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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF Mn(II) COMPLEXES OF ACETYLTHIOPHENE AND ACETYL FURAN SCHIFF BASE DERIVATIVES

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ABSTRACT

Manganese (II) complexes of Schiff bases; 2-acetylthiophene 4-phenylthiosemi-carbazone (AT-PTSC) and 2-furylmethylketone-4-phenylthiosemi-carbazone (AF-PTSC) derived from condensation of 2-acetylthiophene and 2-furylmethylketone (2-acetylfuran) each with 4-phenylthiosemicarbazide in (1:1 molar ratio) ethanol, have been synthesized. The Schiff bases and the Mn(II) complexes were characterized on the basis of melting point/decomposition temperature, solubility, magnetic susceptibility, infrared spectra, molar conductance measurements, elemental and gravimetric analyses. The Mn(II) complexes show moderate values of decomposition temperatures. The Schiff bases and the complexes were soluble in some common organic solvents. Infrared spectral data of the Schiff bases and their complexes, indicate coordination of the Schiff bases to the metal(II) ion via azomethine nitrogen. The effective magnetic moment of the Mn(II) complexes suggested an octahedral geometry. The molar conductance values of the complexes show that the complexes are electrolytes. The results of the elemental analysis of the ligands and their complexes are in good agreement with the calculated values, suggesting a 1:2 (metal-ligand) ratio. Antimicrobial screenings of the ligands and their complexes were conducted against gram-positive (Staphylococcus aureus,) and two gram-negative (Salmonella typhii, and Escherichia coli) bacteria specie. Also three fungi mainly (Candida albicans, Mucus indicus and Aspergillus flavus) were tested. The results showed that both the ligands and the complexes are active against the bacteria and the fungi specie.

Keywords: Ligand, Schiff base, 4-phenylthiosemicarbazide, 2-acetylthiophene, 2-acetylfuran molar conductivity, magnetic susceptibility, elemental analysis.

INTRODUCTION

Condensation between carbonyl compounds (>C=O) and a primary amine, produce a compound containing >C=NR group connected to an aryl or alkyl group, known as a Schiff base (Pierre, 1987). Schiff base therefore is a weakly basic compound, obtained from aldehyde or ketone to form an imine or an anil or azomethine (Nic *et al*., 2006). Schiff base coordinates to active site of transition metals to form complexes through N, O and S donor atoms, which make them important for their biological activity (Mishra *et al.,* 2009). They have been used as analytical reagent, polymer-coating, ink, pigment, fluorescent materials and catalytic reagent (Buhmann *et al.,* 1998).

Thiosemicarbazones are class of sulphur (S) donor Schiff bases that are useful for transition metals due to their metal complexing ability (Abou-Melha *et al*., 2008). Thiosemicarbazone have significant activity against tumor, tuberculosis and leprosy (Ainstcough *et al*. 2007). Clinical and experimental studies on the effect of thiosemicarbazones revealed their activities against cancer (Marina *et al*. 2007). Drug synthesized from N-methyl derivatives of isatin1-β-thiosemicarbazone (methisazone) is found to be active against small pox (Sau *et al*., 2003).

Thiophene-based compounds have widespread use in modern drug design, bio diagnostics, electronic, optoelectronic devices, conductive and electroluminescent polymers (Dore *et al*., 2004). Several reviews of various aspects of thiophene coordination and reactivity in transition metal complexes have been reported (Barbarella and Melucci, 2005). 2-butylthiophene has been employed as a raw material in the synthesis of anticancer agents and 2-octylthiophene has been employed in the synthesis of anti-atherosclerotic agents (Richard *et al*., 2009).

