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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF SALICYLALDOXIME, DIMETHYLGLYOXIME AND BENZOIN WITH Mn (II) AND THEIR BIOLOGICAL ACTIVITY.

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ABSTRACT

The organic ligands contain nitrogen, oxygen and carbonyl and were used for preparation of Metal –Ligand chelated complexes . An ethanolic solution of salicylaldoxime, dimethylglyoxime and benzoin were reacted with aqueous solution of metal salts to give complex with symmetric ligands. Two different ligand solutions were mixed one after other in aqueous metal salt solution to give asymmetric ligand that is mixed ligand complexes having general formula [M(S)(D)] & [M(D)(B)] .The resulting product was found to be solid which have been characterized using FTIR spectrum which shows bands for characteristic frequencies in which –OH,-C=O,-C=N, C-O, M-O and M-N the groups are present. UV-Vis spectroscopy shows that nitrogen and oxygen of ligands donate the electron pair to metal and form the cheated complexes. Thermo Gravimetric Analysis (TGA) of all mixed ligand complexes was carried out to determine the procedural and decomposition temperatures. The temperature range in which decomposition occurs is in between 115^{o}C-440^{o}C. The magnetic properties were determined from Gouy balance method. The μ_{eff}. was found to be from 3.20 BM to 4.88BM as against the calculated 5.93BM value by using spin only formulae. It indicate that the hybridization of complexes is sp^3d^2 having octahedral geometry & is paramagnetic in nature. The complexes were checked for their biological activity by using E.Coli and *B. subtilis* bacteria. Only the mixed ligand complexes of benzoin and Dimethylglyoxime with Mn (II) were found to be biological active.

KEYWORDS: Mixed ligands, salidox, DMG, Benzoin , Manganese.

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INTRODUCTION

The coordination chemistry of multidentate ligands have gained much importance for more than two decades because of their remarkable biological activity and novel structural features .[1-3].In view of this ,we report herein the synthesis ,structural characterization and antimicrobial studies of Mn(II) complexes derived from mixed ligands containing some nitrogen ,oxygen and carbonyl[4-5]. A good example of this is the Mn(II) benzoin by the oxygen, dimethylglyoxime and salicylaldoxime have nitrogen and oxygen as a donor atom to give good yield of products with different geometries[6-7] and these complexes are found to be potentially biologically active[8]. Thus, in recent years metal complexes of this type[Mn(S)(D)] and [Mn(D)(B) shows remarkable biological activity[9]. The organic bidentate ligand, is the important class of ligand in co-ordination chemistry and find extensive application in different fields[10].The ligand contains donor atoms like nitrogen ,oxygen and groups like carbonyl therefore it's interaction with metal ions gives complexes of different geometries and are found to be potentially biologically active[11-12]. Several research papers have been published on synthesis and characterization of transition metal complexes with mixed ligands [13]. The literature survey shows that no work has been done on transition metal complexes of benzoin and dimethylglyoxime, salicylaldoxime and benzoin with Mn (II). The present work describes the investigation of mixed ligand complexes and their characterization [14]. The structure is determined using analytical techniques like; FTIR Spectroscopy, UV- visible spectroscopy, and magnetic susceptibility by Gouy balance method and decomposition temperature is measured by thermo gravimetric method [15-18]

MATERIALS AND METHODS

Metal salts ($MnSO_4.H_2O$); salicylaldoxime; dimethylglyoxime, benzoin, potassium hydroxide (KOH), dimethylformaide (DMF), dimethylsulfoxide (DMSO) and ethanol all were of A. R. grade quality and were from BDH and Merck chemicals. The double glass distill water was used.

