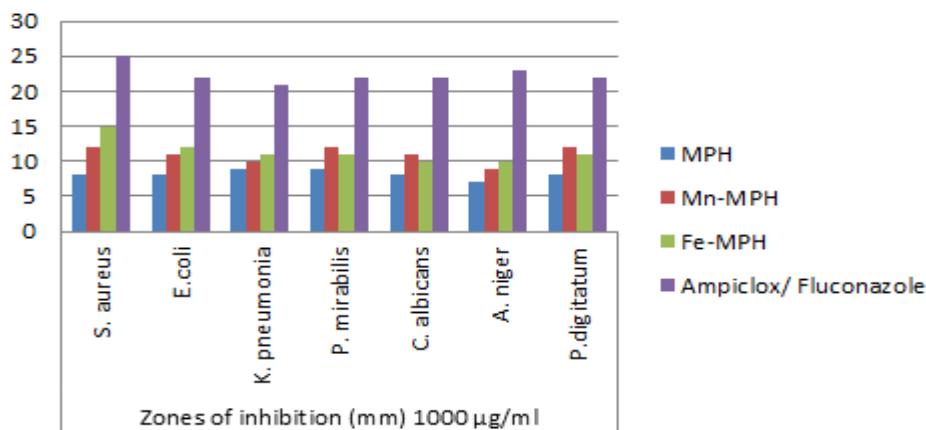


Fig. 1: Histogram of inhibition zones of the ligand and its Mn (II) and Fe (III) complex

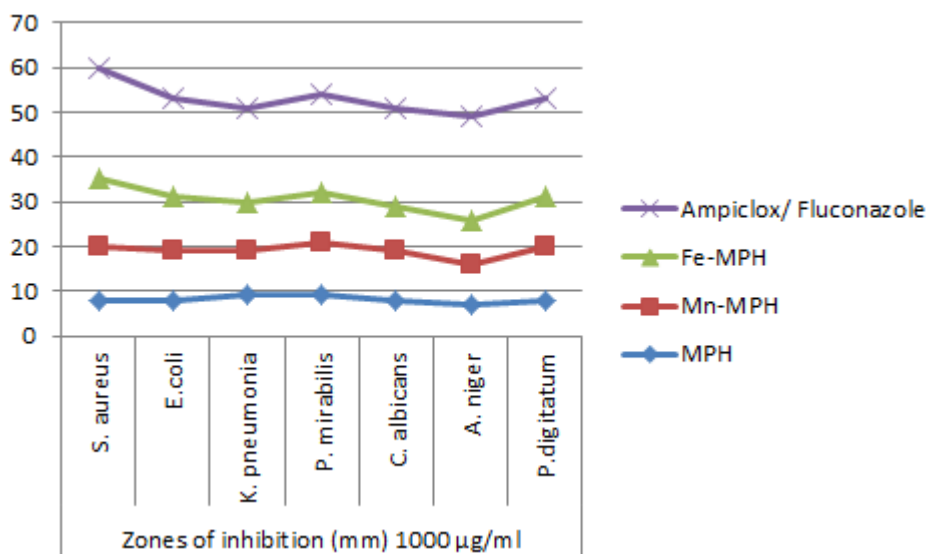


Fig. 2 Line plot of inhibition zones of the ligand and its Mn (II) and Fe(III) complex

6. Discussion

The physical properties of the synthesized compounds are recorded in Table 1. The properties include colour, physical nature, melting points and molar conductivity, the colour ranges from white, brown to pink. The ligand was crystalline while the complexes were powdery in nature. All the compounds were stable to air but melted at relatively high temperatures (268-289°C) indicating that the chelates did not exist in simple form but perhaps in polymeric forms [5]. They melted with decomposition as was apparent by their colour changes. The molar conductivity values were low 0.72 – 0.93 $\Omega\text{cm}^2\text{mol}^{-1}$ corresponding to the non-electrolytic nature of the complexes.