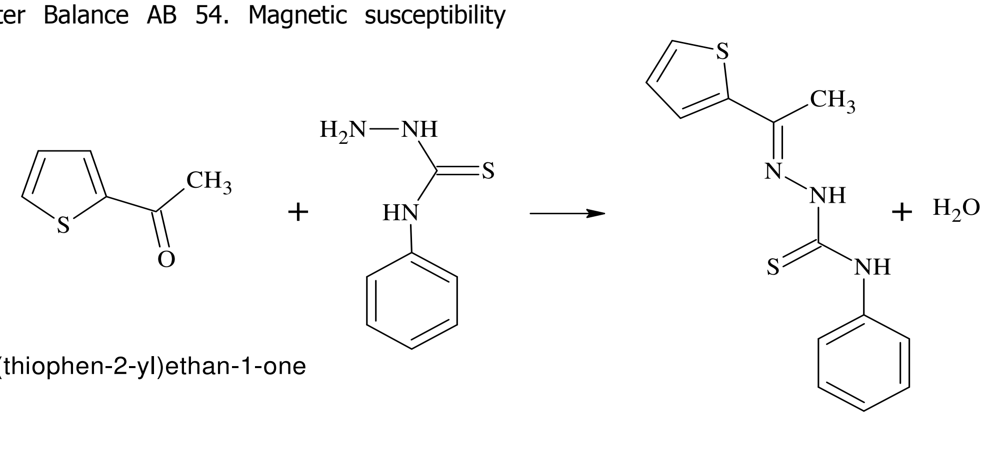
The applications of thiophene and its derivatives as metal complexing agents and in the development of insecticides are well known, (Freeman *et al*., 1994).
Furan is used as a starting point to other special chemicals (Hoydonck *et al*., 2005). Furan derivatives of dihydronaphthalenes, are useful intermediates in the synthesis of other polycyclic aromatic compounds (Filatov *et al*., 2012). Many derivatives of furan have been found useful in condensation and coordination with other compounds and such compounds are biologically active against bacteria, fungi and virus. Schiff base derived from 3-aminodibenzofuran and 2-furan carboxaldehyde was found to be active against tuberculosis and *E. coli* (Aurora *et al*., 2009).
Complexes of the Schiff base; 1,8-bis(thiophene-2-carboxaldimine)-p-menthane (***L***[1]) and 1,8-bis(furan-2-carboxaldimine)-*p*-menthane (***L***[2]) have been very active against Gram positive bacteria; *Bacillus subtilis, Yersinia enterotica, Bacillus cereus, Listeria monocytogenes* and *Micrococcus luteus*, (Ayla *et al.,* 2016). The aim of this research is to synthesize, characterize and conduct antimicrobial studies on Schiff base derived from 2-acetylthiophene and 2-acetylfuran with 4-phenylthiosemicarbazide.

MATERIALS AND METHODS

All the chemicals used in this work were of Analar Grade and were used without further purification. Glass wares used for the preparation were thoroughly washed with detergent, rinsed with distilled water and dried in an oven. The main chemicals; 4-phenylthiosemicarbazide, 2-aceltylthiophene, and 2-acetylfuran (2-furylmethylketone) were all purchased from Sigma Aldrich U. K.
All weighing were carried out using Electrical Meter Balance AB 54. Magnetic susceptibility measurements of the complexes were determined using Sherwood Scientific MSB MK1 Magnetic Susceptibility Balance. Melting point/Decomposition temperatures were determined using a digital WRS-IB Microprocessor Melting Point Apparatus. Infrared spectral analyses were recorded using Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer in the range 4500-250cm^{-1}. Molar conductivity measurements were carried out using George Kent model 5003 conductivity metre. Metal and Elemental Analysis of C, H and N were carried out at Robertson Microlit Laboratories, New Jersey (U.S.A).
All the microbial isolates used in this were obtained from the Department of Medical Microbiology, Aminu Kano Teaching Hospital Kano, and identified at the Department of Microbiology. The antimicrobial screening was conducted in the Department of Microbiology, Bayero University Kano. Standard drugs; Ciprofloxacin for bacteria and Ketoconozole for fungi as reference standards were obtained from Department of Microbiology, Bayero University, Kano. Mueller Hinton agar and Potato dextrose were used as growth media for the microbes.

Preparation of Schiff Base (AT-PTSC)

To a hot solution of 4-phenylthiosemicarbazone (1.67g, 0.01mol) in 70cm^3 ethanol, a solution of 2-acetylthiophene (0.01mol, 1.08cm^3), was added drop wise, followed by the addition of 3 drops of acetic acid. The mixture was refluxed with constant stirring for 3 hours. The solution was transferred into a refrigerator at 5°C for 24 hours. The precipitate obtained was filtered off, washed several times with ether and dried over P_2O_5 in a desiccator for three days (Chandra *et al*., 2009).



1-(thiophen-2-yl)ethan-1-one

(2*E*)-*N*-phenyl-2-[1-(thiophen-2-yl)ethylidene]hydrazine-1-carbothioamide

Scheme 1: Preparation of AT-PTSC Schiff base

Preparation of Schiff Base (AF-PTSC)

The AF-PTSC Schiff base was synthesized using the same procedure for the synthesis of AT-PTSC, only the reagent 2-furylmethylketone (2-acetylfuran) was used instead of 2-acetylthiophene.

