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Synthesis, characterization and biological activities of manganese (II) complexes with N, O and S donor ligands

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Abstract: In this article we report the series of newly synthesized complexes manganese (II) with 3(2'-hydroxyphenyl)-5-(4' substituted phenyl) pyrazolines and dithiophosphates ligands. The metal complexes were characterized by the elemental analysis, magnetic susceptibility, spectral analysis such as ESI mass spectrometry, IR and UV. The biological activities of the synthesized complexes have been studied against bacterial and fungal strains. In this series of complexes dithiophosphate and pyrazoline act as monoanionic bidentate ligand. The coordination in the complexes occurs through the O of phenolic group, N of the azomethine group and S of the dithiophosphoric moieties. The complexes are tetracoordinated having distorted tetrahedral geometry. The synthesized complexes exhibit potential activity against the bacterial strains *E.coli*, *P.Aeruginosa* and *S. aureus* and fungal strains *C. albicans* and *A. niger*. It can be concluded that complexes of manganese have promising antimicrobial activity as compared to the standards taken.

Keywords- Manganese (II), pyrazoline, dithiophosphate

1. INTRODUCTION

In the recent years transition metal complexes have been point of interest in medicinal and bioinorganic chemistry as they are lesser toxic and cost effective as compared lanthanides and other heavy metals [1]. Among all these transition metal, manganese plays an important role as an active site of a number of enzymes such as oxidoreductases, lyases, hydrolases and transferases [2]. It is an essential element used in the development of bones, metabolic breakdown of carbohydrates, synthesis of fats and cholesterol. It is well established that manganese has significant role in water splitting in plants and disproportion of H_2O_2 in microorganism [3-5]. Complexes having two different ligands, with improved structural diversity show adjustable biological properties due to synergistic effects of various donor groups. Among the various ligands, pyrazoline derivatives have a large number of applications in medicinal chemistry [6-12]. Structural diversity in pyrazoline complexes can be achieved by changing the functional groups attached to the pyrazoline moiety which affects the functional behavior of the complexes leading to the tunable biological properties [13]. Likewise, dithiophosphate has two sulphur donor atoms are reported to be used in metal chelation therapy [14], as pesticides [15-16] and fungicides [17-18]. Manganese preferably binds with hard donor atoms like nitrogen and oxygen as compared to soft sulphur donor atoms [19]. Complexes of dithiophosphate with manganese metal have received lesser attention due to the soft sulphur donor atom their synthesis is difficult and self-life is of few days [20]. Thus, in our laboratory we have synthesized complexes of manganese with both pyrazoline and dithiophosphate ligands having two hard and one soft donor atoms i.e., nitrogen, oxygen and sulphur. Both the ligands independently show promising biological activity, to the best of our knowledge no sources are there showing the complexes of manganese (II) with both pyrazoline and dithiophosphate ligands. Therefore, manganese complexes with two different bioactive ligands are reported herewith. In this work we have discussed the synthesis, characterization and biological activities of the manganese (II) complexes with pyrazoline and dithiophosphate.

2. Experimental

All the solvents were of analytical grade (methanol, ethanol, benzene etc.) were dried and purified by the standard methods [21]. Phosphorous pentasulphide (S.D. Fine), benzaldehydes, o-hydroxyacetophenone (CDH), hydrazine hydrate (Rambaxy), acetic acid (CDH) and hydrochloric acid (Ranbaxy) were used as received. Ammonium dithiophosphates and pyrazoline were prepared by the earlier reported method [22-24]. Manganese (II) chloride (SDFL) was used as received.

2.1 **General Procedure**

Synthesis of Manganese (II) complexes with Pyrazoline and O,O' di-alkyl and alkylene dithiophosphate

The complexes of Mn(II) with 3(2'-hydroxyphenyl)5-(4- substituted phenyl) Pyrazolines and O,O' –di-n-propyl and alkylene dithiophosphate of general formula $Mn(C_{15}H_{12}N_2OX)(RO)_2PS_2$ and $Mn(C_{15}H_{12}N_2OX)[S_2\overline{POGO}]$ were prepared as the following reaction scheme in 1:1:1 molar ratio, where X= H, CH_3 ,OCH_3 , Cl, R= $-CH_2CH_2CH_3$ and G= - $CH_2CMe_2CH_2$ - .