2.2. General method for Preparation of the Metal (II) complexes

The metal ligand complexes were synthesized by taking 50 cm^3 ethanolic KOH in which 2.00-3.00 moles of ligand (Dimethylglyoxime, Salicylaldoxime and benzoin) is added to form homogenous solution. One mole of $MnSO_4H_2O$ was dissolved in 50 cm^3 in distilled water. Thus the ligand solution is added into the aqueous Mn(II) solution drop by drop with constant stirring for about 1.5hrs. The solid product formed was separated by filtration & washed with 1:1 ethanol: water & dried in vaccum. The Metal -Ligand complexes were Brown, Gray Brown and faint brown in colour with respect to ligands .The mixed ligands complexes were synthesized by adding solution of dimethylglyoxime (0.30 to 0.50g) dissolved in 50 cm^3 ethanolic KOH solution and salicyladoxime (0.50 to 0.94g) dissolved in50 cm^3 ethanolic KOH; in 50cm^3 aqueous solution of Mn(II) salts (0.5g) were added one by one respectively. This mixture was reflux for 2 hrs. The formed product was separated by filtration and washed with1:1 ethanol: water .The product was dried in vacuum. The mixed ligand complexes of benzoin and dimethylglyoxime were synthesized by adding solution of dimethylglyoxime (0.25 to 0.40g) dissolved in 50 cm^3 ethanolic KOH solution and benzoin (0.30 to 0.50g) dissolved in 50 cm^3 ethanolic KOH; in 50cm^3 aqueous solution of Mn(II) salts (0.5g) were added one by one respectively. The formed product was separated by filtration and washed with1:1 ethanol: water .The product was dried in vacuum.

2.3. Bacterial culture

The strains of bacteria used were Escherichia coli and *B. subtilis*. The identity of all the strains was confirmed. A bacterial suspension was prepared and added to the sterilized medium before solidification [19]. The media with bacteria was poured into sterilized Petri dishes under aseptic condition. The weight 100ug/ml of Mn (II) ligand complexes in DMSO solvent were placed on the surface of the culture and incubated at 37^0C for 24 hours [20-22]. The zones of inhibition was formed by these complexes was recorded in mm by scale [22-24].

RESULTS AND DISCUSSION

1. Physical Measurements and Analysis

IR spectra were recorded as KBr discs using IRAffinity-1 Fourier transform infrared spectrophotometer SHIMADZU in the range of 4000-400 cm^{-1}. Electronic Spectra were obtained using UV-1800 SHIMADZU spectrophotometer at 26^0C in 10^{-3} in DMF and DMSO. Elemental analysis was done C, H, N using qualitative organic analysis scheme. Magnetic properties were determined from Gouy balance method using analytical single pan balance (TapsonS-200J) and magnetic field was provided by electromagnet (Em-10), auto transformer. The metal percent in complex was determined using the simple volumetric estimation. Thermo gravimetric Analysis (TGA) is set up.*by using thermo balance K-14 super of 100mg capacity with an accuracy of ±0.1 mg. The elemental analysis data, decomposition temperature, Colour and percentage yield were given in Table 1.*

Table 1
The physical properties and data of the ligands (S, B, D) with their metal

Sr. no	Compound	Color	Melting Point ^{0}C	Yield %	C, H, N Analysis found (Calc.)(%)				
					C	H	O	N	M
1	S (Salidox)	White	61^0C	-----	------	-------	-----	-----	-----
2	B (Benzoin)	Whitish faint brown	134^0C	-----	-------	-----	-----	------	----
3	D (DMG)	White	241^0C	-----	-----	-----	------	-----	------
4	[Mn(Salidox)$_2$2H$_2$O]	Grey Brown	192d*	78.64	40.88 (40.68)	4.36 (4.35)	24.75 (23.97)	13.00 (12.87)	16.99 (16.98)
5	[Mn(DMG)$_2$2H$_2$O]	Brown	230d*	57.63	29.92 (30.01)	5.64 (5.62)	29.87 (28.97)	17.44 (17.65)	17.10 (17.12)
6	[Mn(Benzoin)4H$_2$O]	Light Brown	>300^0C	55.96	49.47 (49.45)	28.27 (28.27)	5.66 (5.45)	-------	16.24 (16.23)
7	[Mn(S)(D)2H$_2$O]	Brownish metallic Grey	320d*	88.57	37.19 (36.98)	4.54 (4.56)	27.02 (27.10)	11.83 (11.98)	15.46 (15.44)
8	[Mn(B)(D)2H$_2$O]	Dark Brown	280^0C	88.52	52.06 (52.07)	4.85 (4.05)	23.10 (23.15)	6.74 (6.71)	13.23 (13.21)

d*=Decomposition, B= Benzoin; S= Salicyladoxime (Salidox), D =Dimethylglyoxime (DMG).

