Spectral, Thermal, Fluorescence and Antimicrobial studies of binuclear Mn(II) Complexes with bis-(Carboxyamides) derived from 4,4'-diaminobiphenyl, 1,4-diaminobenzene with anhydrides

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Abstract- The Binuclear Mn(II) Complexes of bis-carboxyamides derived from 4,4'-diaminobiphenyl 1,4-diaminobenzene with Phthalic, Succinic and Maleic anhydrides. The Complexes were characterized using elemental, spectral electrochemical, fluorescence, thermal and antimicrobial activities. The ligands act as doubly bidentate towards the metal ion coordination through amide carbonyl oxygen and acid carbonyl oxygen. The geometry and antimicrobial activities of the complexes have been discussed.
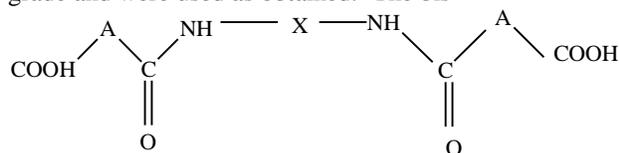
Keywords- Bis-Carboxyamide, 4,4'-diaminobiphenyl, 1,4-diaminobenzene

1. INTRODUCTION

Now a days there has been a growing interest in the transition metal complexes bearing carboxyamide type ligands due to their pharmacological and biological importance[1-5]. Manganese is an important metal in biological and electrochemical studies[6,7].The binuclear coordination compounds of manganese have been highly considered in magnetic and catalytic activity areas[8]. A number of reports on binucleating carboxyamide ligands with transition metals are available[9-12], no study on the Mn(II) complexes of such ligands has been reported. In this paper, we report the synthesis and spectral properties of Mn(II) complexes of bis-(carboxyamide) ligands derived from 4,4'- diaminobiphenyl, 1,4 – diaminobenzene reacted with Phthalic, Succinic and Maleic anhydrides. The structure of the carboxyamide ligand shown in fig. 1.

2. EXPERIMENTAL

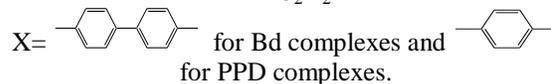All chemicals were of analytical reagent grade and were used as obtained. The bis-(carboxyamide) ligands were prepared by substantially modifying a published procedure[13].

2.1 Synthesis of ligands:

A solution of 4,4' diaminobiphenyl (1.84g, 0.01mol) dissolved in 30ml of absolute ethanol was mixed with a solution of 2.96 g (0.02 mol) of Phthalic anhydride (or) 2g (0.02mol) of Succinic anhydride (or) 1.96g (0.02mol) of Maleic anhydride in 30 ml of absolute ethanol and refluxed for 4 hrs. The solid separated was filtered, washed with ether and dried[9,14]. It was found to be the ligands $Bd(PAH)_2$, $Bd(SAH)_2$ and $Bd(MAH)_2$

A solution of 1.08g (0.01moles) of 1,4 – diamino benzene in absolute ethanol (30 ml) was refluxed with 2.96 g (0.02moles) of phthalic anhydride (or) 2g (0.02moles) of Succinic anhydride (or) 1.96 (0.02 moles) of Maleic anhydride in 30ml of absolute ethanol and refluxed for 4hrs. On cooling the carboxyamides precipitates out. The product was filtered, washed with ether and dried.It was found to be the ligands $PPD((PAH)_2$, $PPD(SAH)_2$ and $PPD(MAH)_2$.

Fig.1- The structure of ligand : $A=C_6H$ or $A=C_2H_4$ or $A=C_2H_2$

$X=$ ⬡—⬡ for Bd complexes and ⬡ for PPD complexes.

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2.2 Synthesis of complexes:

A solution of 0.480 g (0.002mmol) of Bd(PAH)$_2$ in 30ml of absolute ethanol was refluxed with a solution containing 0.252 g (0.002 mmol) of Mn(II)acetate dihydrate in 30ml of absolute ethanol for 4 hrs in a 100ml round bottomed flask. On cooling, the metal complexes were precipitated out. The solid formed was filtered, washed with ethanol and ether and dried. A similar procedure was followed for the synthesis using the ligand Bd(SAH)$_2$, Bd(MAH)$_2$, PPD((PAH)$_2$, PPD(SAH)$_2$ and PPD(MAH)$_2$. The following reaction takes place during the formation of complexes.