7. Infrared spectra

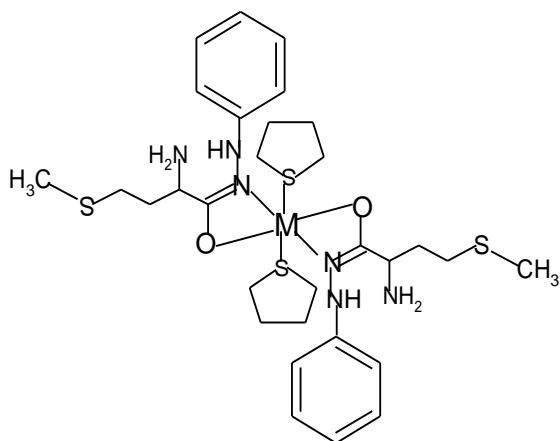
Infrared spectra were recorded within the range 370-4000 cm^{-1} . The selected infrared bands shown in Table 2 gives the vibrational frequencies of relevant functional groups in the synthesized compounds. The bonds formed between the ligands and the metal ions were elucidated by comparing the spectra of the ligands with those of the complexes. A vibrational band with strong intensity at 3420 cm^{-1} assigned to $\nu(\text{OH})$ stretching vibration disappeared due to deprotonation and coordination of the carbonyl oxygen to the metal ion [9]. The infrared spectrum

of the ligand also showed relatively strong bands at 3060-3330 attributed to $\nu(\text{NH}_2)$ and $\nu(\text{NH})$ stretching vibrations. In the spectra of the chelates the frequency assigned to the - NH_2 functional group is shifted to higher frequency values by 100-300 cm^{-1} confirming the bonding of the nitrogen to metal ion. Medium intensity band observed at 3280 cm^{-1} was assigned to $\nu(\text{NH})$, others at 930 cm^{-1} for (N-N) and 1020 cm^{-1} for (C-O). The band attributed to the azomethine group $\nu(\text{C}=\text{N})$ stretching vibration was observed at 1648 cm^{-1} . This was shifted to 1596 cm^{-1} and 1615 cm^{-1} in the spectra of the Fe (III) and Mn (II) complexes respectively. The M-N band in the Fe and Mn complexes were seen at 509 and 421 cm^{-1} while the M-S was at 391 cm^{-1} and 383 cm^{-1} and the M-O at 433 cm^{-1} and 429 cm^{-1} respectively. These observations were all in conformity with documented reports of [10, 11, 12 & 13].

8. Electronic absorption spectra

The electronic absorption spectrum of the ligand, methioninephenylhydrazone has three essential bands observed at 42,550, 38,462 and 33,680 cm^{-1} , each assignable to $n-\sigma^*$, $\pi-\pi^*$ and $n-\pi^*$ transitions which are caused by intraligand delocalization of electrons within the heteroatomic and double bond network system. These transitions occur in the molecules of the complexes but are shifted to lower intensities due to coordination to the metal

ions. whose d-d and charge transfer transition are reflective. Thus giving rise to configurational geometries of the resulting chelates. Mn(II) complex has weak bands observed at 16052, 23640 and 29422cm⁻¹ assignable to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴T_{2g} transitions including charge transfer while the Fe(III) complex also displayed weak absorption at 12694, 18761 and 31250cm⁻¹ assignable to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴T_{1g} and charge transfer both attributable to octahedral configurations [14,15].



Where M= Fe(III) or Mn(II)

Fig.1: Proposed structure for the complexes.

9. Antimicrobial Studies

The ligand and mixed ligand complexes were screened for antimicrobial activity on gram positive bacteria–staphylococcus aureus, gram negative bacteria Escherichia coli, fungi- Candida albican and Aspergillus niger. The data showing the zones of inhibition for the above named microbes are presented in Table 3. It is clear and is in conformity with the report of [16, 17] that the ligand show less zone of inhibition than the chelates. For instance, the Mn(II) complex displays 15mm zone of inhibition on S. aureus, 12mm on E. coli, For Fe(III) complex, the zone measured 12mm against S. aureus, 11mm against E. coli while zone caused by the ligand was just 8mm for both bacteria. For the fungi, the average zone was 10mm for the two fungi. Though these zones of inhibition were less than those caused by the standards.

10. Conclusion

The ligand methionine-phenylhydrazone along with its Fe(III), Mn(II) mixed ligand complexes with thiophene were successfully prepared at room temperature. The complexes were stable in air and heat, soluble in common coordinating solvents such as acetone, methanol, ethanol, DMF and DMSO. Elemental analysis, infrared and electronic absorption spectra revealed that the primary ligand was bidentate, coordinating through the nitrogen atom of azomethine group and oxygen atom of the carbonyl group in a 2:1:2 ligand to metal to ligand (secondary ligand-thiophene) molar ratio. The prepared complexes displayed octahedral geometry. The complexes gave enhanced inhibition zones against *S. aureus*, *E. coli*, *C. albicans* and *A. niger*, when compared to the free ligand.

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