2. Infrared spectra of free ligands

The characteristics vibrations & assignments of ligand dimethylglyoxime, benzoin, salicylaldoxime and their complexes were described in Table.2.The spectrum of ligand dimethylglyoxime exhibited weak bands at 3209 cm^{-1} and 3033 cm^{-1} this could be attributed to ν_{O-H} and ν_{C-H} ,respectively[25] While the another band at 1425 cm^{-1} which belong to $\nu_{C=N}$, and ν_{C-O}, observed at 1278 cm^{-1} . In spectrum of ligand salicyladoxime, it was noticed that the broad band at 3209 cm^{-1} and 2974 cm^{-1} which could be attributed to ν_{O-H} and ν_{C-H} respectively .The other strong band was appeared at 1425 cm^{-1} is due to the $\nu_{C=N}$. In case of benzoin the 3418 cm^{-1} ,3001 cm^{-1} 1679 cm^{-1} ,1466 cm^{-1} and 1278 cm^{-1} band belong to ν_{O-H} , ν_{C-H} , $\nu_{C=O}$, $\nu_{C=C}$, ν_{C-O}, respectively [26]

3. Infrared spectra of Complexes

The infrared spectra of the prepared complexes exhibited , $\nu_{C=N}$ in the range of 1598 cm^{-1} to 1634 cm^{-1} which shows a shifting to the lower frequencies 1425 cm^{-1} to1450 cm^{-1} compared with ligand like salicyladoxime and dimethylglyoxime[27].This indicate the coordination of ligand with metal ions through nitrogen atoms in their structures. The other bands are appeared in the range of 1278 cm^{-1} in benzoin which belong to ν_{C-O} & its complex shows band at 1114 cm^{-1} having lower frequency .This lower in frequencies is due to the coordination of ligand with metal ions through oxygen atom in their Mixed ligand cheated complexes[28]. The spectrum shows the band for the carbonyl group in the complexes in the range 1645 cm^{-1} to 1698 cm^{-1} .But the Carbonyl group shows the frequencies shifting from 1679 cm^{-1} to 1645 cm^{-1} & 1632 cm^{-1} indicating that it coordinate with metal in ligand of Benzoin and Salicyladoxime complexes[29]. The disappearing of band for ν_{O-H} vibration in the spectra of complexes is indicating the coordination of phenolic oxygen with metal ions [30].

4. M-Ligand Bond

The infrared of prepared complexes have shown weak bands in the range of 502-585 cm^{-1} and 444 cm^{-1}-472 cm^{-1} . This was attributed to the ν_{M-O} and ν_{M-N} respectively [31].

Table-2

The characteristic band of IR-absorption band of ligands and their complexes

Sr. no	Complexes	IR-Absorption band in cm^{-1}							
		νO-H	νC-H	νC=O	νC=N	νC=C	νC-O	νM-N	νM-O
1	S (Salidox)	3209	2974	----	1598	-----	----	----	-----
2	B(Benzoin)	3418	3061	1679	-----	1466	1278	----	-----
3	D (DMG)	3209	3033	-----	1693	-----	-----	----	-----
4	[Mn(Salidox)$_2$2H_2O]	---	3050	1598	1425	1438	1270	472	585
5	[Mn(DMG)$_2$2H_2O]	--	3107	----	1425	----	---	------	502
6	[Mn(Benzoin)4H_2O]	---	3030	1645	-----	1466	1114	453	----
7	[Mn(S)(D) 2H_2O]	--	2986	1632	1598	1435	1122	444	544
8	[Mn(B)(D) 2H_2O]	--	2976	1698	1450	1450	1143	458	512

5. Thermal Properties

The thermal decomposition of metal –Oxalate has been the subject of many researches. The thermal decomposition of metal –chelated yet have been not studied. The thermo gravimetric data was used to determine the dehydration and decomposition temperatures (Table.3).The TG curves for [Mn(Benzoin)4H_2O], [Mn(DMG)$_2$2H_2O] ,[Mn(Salidox)$_2$2H_2O], [Mn(D)(S)2H_2O] and [Mn(D)(B)2H_2O] are shown in (Fig.1). During this period of non-isothermal heating, the sample undergoes some transformation in air atmospheres. The final product formed in the TGA study of all complexes is MnO_2 [32].