Step 1:

$$MnCl_2 + C_{15}H_{12}N_2OX \xrightarrow[4\text{-}6\ hrs]{Benzene,methanol} MnCl(C_{15}H_{12}N_2OX) + HCl \uparrow$$

Step 2:

$$MnCl(C_{15}H_{12}N_2OX) + [(RO)_2PS_2]NH_4 \xrightarrow[3\text{-}4\ hrs]{methanol} Mn(C_{15}H_{12}N_2OX)[(RO)_2PS_2] + NH_4Cl \downarrow$$

$$MnCl(C_{15}H_{12}N_2OX) + [S_2\overline{POGO}]NH_4 \xrightarrow[3\text{-}4\ hrs]{methanol} Mn(C_{15}H_{12}N_2OX)[S_2\overline{POGO}] + NH_4Cl \downarrow$$

Procedure: Methanolic solution of manganese (II) chloride was added dropwise to the benzene solution of pyrazoline. The reaction mixture was refluxed under inert atmosphere for 4-6 hours. The color changed to blackish brown. The reaction mixture was cooled to room temperature and methanolic solution of ammonium dithiophosphate was added with constant stirring. The content was further stirred for 3-4 hours. The reaction mixture was filtered through the alkoxy funnel to separate out ammonium chloride. The solvent was removed under reduced pressure and blackish brown colored solid was obtained. The proposed structures of the complexes are given in the figure 1. The physical details of all complexes are summarized in the table 1.

Table 1: Physical characteristics

S.No.	Complex	Mol. Wt. Found (calc'd)	Yield (%)	M.P.(°C)	State/Colour
1	$Mn(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	507.20 (505.49)	72	265	Amorphous/ Blackish Brown
2	$Mn(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	522.67 (519.52)	85	192	Amorphous/ Blackish Brown
3	$Mn(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	539.46 (535.52)	87	253	Amorphous/ Blackish Brown
4	$Mn(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	542.32 (539.94)	94	209	Amorphous/ Blackish Brown
5	$Mn(C_{15}H_{12}N_2OH)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	493.45 (489.45)	90	197	Amorphous/ Blackish Brown
6	$Mn(C_{15}H_{12}N_2OCH_3)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	505.34 (503.48)	89	231	Amorphous/ Blackish Brown
7	$Mn(C_{15}H_{12}N_2O.OCH_3)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	520.67 (519.48)	78	175	Amorphous/ Blackish Brown
8	$Mn(C_{15}H_{12}N_2OCl)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	526.48 (523.90)	92	231	Amorphous/ Blackish Brown