Preparation of the Schiff base Manganese(II) complexes

Mn(II) complexes for the Schiff bases (AT-PTSC and AF-PTSC) derived from 2-acetylpyridine and 2-furylmethylketone with 4-phenyl thiosemicarbazide, were prepared by the addition of 0.002mol of each the Schiff bases in $20cm^3$ethanol to the solution containing 0.001mol of each of the Mn(II) salts in $10cm^3$ ethanol. Each of the mixture was then refluxed for 3 hours with stirring. On cooling, the precipitate obtained was filtered, washed with diethyl ether and dried over P_2O_5 in a desiccator for three days (Gehad *et al.*, 2006).

Infrared Measurements

Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer in the range 250-4500cm^{-1} was used. A small amount of powder sample (about 1-2% of KBr amount) was taken and mixed with KBr powder and then analyzed using infrared analyzer. The results obtained are shown in Table 4.

Molar Conductance Measurement

Molar conductivity measurements were carried out on 1 x 10^{-3} $moldm^{-3}$(0.001M) solution of each of the metal complexes in Dimethyl Formamide (DMF) at 25°C. The molar conductance is calculated using the equation, (Mohd, *et al.,* 2013).

$$\Lambda_M = \frac{1000L}{C}$$

Where Λ_M = molar conductance, L = specific conductance and C = concentration of the complex. The results are presented in Table 5.

Elemental Analysis

The analysis was carried out using Perkin-Elmer CHN 2400 Elemental Analyzer based on the classical Pregl-Dumas method. About 20 mg of each of the samples for analysis was encapsulated in an aluminium vial and inserted automatically into the combustion zone of the analyser using a single-sample auto injector. In the presence of excess oxygen and combustion reagents, the samples were combusted completely and reduced to the elemental gases CO_2, H_2O and N_2. All the results were computed automatically and were given as percent weight of each element. The results are shown in Table 6.

Antimicrobial Test

The *In vitro* antimicrobial activity of the ligand (AP-PTSC) and its complexes were tested against Gram-positive (S*taphylococcus aureus,*) and two Gram-negative (*Salmonella typhii, and Escherichia coli*) pathogenic bacteria. Also three fungi mainly (*Candida albicans*, *Mucus indicus* and *Aspergillus flavus*) were used. Muller Hilton Agar media for bacteria while Potato Dextrose Agar (PDA) for fungi were used and were prepared in distilled water. The ligands and the complexes were dissolved separately in Dimethyl Sulphoxide (DMSO) to obtain three different concentrations (15 µg/ml, 30 µg/ml and 60 µg/ml), which were used to check the antimicrobial activities by well diffusion method. The discs were saturated with the dissolved compounds in Dimethyl sulphoxide (DMSO) and then placed in petridishes containing the culture media. The petri dishes were incubated at 37^{o}C and the inhibition zone was measured after 24hours for bacterial strain and 48hours for fungal isolates and compared with standard drugs (Ciprofloxacin for bacteria and Ketoconozole for fungi) (Sheikh *et al*., 2004).

RESULTS AND DISCUSSION

The results of some physical properties, solubility, magnetic susceptibility, FTIR, molar conductance, elemental analysis and antimicrobial studies of the Schiff bases and the Mn(II) complexes are presented

Reaction between 2-acetythiophene and 2-acetylfuran (2-furylmethylketone) each with 4-phenylthiosemicarbazide in (1:1 molar ratio) in ethanol produced a Schiff base; 2-acetylthiophene-4-phenylthiosemicarbazone and 2-acetylfuran-4-phenylthiosemicarbazone (AT-PTSC and AF-PTSC). Mn(II) complexes were synthesized from these Schiff bases in (2:1 molar ratio) in ethanol. The Schiff bases AT-PTSC and AF-PTSC together with $[Mn(AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$ complexes were subjected to spectroscopic analyses based on melting point/decomposition temperature, solubility, magnetic susceptibility, infrared (IR) spectra, molar conductance measurements, elemental and gravimetric analysis.

Physico-Chemical Properties of the Schiff Base and its Metal(II) Complexes.

Both the AT-PTSC and AF-PTSC Schiff bases are light yellow powders with a yield of 85.2% and 85.1%, a melting point of 176^{o}C and 178^{o}C. The complexes $[Mn(AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$ are pale brown and brown, a decomposition temperature of 215^{o}C and 220^{o}C and a yield of 79.6% and 75.8% (Table 1).