6.Thermogravimetric Analysis of **Mn(II) ligands Complexes**

The TG curve for [Mn(Benzoin)4H_2O] shows that ,the thermal decomposition of complex at temperature below 350ºC occurs in three well –defined steps .The first step occurs in the temperature range 124ºC to 140ºC is accompanied by a weight loss of 10.18 % as against the calculated weight loss 10.64 % attributed for the dehydration of complex and is equivalent to two water molecules .The complex is stable up to 178ºC then decomposed in second step. This step shows weight loss 11.95 % at in accordance with calculated weight loss 12.37 % due to further dehydration of Mn-Benzoin complex in the temperature range 180ºC-238ºC and is equivalent to another two water molecules of the complex [33] .The third decomposition step occurs in the temperature range 280ºC-345ºC accompanied by a weight loss 67.29 % compared with theoretical weight loss of 67.44 % attributed to the decomposition of the intermediate step in *to* MnO_2 residue & evolution of other by product as gases (Fig.1.Curve-A).The TG curve (Fig.1.Curve.B) for bis (dimethylglyoxime) Manganese (II) dihydrated complex heated from 26ºC to 300 ºC at 5 ºC min^{-1} under air atmosphere. The practical mass loss is 11.07 % in the temperature range 115ºC-140ºC which is in accordance with calculated weight loss 11.21 % attributed for dehydration of complex. The second step; weight loss; 22.28 % in the temperature range 162ºC - 182ºC and is in accordance with calculated weight loss 23.13 % attributed to loss of 1.5 O_2 and water molecules. The last step shows weight loss 59.17 % in accordance with calculated 60.33% in the temperature range 220ºC-280ºC The remaining residue is about 5.33 % of MnO_2. The TG curve (Fig.1.C.) shows that the dehydration takes place in the temperature range 192ºC-263ºC which was attributed loss of water from the complex .The weight loss is 29.43 % which is in accordance with calculated weight loss of 29.70%.The second decomposition steps occurs in 320ºC-378ºC showing weight loss 40.49 % in accordance with calculated weight loss 45.49 % and formation of end product of Manganese dioxide. The thermal decomposition of this complex shows two distinct steps curves (Fig.1.D). First step is attributed for dehydration with weight loss 35.47 % in accordance with calculated weight loss of 37.63 % in the temperature range 152ºC-340ºC.The another shows decomposition of organic molecules with weight loss 61.80% in the temperature range 380 ºC - 422ºC in accordance with calculated weight loss 63.69%. The TG curve E (Fig.1.) for [Mn (DMG)(Benzoin)2H_2O] heated under non-isothermal condition. It shows two steps with weight loss 15.86% and 73.56 % in the temperature range144ºC-240ºC and 348ºC - 375ºC in accordance with calculated weight loss 16. 37 % and 74.96 % respectively .The weight loss in step first was due to dehydration and step second due to the ligand was broken down in to many organic fragments. In general, the final decomposition product in all the Mn (II) complexes was found to be manganese dioxide. The data of thermal analyses is summarized in table.3.

Table.3

Thermal Analysis data of the Mn(II) complexes

Sr.No.	Complexes	Decomposition stage	Temp. range ºC	Weight loss Found (calcd.) %	Decomposition Assignment	Residue Remained Fond (Calcd.) %
1	**[Mn(Benzoin).4H_2O]**	Stage-1	124-140	10.18 (10.64)	-2 H_2O	MnO_2 9.95 (10.17)
		Stage-2	180-238	11.95(12.37)	-2H_2O	
		Stage-3	280-345	67.29 (67.44)	-$C_{12}H_{12}$	
2	**[Mn(DMG)$_2$.2H_2O]**	Stage-1	115-140	11.07 (11.21)	-2 H_2O	MnO_2 5.33 (7.48)
		Stage-2	162-182	22.28 (23.13)	-2 H_2O,-1/2 O_2	
		Stage-3	220-280	59.17 (60.33)	-2N_2, 2C_2H_6	
3	**[Mn(Salidox)$_2$ 2H_2O]**	Stage-1	192-263	29.43(29.70)	-2 H_2O , 2NO	MnO_2 25.08 (29.81)
		Stage-2	320-378	40.49(45.49)	-2C_7H_7	
4	**[Mn(D)(S).2H_2O]**	Stage-1	152-340	35.47 (37.63)	--2 H_2O,-3NO	MnO_2 0.57 (0.84)
		Stage-2	380-422	61.80 (63.69)	-$C_{11}H_{13}$	
5	**[Mn(D)(B).2H_2O]**	Stage-1	144-240	15.86 (16.37)	-2 H_2O, O_2	MnO_2 8.67 (10.57)
		Stage-2	348-375	73.56(74.96)	-2NO,-$C_{16}H_{18}$	