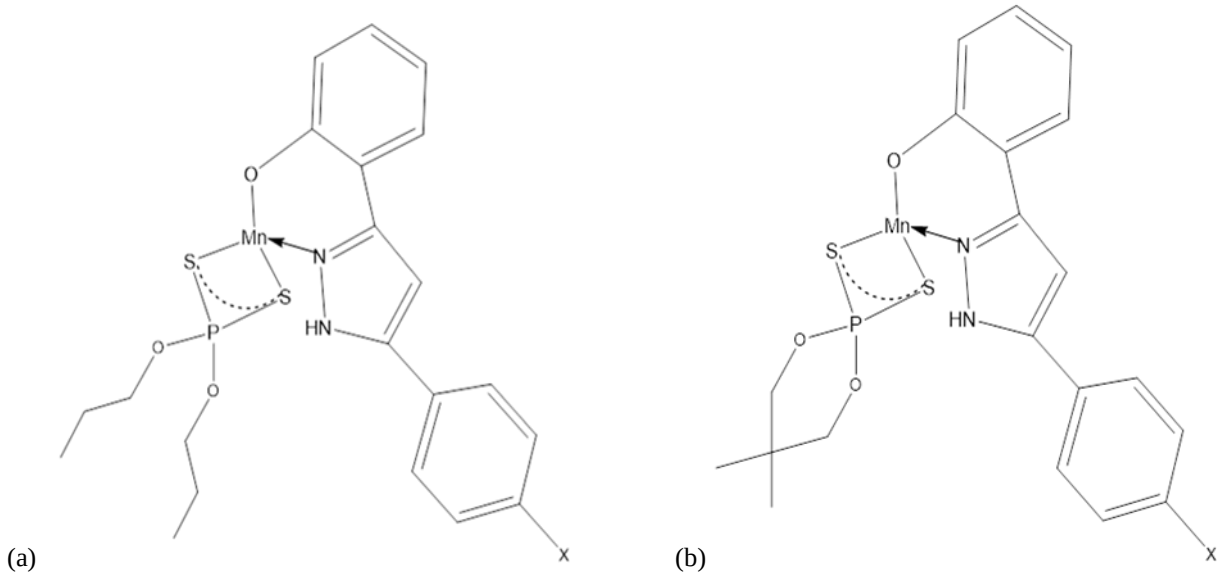

Figure 1 : Proposed structure of (a) $Mn(C_{15}H_{12}N_2OX)[(C_3H_7O_2)PS_2]$
(b) $Mn(C_{15}H_{12}N_2OX)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$

2. **Physical measurements**

Molecular weights were determined by the Electronspray ionization mass (ESI-MS positive) spectra on Water Alliance E2695/HPLC- TQD mass spectrometer. Elemental Vario EL III was used for elemental Analysis (C,H,N and S). Magnetic measurements were carried out on Gouy balance (Broker Magnetic Balance) at room temperature. IR Spectra were recorded on Thermo Nicolet iS50 in the range of 4000-100 cm-1. Phosphorous and chlorine ware estimated by the carius and Volhard's method respectively. Manganese was estimated as $Mn_2P_2O_7$ using analytical method [21].

3. **Antimicrobial Assay**

Antibacterial and antifungal activities of complexes 3 and 7 were studied. The antimicrobial activities of the synthesized complexes were evaluated using well diffusion method [25]. *E.coli*(MT 2124) , *P. Aeruginosa* (MTCC 2295) and *S.aureus* (MTCC 737) are the negative and positive strains against which antibacterial activity is evaluated. The fungal strains *C. albicans* (MTCC 31017) and *A. niger* MTCC 4325 were used. Carbapenem and Fluconazole were used as the standard reference against bacterial and fungal strains. The antimicrobial activities were compared with ligands and metal salts.

4. RESULTS AND DISCUSSION

All these manganese complexes are blackish brown, amorphous solid which are non-hygroscopic and stable at room temperature. All the complexes are soluble in chloroform and DMSO. The molecular weights of the complexes show that the complexes are monomeric nature. The elemental analysis of (C, H, N, O, S and Mn) is given table 2 which is in good agreement to the stoichiometry proposed**.**

Table 2: Elemental Analysis

S. No.	Complex	%C found (calc'd)	%H found (calc'd)	%N found (calc'd)	%O found (calc'd)	%S found (calc'd)	%Mn found (calc'd)
1	$Mn(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	61.69 (61.98)	5.36 (5.37)	5.52 (5.54)	9.46 (9.49)	12.68 (12.64)	10.83 (10.86)
2	$Mn(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	50.56 (50.86)	5.59 (5.62)	5.35 (5.39)	9.18 (9.23)	12.27 (12.34)	10.51 (10.57)
3	$Mn(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	48.98 (49.34)	5.19 (5.45)	5.41 (5.23)	11.86 (11.95)	11.88 (11.98)	10.18 (10.26)
4	$Mn(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	46.51 (46.71)	4.83 (4.85)	5.16 (5.18)	8.85 (8.89)	11.83 (11.87)	10.13 (10.17)
5	$Mn(C_{15}H_{12}N_2OH)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	48.68 (49.07)	4.69 (4.74)	5.67 (5.72)	9.72 (9.80)	12.99 (13.10)	11.13 (11.2)
6	$Mn(C_{15}H_{12}N_2OCH_3)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	49.91 (50.09)	4.98 (5.01)	5.54 (5.56)	9.5 (9.53)	12.69 (12.73)	10.87 (10.91)
7	$Mn(C_{15}H_{12}N_2O.OCH_3)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	48.44 (48.55)	4.83 (4.85)	5.38 (5.39)	12.29 (12.32)	12.31 (12.34)	10.55 (10.57)
8	$Mn(C_{15}H_{12}N_2OCl)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	45.62 (45.85)	4.21 (4.23)	5.32 (5.35)	9.12 (9.16)	12.18 (12.24)	10.43 (10.48)

4.1 Infrared Spectral Studies

The important bands in the spectra of Manganese complexes are in the range of 4000-100 cm^{-1} and are summarized in the table 3.