The variation in colour of the Schiff bases with their corresponding complexes indicates coordination of each of the Schiff base with the Mn(II) ion. The colour of the compounds is attributed to 'd-d' orbital transition of electron between one energy level to another, by their magnitude of splitting, which in turn depends on the geometry of the complex, the nature of the ligand and charge transfer (Rodgers, 1994).

The decomposition temperatures of the complexes are relatively high, indicating good thermal stability of the complexes.

Both the Schiff bases and their Mn(II) complexes are soluble in acetone, dichloromethane, chloroform and DMSO but slightly soluble in methanol and ethanol, except $[Mn(AF\text{-}PTSC)_2]Cl_2$ which is insoluble in methanol, (Tables 2). The solubility of the Schiff bases and their Mn(II) complexes in the common solvents indicated their low polarity which can be used to determine the suitable solvents that could be utilized for subsequent spectroscopic measurements (Jones and Fleming, 2010).

The magnetic susceptibility as presented in (Tables 3) are 6.0BM and 5.9BM for $[Mn(AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$, indicating paramagnetic high spin octahedral geometry (Gehad *et al*., 2006).

The Schiff bases show broad band spectra at $1648cm^{-1}$ and $1522cm^{-1}$, that are attributable to υ(C=N) stretching vibration, which is shifted downward in the spectra of the complexes at range of $1633\text{-}1510cm^{-1}$. This indicates coordination of the Schiff bases to each of the Mn(II) ion via azomethine nitrogen. The spectra of the Schiff bases at $3289cm^{-1}$ and $3281cm^{-1}$ assignable to υ(N-H) stretching vibration shifted downward and upward in the spectra of the complexes at $3280cm^{-1}$ and $3287cm^{-1}$, which resupports coordination of the Schiff bases to the Mn(II) ion. The band spectra of the complexes at the region of $529\text{-}548cm^{-1}$ and $403\text{-}405cm^{-1}$ are assignable to υ(M-N) and υ(M-S) respectively, which is another indication for the coordination of the Schiff base to the metal(II) ion, (Awadelkareem *et al*., 2012), (Tables 4).

The molar conductivities of $[Mn(AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$ were carried out in DMF and their 10^{-3} M solutions are $126.02\Omega^{-1}cm^2mol^{-1}$ and $123.53\Omega^{-1}cm^2mol^{-1}$ as shown in (Table 5). These values indicate electrolytic nature of the complexes, (Gehad *et al*., 2006; Mohd, *et al.,* 2013).

The results of the elemental analysis (C, H and N) for the Schiff bases and their respective Mn(II) complexes are as presented in Table 6. The values are in agreement with the proposed formulas of the ligands, and their corresponding Mn(II) complexes, suggesting 2:1(ligand-metal ratio).

Antimicrobial test of the AT-PTSC and AF-PTSC Schiff bases and their Mn(II) complexes were carried out against three bacteria isolates; Gram-positive (*Staphylococcus aureus,*), Gram-negative (*Salmonella typhii, and Escherichia coli*) and three fungi (*Candida albicans, Mucus indicus and Aspergillus flavus*). Concentrations of 15, 30 and 60(μg/disc) were used, standard drugs ciproflaxacin and ketoconozole for bacteria and fungi, were served as controls, (Tables 7-8). The results of the tests indicate moderate antimicrobial activity against the tested microorganisms when compared with the standards, and this activity increases by increasing concentration. Also the metal complexes show higher activities than free ligand, except in the case of $[Mn(AT\text{-}PTSC)_2]Cl_2$ where its activity against *Staphylococcus aureus,* is lower than that of the Schiff base. However, the activities of both the ligand and the complexes are less than that of the standard drugs used. The activities of the compounds can be explained on the basis of chelation theory, which states that; the chelation tends to make the complex acts as a more powerful and potent bactericidal or bacteriostatic agent than the ligand (Sengupta *et al.,* 1998).