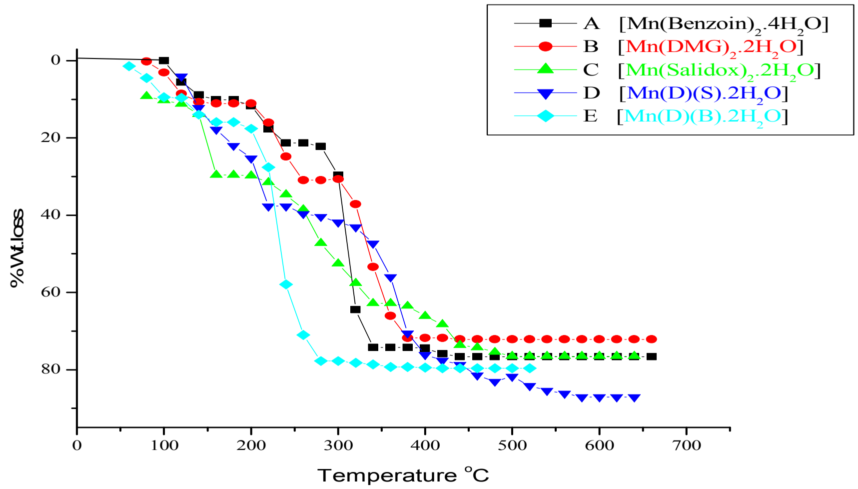


Figure.1
TG-Curves for Mn(II) –Complexes.

7. The Electronic Spectra –
UV-Visible spectrum of complexes was measured in DMF solvent Figure 2. Electronic spectral data of mixed ligand complex [Mn(S)(D).2H_2O] of shows bands in the range of 309 nm-527nm suggesting the existence of charge transfer and due to $^6A_1g \rightarrow$ ^6T_1g transition. The observed data confirmed the presence of an octahedral geometry [34-37]. The magnetic moment value of the complex displays the presence of a high spin complex[38].

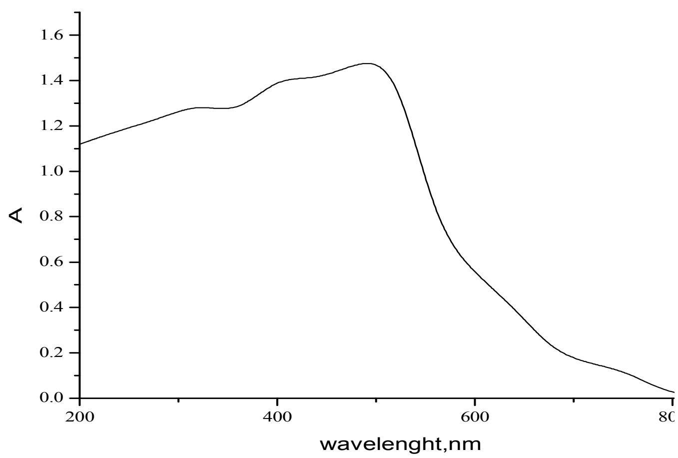


Figure.2
Electronic spectra of Mn (II) mixed ligand complexes of [Mn(S)(D).2H_2O]