Table 3: IR Spectra

S.No	Complex	[N-H]	[C-N]	[(P)-O-C]	[P-O-(C)]	[P=S]	[P-S]	[Mn-O]	[Mn-N]	[Mn-S]
1	$Mn(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	3392	1612	1054	854	659	554	576	442	392
2	$Mn(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	3372	1604	1042	862	649	562	598	432	409
3	$Mn(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	3354	1600	1029	879	643	547	602	452	416
4	$Mn(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	3365	1610	1067	882	648	561	573	436	420
5	$Mn(C_{15}H_{12}N_2OH)[S_2POCH_2C(CH_3)_2CH_2O]$	3420	1592	1062	892	652	559	571	467	396
6	$Mn(C_{15}H_{12}N_2OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	3399	1608	1039	899	650	541	569	472	382
7	$Mn(C_{15}H_{12}N_2O.OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	3378	1587	1052	882	679	561	586	463	411
8	$Mn(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3)_2CH_2O]$	3405	1612	1063	869	662	542	610	429	402

The bands of medium intensity in the region of 3354-3420 cm^{-1} are attributed to υ [N-H] stretching [26]. The bands of C=N are observed in the region of 1612-1587 cm^{-1} which shifted to lower wavelength suggesting the coordination of the azomethine nitrogen [27-32]. The bands in the regions of 1029-1067 cm^{-1} and 854-899 cm^{-1} ascribed to [(P)-O-C] and [P-O-(C)] modes respectively [33-37]. The sharp medium intensity bands in the region 643-679 cm^{-1} may be assigned to υ [P=S] mode [38] while the bands of [P-S] are observed in regions of 541-567 cm^{-1} [39]. It has been that these bands have shifted towards lower frequency region as compared to parent dithiophosphate ligands, which may be due to bidentate mode of dithiophosphate ligands bonding. The disappearance of the peak around 3080 cm^{-1} which is assigned to (O-H) stretching of pyrazoline moiety suggests that the oxygen is covalently bonded to manganese which is confirmed by the peak obtained in region 610-559 cm^{-1} [40]. The appearance of the bands at 429-472 $cm^{-1}$and 382-420 cm^{-1} is ascribed to [Mn-N] and [Mn-S] respectively [41-43].

4.2 Magnetic moment

Magnetic moment values (5.80-6.04) of manganese (II) complexes are summarized in the table 4. Magnetic measurements show that all these complexes are paramagnetic in nature with five unpaired electrons. These values are according to earlier reported data of the manganese (II) high spin complexes [44-46].

4.3 Electronic Spectra

All the manganese (II) dithiophosphate and pyrazoline complexes are in d^5 state , therefore there is a strong possibility for sp^3 hybridisation , indicating tetrahedral geometry around the manganese metal with reference to the earlier reported data [47] for $[Mn_4(Sph)_{10}]^{2-}$,$MnCl_2$, $MnCl_2.2CH_3CN$ [48] some bands are quite similar to those reported for $MnCl_2$. Some additional bands are also observed which are of low intensity due to spin and Laporte forbidden nature. The electronic and magnetic moment of the complexes are listed in the table 4.The bands in the region of 18024-18950 cm^{-1}, 19217- 21650 cm^{-1} and 23567-24584 cm^{-1} is attribute to $^6A_1 \longrightarrow {}^4T_1$, $^6A_1 \longrightarrow {}^4T_2(G)$ and $^6A_1 \longrightarrow {}^4T_2(D)$ respectively showing the distorted tetrahedral geometry of the complex [49] . The charge transfer bands are observed in region of 41532- 42251 cm^{-1} [50].