From the results of analysis of the complexes and the available literature data, the following general molecular structures for $[Mn(AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$ are proposed:

Table 1: Some Physical Properties of (AT-PTSC and AF-PTSC) Schiff Bases with their Mn(II) Complexes

Ligand /Complex,	Colour	Melting point (°C)	Decomposition Temperature (°C)	Percentage (%) Yield
AT-PTSC	Light yellow	176	-	85.2
AF-PTSC	Light yellow	178	-	85.1
$[Mn(AT\text{-}PTSC)_2]Cl_2$	Pale brown	-	215	79.6
$[Mn(AF\text{-}PTSC)_2]Cl_2$	Brown	-	220	75.8

AT-PTSC and AF-PTSC = Schiff bases derived from 2-acetylthiophene and 2-acetylfuran with 4-phenylthiosemicarbazide. $[Mn (AT\text{-}PTSC)_2]Cl_2$ and $[Mn(AF\text{-}PTSC)_2]Cl_2$= Mn(II) complexes for the Schiff bases derived from 2-acetylthiophene and 2-acetylfuran with 4-phenylthiosemicarbazide.

Table 2: Solubility Data of AT-PTSC and AF-PTSC Schiff Bases with their Mn(II) Complexes

Ligand/Complex	Water	Methanol	Ethanol	n-hexane	Ether	Acetone	Dichloromethane	Chloroform	DMSO	Benzene
AT-PTSC	IS	SS	SS	IS	IS	S	S	S	S	IS
AF-PTSC	IS	SS	SS	IS	IS	S	S	S	S	IS
$[Mn(AT\text{-}PTSC)_2]Cl_2$	IS	SS	SS	IS	IS	S	S	S	S	IS
$[Mn(AF\text{-}PTSC)_2]Cl_2$	IS	IS	SS	IS	IS	S	S	S	S	IS

Key: IS => Insoluble, SS =>Slightly Soluble, S => Soluble

Table 3: Magnetic Susceptibility Values of AT-PTSC and AF-PTSC Mn(II) Complexes

Complex	Gram susceptibility $(X_g)10^{-6}$	Molar Magnetic Susceptibility $(Xm)10^{-3}$	Magnetic Moment μ_{eff} (B.M)	Magnetic Property
$[Mn(AT\text{-}PTSC)_2]Cl_2$	24.0	0.16	6.0	Paramagnetic
$[Mn(AF\text{-}PTSC)_2]Cl_2$	22.7	0.15	5.9	Paramagnetic

Table 4: Infrared Spectra Data of AT-PTSC and AF-PTSC their Mn(II) Complexes

Compounds	υ (C=N) (cm^{-1})	υ (N-H) (cm^{-1})	υ (C=S) (cm^{-1})	$υ(M\text{-}S)_{Thio}$ (cm^{-1})	υ(M-S) (cm^{-1})
AT-PTSC	1648	3289	852	-	-
AF-PTSC	1522	3281	750	-	-
$[Mn(AT\text{-}PTSC)_2]Cl_2$	1633	3280	849	529	405
$[Mn(AF\text{-}PTSC)_2]Cl_2$	1510	3287	753	548	403

Table 5: Molar Conductance Measurement for AT-PTSC and AF-PTSC Mn(II) Complexes

Compound	FW $gmol^{-1}$	Conc. ($Moldm^{-3}$) x 10^{-3}	Specific Conductance x 10^{-4} $S\Omega^{-1}$	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$
$[Mn(AT\text{-}PTSC)_2]Cl_2$	676.63	2.36	2.98	126.02
$[Mn(AF\text{-}PTSC)_2]Cl_2$	644.50	1.86	2.30	123.53

Table 6: Elemental Analysis of AT-PTSC and AF-PTSC with their Mn(II) Complexes

Ligand/Complex	%C (Calc) Found	%H (Calc) Found	%N (Calc) Found	%M (Calc) Found
AT-PTSC	(56.70) 56.50	(4.76) 4.90	(15.26) 14.90	
[Mn (AT-PTSC)$_2$]Cl$_2$	(46.15) 45.90	(3.87) 3.60	(12.42) 12.40	(8.12) 8.32
AF-PTSC	(60.21) 60.30	(5.05) 5.30	(16.20) 16.30	
[Mn (AF-PTSC)$_2$]Cl$_2$	(48.45) 48.20	(4.07) 4.30	(13.04) 13.10	(8.52) 8.56

Table 7: Antibacterial Activity of AT-PTSC and AF-PTSC with their Mn(II) Complexes

Compound	AT- PTSC	Mn(AT-PTSC)$_2$Cl$_2$	AF-PTSC	Mn(AT-PTSC)$_2$Cl$_2$	Ciprofloxacin (At all con.)
Isolate/Concentration	15 30 60	15 30 60	15 30 60	15 30 60	15 30 60
Staphylococcus aureus (μg/disc)/ inhibition (mm)	7 8 10	6 6 0	6 6 6	10 14 18	34 34 34
Escherichia coli (μg/disc)/ inhibition (mm)	8 9 11	9 13 15	6 8 10	8 11 13	40 40 40
Salmonella typhirium (μg/disc)/inhibition (mm)	6 9 12	9 11 15	7 11 15	10 14 19	43 43 43