2Mn(CH$_3$COO)$_2$.4H$_2$O + 2Ligand $\xrightarrow{\text{ETOH}}$

[MnL(H$_2$O)$_2$]$_2$ + 4CH$_3$COOH
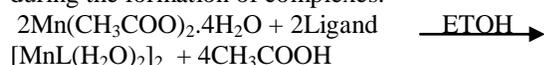
2.3 Analysis and measurements:

The elemental analysis was carried out on a FLASH EA SERIES 1112 C,H,N,S analyser. IR spectra were recorded on JASCO Spectrophotomer in the 4000-400Cm-1 range using KBr Pellets.The UV-Vis Spectra were recorded on JASCO variant 630 Spectrophotometer. The electrochemical studies were performed with a three electrode configuration using a CHI-643B series electrochemical workstation. Working electrode was a glassy carbon electrode(3mm) disk, Platinum wire as Counter electrode and KCl saturated Ag/AgCl as a reference electrode. Tetrabutyl ammonium perchlorate (0.1M) was used as the supporting electrolyte. The fluorescence emission spectrum were recorded with JASCO FP-6300. Thermal Analysis were done on a PerkinElmer STA 6000.

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis

The analytical data pertaining to the C,H,N and Manganese contents of the complexes being reported in Table 1 . The data indicates formulation of the complexes with a Manganese: ligand ratio 1:1. The ligands being capable of binding to two metal centers, this will lead to the complexes being formulated as Mn$_2$(ligand)$_2$ (H$_2$O)$_4$. This conjecture is supported by the closeness of the experimental and the theoretical values.The metal content in the complexes were estimated by standard methods.

Table 1. Analytical data of the Ligand and Mn(II) Complexes.

Compound	Molecular Formula	Found (calcd) %			
		C	**H**	**N**	**Mn**
L1 - Bd(PAH)$_2$	C$_{28}$H$_{20}$N$_2$O$_6$	70.07 (70.0)	4.03 (4.17)	5.59 (5.83)	- -
Mn$_2$-Bd(PA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{56}$H$_{44}$N$_4$O$_{16}$	59.16 (59.36)	3.82 (3.87)	4.85 (4.92)	9.85 (9.65)
L2 - Bd(SAH)$_2$	C$_{20}$H$_{20}$N$_2$O$_6$	62.17 (62.5)	5.18 (5.21)	7.19 (7.29)	- -
Mn$_2$-Bd(SA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{40}$H$_{44}$N$_4$O$_{16}$	50.54 (50.75)	4.58 (4.65)	5.83 (5.92)	11.58 (11.61)
L3 - Bd(MAH)$_2$	C$_{20}$H$_{16}$N$_2$O$_6$	63.06 (63.16)	4.11 (4.21)	7.26 (7.36)	-
Mn$_2$-Bd(MA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{40}$H$_{36}$N$_4$O$_{16}$	51.08 (51.18)	3.64 (3.84)	5.86 (5.97)	11.90 (11.70)
L4 - PPD(PAH)$_2$	C$_{22}$H$_{16}$N$_2$O$_6$	65.31 (65.35)	3.88 (3.96)	6.85 (6.93)	-

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Mn$_2$-PPD(PA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{44}$H$_{36}$N$_4$O$_{16}$	55.54 (55.59)	3.34 (3.36)	5.86 (5.89)	11.54 (11.56)
L5 - PPD(SAH)$_2$	C$_{14}$H$_{16}$N$_2$O$_6$	55.50 (55.55)	5.15 (5.19)	9.04 (9.09)	-
Mn$_2$-PPD(SA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{28}$H$_{36}$N$_4$O$_{16}$	44.28 (44.33)	4.12 (4.22)	7.36 (7.38)	14.45 (14.48)
L6 - PPD(MAH)$_2$	C$_{14}$H$_{12}$N$_2$O$_6$	55.23 (55.26)	3.90 (3.95)	9.18 (9.21)	-
Mn$_2$-PPD(MA)$_2$(H$_2$O)$_4$	Mn$_2$C$_{28}$H$_{28}$N$_4$O$_{16}$	44.75 (44.81)	3.18 (3.20)	7.43 (7.46)	14.61 (14.64)