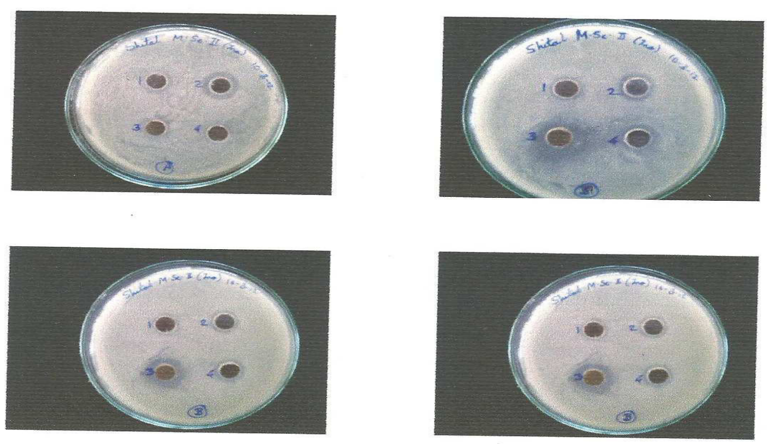
8. Magnetic Properties
The magnetic moment μ_{eff} for complexes of Mn^{+2} (d^5) were found to be 5.93 B.M . Which within the expected spin only values [39].The lower value of Mn^{+2} (d^5) complexes shows 4.88 BM-5.23BM may be due to the no orbital contribution[40-41] . The complexes show paramagnetic due to five unpaired electron[42].The geometry of complexes were found to be Octahedral in nature [43].The hybridization of complexes was attributed sp^3d^2 .All the data and remarks are found in table 4.

Table 4
The Magnetic properties of the complexes at 27 ^{O}C

Complexes	No. of Electron	No. Of Unpaired Electron	Electron Configuration	Term Symbol	Orbital Contribution	μ_{eff}	
						Found	Calculated
[Mn(Salidox)$_2$2H_2O]	d^5	5	$t^3{}_{2}g$, e^2g	S^6	NO	5.05	5.93
[Mn(DMG)$_2$2H_2O]	d^5	5	$t^3{}_{2}g$, e^2g	S^6	NO	5.23	5.93
[Mn(Benzoin)4H_2O]	d^5	5	$t^3{}_{2}g$, e^2g	S^6	NO	5.18	5.93
[Mn(S)(D)2H_2O]	d^5	5	$t^3{}_{2}g$, e^2g	S^6	NO	3.02	5.93
[Mn(B)(D)2H_2O]	d^5	5	$t^3{}_{2}g$, e^2g	S^6	NO	4.88	5.93

9.Antimicrobial susceptibility test

The synthesized complexes were screened for their *in vitro* antimicrobial activity against *Escherichia coli* and *B. subtilis* by measuring the zone of inhibition in mm. The antimicrobial activity was performed by agar well diffusion method at concentration 100 µg/m [43-44].The synthesized complexes shows potential antimicrobial activity by well diffusion method. The zone of inhibition based upon zone size around the wells was measured. The measured zone of inhibition against the growth of microorganism is listed in Table 5.It is found that the metal complexes have higher antimicrobial activity. A total of three complexes of Mn (II) shows antimicrobial activity (figure 3.).



Where,

A = E-coli

B = B-Substilus

1 = Mn DMG in DMSO solution

2 = Mn Benzoin in DMSO solution

3 = Mn DMG Benzoin in DMSO solution

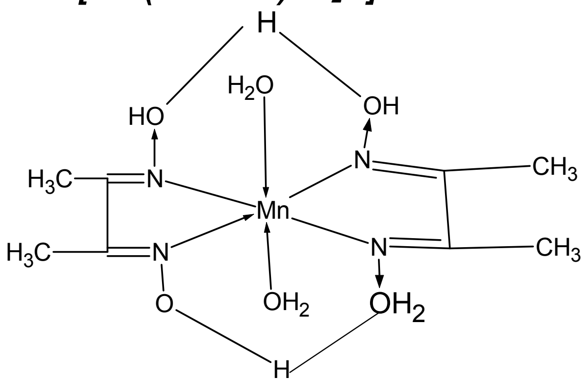
4 = DMSO solution

Figure.3
Photograph of Antimicrobial Activity of Mn(II) complexes.

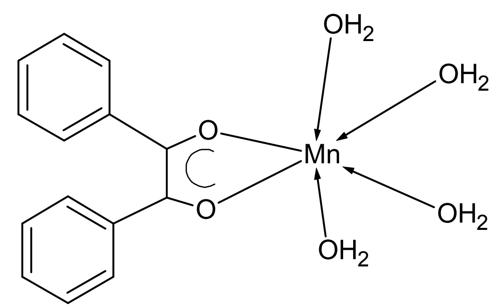
Table-5
Antibacterial activities of Mn(II) ligands Complexes