Table 4: Magnetic moment and Electronic Spectra

S.No.	Complex	Magnetic Moment	Electronic Spectra
1	$Mn(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	5.80	18621, 19950, 24512, 41556
2	$Mn(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	6.01	18530, 19217,24525,41532
3	$Mn(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	6.00	18923, 20009, 23871, 42071
4	$Mn(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	5.92	18950, 19967, 23720, 41841
5	$Mn(C_{15}H_{12}N_2OH)[S_2POCH_2C(CH_3)_2CH_2O]$	5.87	18621, 20015, 23950 41970
6	$Mn(C_{15}H_{12}N_2OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	5.97	18618, 21650, 23567, 42251
7	$Mn(C_{15}H_{12}N_2O.OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	5.94	18024, 20584, 24241, 42078
8	$Mn(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3)_2CH_2O]$	6.04	18270, 21513, 24584, 42150

4.4 **Biological Studies**

4.4.1 **Antibacterial activity**

The antibacterial activities of synthesised complexes were tested against bacterial species i.e., *E.coli*, *P. Aeruginosa* and *S. aureus*. Carbapenem was used as the standard reference. The data is summarized in the table 5. The well diffusion method was used to evaluate the antimicrobial study. The complexes were compared with metal salt, respective ligands and standard reference.

The complexes of manganese with 3-(2' hydroxyl phenyl)-5-(4'- methoxy phenyl) pyrazoline and O,O'-alkylene dithiophosphate (complex 7) has moderate the zone of inhibition (49.3 mm against *E.coli*, 52.6 mm against *P.Aeruginosa* and 49.9 mm against *S. aureus*). Complex 3 i.e, manganese with 3-(2' hydroxyl phenyl)-5-(4'-methoxy phenyl) pyrazoline and O,O' alkyl dithiophosphate shows the maximum zone of inhibition as compared to complex 7. It is observed that on complexation with pyrazoline and open chain dithiophosphate, manganese shows a better inhibitory effect as compared to the metal salts, respective ligands, complex 7 and standard drug. The greater efficiency of complexes as an antibacterial drug may be due to the presence of electron donating groups, which may increase the electron density on the metal centre. This makes complex more basic and complex may become prone to protonation, which may lead to a less stable and more labile complex. Electron –donating groups can also act as polar components, allowing them to form hydrogen bonds and hydrophilic interactions with amino acids in bacteria These interactions may disrupt the normal structure and function of enzymes and proteins by altering or damaging their amino acid components , ultimately leading to the death of the bacteria. [51].

Table 5: Antibacterial Activity

		Zone of inhibition (mm)						
S. No.	**Pathogen**	**Mn**	**Pyrazoli-ne[1]**	**Dtp[2]**	**Dtp[3]**	**Complex 3**	**Complex 7**	**Carbapenem (500µg/ml)**
1.	*E. coli*	18.4	25.9	26.1	31.3	49.3	41.7	40.4
2	*P. Aeruginosa*	17.9	24.6	32.4	26.9	52.6	44.6	42.8
3.	*S .aureus*	16.7	23.7	30.1	28.2	49.9	47.6	45.1