3.2. Infrared spectral studies

The infrared spectra of the complexes were recorded in KBr pellets in the range of 4000- 400 cm-1. The data of the ligand and complexes were summarized in Table 2 and Fig.2. The infrared spectral data of the ligands and Mn(II) complexes shows a wide range of absorptions due to amide carbonyl, acid carbonyl, ν NH stretching of the amide group. The ν OH stretching of the carboxylic acid group normally occurs around 3560-3500cm^{-1} in the monomer. The ν NH stretching absorption due to the presence of amide group occurs around 3400-3200 cm^{-1}

Table 2. IR Spectral data (in cm^{-1} and CV data of the Ligand and Mn(II) – Complexes

Compound	OH str/ NH str (amide)	Amide I C=O Amide II (N-H bend)	Acid C=O	Mn-O	Epc (V)	Epa (V)
Bd(PAH)$_2$	3458, 3350	1636, 1556	1718	-	04891	0.8928
Mn$_2$-Bd(PA)$_2$(H$_2$O)$_4$	3439	1628, 1560	1708	531	0.5323	0.652
Bd(SAH)$_2$	3417, 3331	1657, 1557	1710	-	0.4824	0.9595
Mn$_2$-Bd(SA)$_2$(H$_2$O)$_4$	3423	1616, 1560	1722	666	0.5357	0.9190
Bd(MAH)$_2$	3417, 3330	1630, 1559	1709	-	0.4923	0.7392
Mn$_2$-Bd(MA)$_2$(H$_2$O)$_4$	3423	1640, 1561	1720	529	0.5357	0.722
PPD(PAH)$_2$	3440, 3360	1656, 1545	1710	-	0.1219	0.7178, 0.9795
Mn$_2$-PPD(PA)$_2$(H$_2$O)$_4$	3397	1630, 1550	1700	531	-0.5742 0.2639	-0.4148
PPD(SAH)$_2$	3292, 3330	1660, 1550	1700	-	0.3555	0.7259, 1.0397
Mn$_2$-PPD(SA)$_2$(H$_2$O)$_4$	3294	1650,1554	1725	661	-0.5860	0.756
PPD(MAH)$_2$	3286, 3193	1630, 1553	1700	-	0.3450	0.7200
Mn$_2$-PPD(MA)$_2$(H$_2$O)$_4$	3340	1660,1560	1710	539	0.2639 0.6515	0.7115

The possible sites of binding of the metal are the amide carbonyl and the carboxylate oxygen atoms. The amide absorption due to ν NH bending of the secondary amide occurs at 1560-1600cm-1. This band does not undergo any perceptible shift upon complexation indicating the non-involvement

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of the amide N atom. The secondary amide carbonyl absorbs around 1660-1630Cm^{-1} in the ligand. In the case of complexes these absorption shifted to approximately 10-30cm^{-1} lower and higher values indicating the involvement of the amide carbonyl oxygen atom. The acid carbonyl which absorbs around 1700-1718cm^{-1} in the ligands also gets shifted to higher and lower values by nearly 10-28cm^{-1} upon

complexation, implying the involvement of acid carbonyl in binding to the metal. Comparison of the values observed for the present complexes with the literature values indicate that the carboxylate group is bound through the C-O$^-$ moiety. The ν C=O has been reported to shift to lower and higher frequencies when involved in binding to the metal[15].

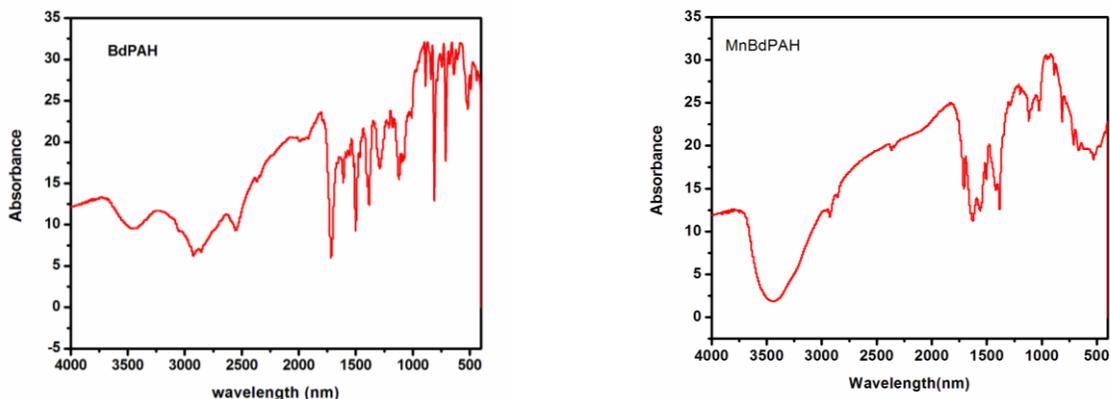**Fig.2**. IR Spectra of Bd(PAH)$_2$ and Mn$_2$Bd(PA)$_2$(H$_2$O)$_4$