Complexes	Diameter of Zone of Inhibition (mm)	
	E.Coli	***B. subtilis***
[Mn(Benzoin)4H_2O]	1.0	3.0
[Mn(DMG)2.2H_2O]	1.8	2.5
[Mn(D)(B).2H_2O]	2.1	6.2

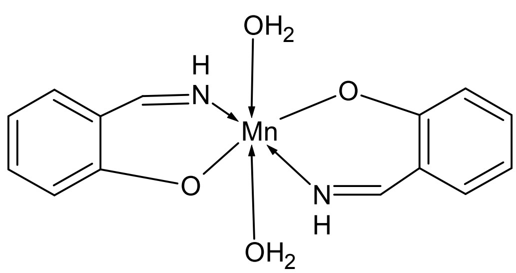
1.[Mn(Benzoin)4H_2O]



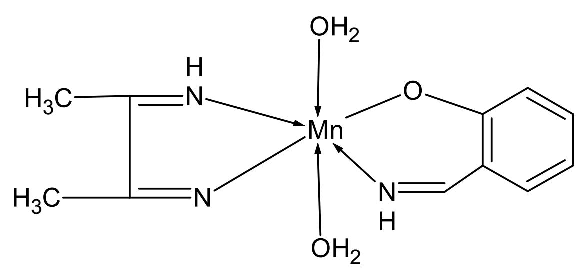
2. [Mn(DMG)$_2$2H_2O]



3.[Mn (Salidox)$_2$2H_2O]



4.[Mn(DMG)(Salidox)2H_2O]



5.[Mn(DMG)(Benzoin)2H_2O] Complex

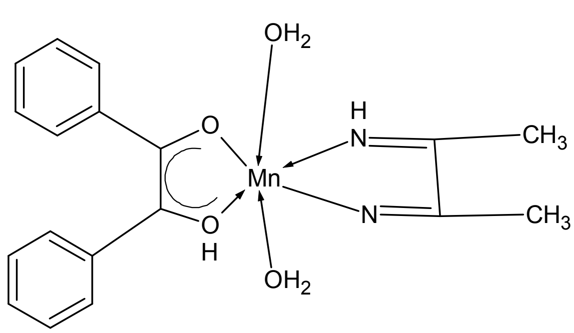


Figure .4
Suggested structure of the Mn(II) Complexes

CONCLUSION

The mixed ligand complexes of salicylaldoxime, dimethylglyoxime and Bezoin with the general formulae [Mn(S)(D)2H_2O] & [Mn(D)(B) 2H_2O] are found to be totally new and unreported . The FTIR of ligand & complexes shows the nitrogen and oxygen of ligand atoms to coordinate with the Mn(II). Also from the UV-Visible spectra and Gouy balance method it can be suggested that the octahedral geometry and paramagnetic nature of complexes is confirm. All the newly synthesized Metal -Ligands complexes of symmetric as well as mixed Mn(II)-ligands were analyzed with different spectral techniques and screened in vitro for their antibacterial activity against both *Escherichia coli* and *B. subtilis*. The result of antimicrobial screening reveals that the three complexes have exhibited good biological activity against all strains. The suggested structures of complexes are shown in figure 4