1.$(C_{15}H_{12}N_2O.OCH_3)$, 2.$[(C_3H_7O)_2PS_2]$, 3. $[S_2POCH_2C(CH_3)_2CH_2O]$

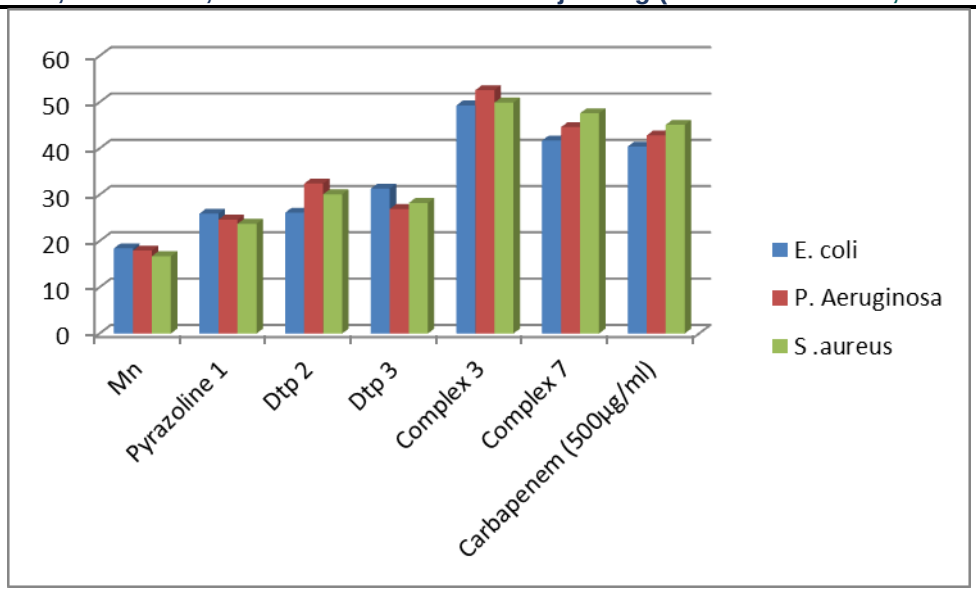

Figure 2: Antibacterial Activity

4.4.2 Antifungal activity

The data of antifungal activities are summarized in table 6. In this study, manganese complexes exhibited significant activities against *A. niger* and *C. albicans* with increased zone of inhibition as compared to Fluconazole (standard antifungal drug). Results show that Complex 3 with open chain dithiophosphate exhibit maximum antifungal activity (38.7 mm for *A. niger* and 41.3 mm for *C. albicans*) as compared to manganese salt, ligands and standard drug. The complex exhibit effective inhibition because sulphur in dithiophosphate contributes to the lipophilic properties which enhance their interaction with the fungal cell wall and membrane structures [52].

Table 6: Antifungal Activity

		Zone of inhibition (mm)						
S. No.	**Pathogen**	**Mn**	**Pyrazo-line [1]**	**Dtp [2]**	**Dtp [3]**	**Complex 3**	**Complex 7**	**Fluconazole**
1.	*A. niger*	15.2	21.6	23.2	27.9	38.7	34.7	32.9
2	*C. albicans*	16.9	22.5	25.4	23.7	41.3	36.5	35.4

1.($C_{15}H_{12}N_2O.OCH_3$) , 2.[$(C_3H_7O)_2PS_2$], 3. $[S_2POCH_2C(CH_3)_2CH_2O]$

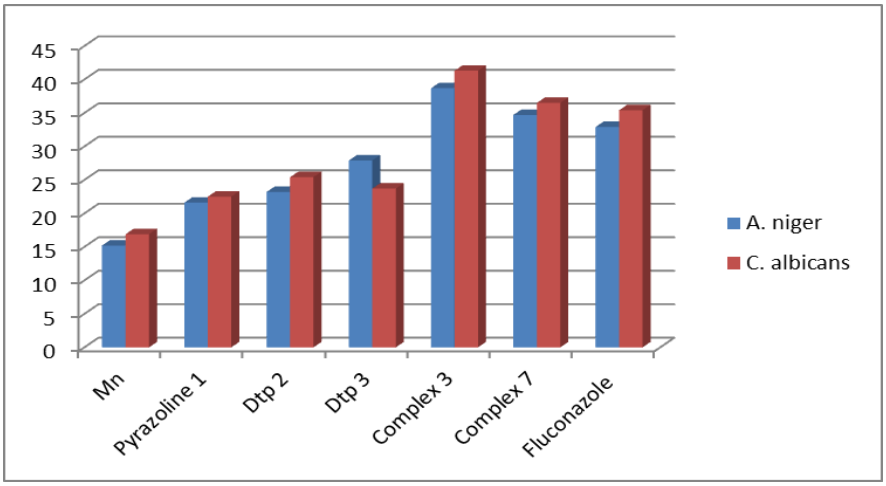

Figure 2: Antifungal Activity

5. Conclusion

The new complexes of manganese have been prepared and characterised by the elemental analysis, IR, UV. These investigations suggest that, all manganese complexes are tetracoordinated having distorted tetrahedral geometry with monoionic and bidentate ligands. All the complexes are monomeric in nature which is confirmed by the molecular weight data. Biological activities (antibacterial and antifungal) reveal that the complexes have significant antibacterial and antifungal activity in comparison to metal salt and ligands.

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