Table 8: Zone of Inhibition (mm) for Antifungal of AT-PTSC and AF-PTSC with their Mn(II) Complexes

Compound	AT- PTSC	Mn(AT-PTSC)$_2$Cl$_2$	AF-PTSC	Mn(AT-PTSC)$_2$Cl$_2$	Ciprofloxacin (At all con.)
Isolate/Concentration	15 30 60	15 30 60	15 30 60	15 30 60	15 30 60
Mucus indicus (μg/disc)/ inhibition (mm)	7 8 9	11 13 16	6 6 6	6 8 10	34 34 34
Aspergillus flavus (μg/disc)/ inhibition (mm)	6 6 6	6 9 11	6 8 10	12 14 16	40 40 40
Candida albican (μg/disc)/inhibition (mm)	7 9 11	8 10 13	6 10 12	8 10 13	43 43 43

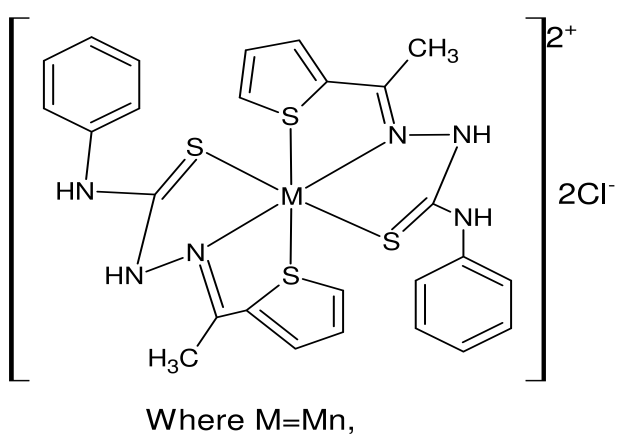
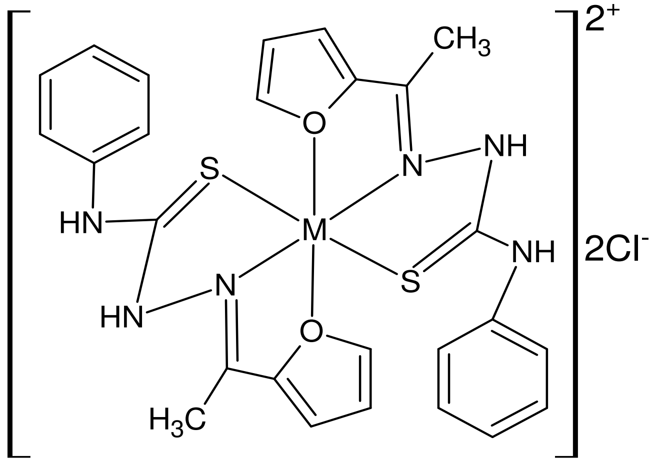


Figure 1: Proposed Structure of 2-acetythiophene-4-phenylthiosemicarbazone (AT-PTSC) Metal(II) Complexes.



Where M=Mn.

Figure 2: Proposed Structure of 2-acetylfuran-4-phenylthiosemicarbazone (AF-PTSC) Metal(II) Complexes.

CONCLUSION

Schiff bases 2-acetylthiophene-4-phenylthiosemicarbazone (AT-PTSC) and 2-acetylfuran-4-phenylthiosemicarbazone (AF-PTSC) together with their Mn(II) complexes were successfully synthesized and characterized. The decomposition temperature indicates the good stability of the complexes. The IR values assignable to υ(N-H) and υ(C=N) stretching vibrations show coordination of the ligand to the metal ion via azomethine nitrogen. Molar conductance values range from $126.02\Omega^{-1}cm^2mol^{-1}$ and $123.53\Omega^{-1}cm^2mol^{-1}$, showing that the solutions of the complexes are electrolytes. The values of the magnetic susceptibility of the complexes indicated an octahedral geometry. The elemental analysis values indicates 2:1(ligand-metal ratio). The antimicrobial test shows that both the ligand and the complexes have good activity against the isolates used. Finally the structures of the complexes have been proposed.

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