REFERENCES

1. Panchal P.K& Patel M.N.,Synth React Inorg Met-org chem.,2004 (34) :1277
2. Thomson K.S; Meneilli J.H & Org. C,Chem. Rev,1999 (99) 2561
3. Maurya M R ,bharti n, Naqui F & Azam A, Bioinorganic Med. Chem. Lett. 2000 (10):2243
4. Akbar M.A. and Bose.R ,J.Inorg. nucl.Chem.1977,(39) :265
5. Harlai S and Varshney A.K., Bioinorganic Chem Appl.2006
6. El-ajaily1, M.M. and Maihub, A.A., International Journal ofChem.Tech. Research. 2010,2(3):1579-1580.
7. Birendra Kumar, Kiran kumara Prasad , Sanjay Kumar Srivastawa oriental journal of chemistry 2010,26(4):1413-1418.
8. Sarika R.Youl, Amit R.Yaul, Gaurav B. pethe ,Anand S.Aswar ,American-Eurasian journal of scientific research 2009,4(4):229-234.
9. Aliyu, H.N., A.S.Mohammed, Bayer Journal of Pure and Applied Science, 2009,2(1):132-134.
10. Shayma A.Shaker, H.A.Mohammed , Abbas Ali Salih, 2010,4(10):5178-5183.
11. Pramila Yadav, Pratibha Sharma VSRDTNTJ,, 2012 ,3(10): 371-373.
12. Catherine P. Raptopoulou , Yiannis Sanakis, Athanassios K. Boudalis, Vassilis Psycharis 2005,24:711–721
13. Erdal CANPOLAT, Mehmet Kaya, Seher G¨UR Turk J Chem (2004) ,28 : 235 – 242.
14. Wies Awaferenc, Agnieszka Walkow Dziewulska, Janusz Chru Ciel J.Serb.Chem.Soc. 2003, 68(10):751–763.
15. Boraey. H. A., Journal of Thermal Analysis and Calorimetry,2005, 81:341
16. M. KurtogluDOI: 10.2298/JSC091118102K
17. H. N. Aliyu and H. J. Abdullahi Bayero Journal of Pure and Applied Sciences,2009, 2(2): 110 – 112
18. Domenico Cupertino a, Mary McPartlin b, Andreas M. Zissimos, Polyhedron, 2001,20 ,:3239–3247
19. M.M. El-ajaily1*and A.A. Maihub, International Journal of ChemTech Research , 2010,2(3):1579-1580.
20. Joshi Krushnalal. T1, Pancholi A. M1, Pandya K. S2 and Thakar A. S 2011, 1 (2):63-69
21. U. Schillinger and F.K. Lucke, Appl. Environ. Microb.,1989 55(8):1901 .
22. M. D.grak, A. I.cim and M.H. Alma, Physiotherapy Research,,1999 13:584 .
23. Mukerrem Kurtoglu,J. Serb. Chem. Soc.2010, 75 (9):1231–1239)
24. S. C. Nayak, B.P. K. Das, K. K. Sahoo ,Chem. Pap. 2003, 57(2) : 91—96
25. Nakamoto,T.O, K., Infrared Spectra of Inorganic and Coordination Compounds. 2nd ed. New York, NY: Wiley-Interscience; 1970

26. Sing B, Narang K.K, Srivastava R., Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 32, nr. 9, 2002, p 1577
27. Emel M and Vefa A, J Chem Research (S), 1999, 142-143.
28. Nayak S C, Das P K and Sahoo K K, Chem Pap., 2003, 57(2), 91-96.
29. Silverstein R M, Bassler, G C and Morril T C, Spectrophotometric Identification of Organic Compounds; 4th Edn., Wiley: New York, 1981.
30. Socrates G, Infrared Characteristic Group Frequencies; John
31. Keypour H, Salehzadeh S, Pritchard R G and Parish R V, Transition Met Chem.,1998, 23, 605- 607.
32. E. Dubler and G. Hanggi, Thermochim. Acta, 1994, 234: 201.
33. M.I. Dhar and O. Singh, Thermochim. Acta, 1991, 191:285.
34. El-ajaily M M, Maihub A A, Ben-Gwerief S F, Belazi A M and El-zweay R S, Oriental J Chem., 2007, 23(1): 97-104.
35. Shayma A. Shaker, Yang Farina, Abbas A. Salleh, European Journal of Scientific Research,2009;33(4):702-709.
36. Nicholls, D., (1984). “Complexes and first Row transition elements”
37. Ugranker M M, and Pradhanada B,Transition Met Chem,1990,15:361
38. Sanja O. Podunavac-Kuzmanović, Siniša L. Markov and Ljiljana S. Vojinovi, APTEFF, 2004,35:280.
39. Cotton, F. A. and Wilkinson, G., (1998),“Advanced inorganic chemistry
40. Y.K. Gupta, S.C. Agarwal , S.P. Madnawat,Ultra Scientist 2012; 24(2)B: 370-374 .
41. Chakrawati.P.B,J Indian Chem Soc,2001;78:273.
42. Ravanasiddap[pa M.,Sureshg T., Syed K.,Radhavendray S.C.Basavaraja C. and Angadi S.D. E-J.Chem.2008,5(2):395-403
43. Leena Chordia and Alok Chaturvedi,J.of the Chainnese chem. Soc.2009,56:636-641
44. Mishra A.P.,Tiwari A.,Gupta S.K,and Jain Rajendra,2012,9(3):1113-1121