The infrared spectra of the complexes exhibit strong bands in the region 529-666cm^{-1} indicating the presence of ν(Mn-O) bonds [16-18].The medium intensity band appearing in the region 1050- 1125 cm^{-1} in the spectra of Mn(II) complexes has been assigned to the resulting modes of coordinated water[19].The above analysis of the infrared spectra of the complexes shows that the ligand binds through the carboxylate and the amide carbonyl groups to the metal ions. From this an Octahedral coordination around the Manganese atom containing a [Mn(ligand)(H$_2$O)$_2$]$_2$ is indicated.

3.3 Electronic spectral studies

Electronic spectra of the complexes were recorded in DMSO medium in the range of 200-900nm.The ligands shows shoulders in the region around 33333cm^{-1} (300nm) and 27027cm^{-1} (370 nm). The binuclear Mn(II) Complexes exhibits shoulders in the region around 19047- 23255cm^{-1}(525nm - 430nm) when compared to ligands the shape and intensity somewhat different. These may be assigned to the ligand to metal charge transfer, possibly superimposed upon other intra ligand transitions [20-22]. These bands are corresponding to 6A$_{1g}$ $\longrightarrow$ 4T$_{1g}$, (G) and 6A$_{1g}$ $\longrightarrow$ 4T$_{2g}$(G) transitions which are compatible to an octahedral geometry around Mn (II) ion [23-26].

3.4 Electrochemical studies

The Cyclic voltammogram of Mn(II) complexes (MnL1-MnL6) are recorded in the potential range -0.80V to 1.2V.

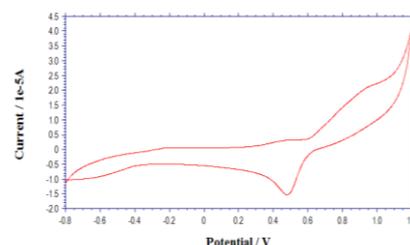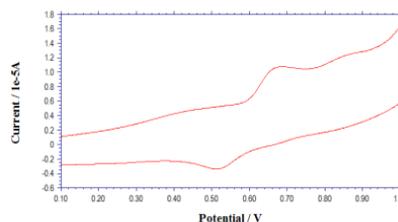**Fig.3**. Cyclic Voltammogram of Bd(PAH)$_2$

Fig.4. Cyclic Voltammogram of Mn$_2$Bd(PA)$_2$(H$_2$O)$_4$

The electrochemical data of the bis-(carboxyamide) ligands show a quasi irreversible

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reduction in the range 0.12V to 0.49V vs Ag/AgCl. This reduction may be attributed to the reduction of the carboxylic acid group[27]. The Cyclic Voltammetric data for the ligand and Manganese complexes given in Table 2. All the Mn(II) complexes show similar cyclic voltammogram. The complexes shows a reduction peak in the region -0.5860V- 0.6515V and the corresponding oxidation peaks appear in the region -0.4148V-0.919V . The Mn (II) complexes shows both reduction and oxidation in cathodic and anodic potential respectively. Based on the above result Mn(II) Complexes followed quasi irreversibility reactions.[28-30]

3.5 Fluorescence studies

The Photoluminescence properties of the carboxamide ligand and their complexes were studied at room temperature for 10^{-4}m solution for all compounds in DMSO. Excitation and emission slit widths were set at 20nm with a scan speed of 500nm/min.

Table:3 Fluorescence Characteristics of Ligand and its Metal Complexes:

Compound	Excitation Wavelength(nm)	Fluorescence Wavelength (nm)	Intensity
Bd(PAH)$_2$	320	411	6500
Mn$_2$-Bd(PA)$_2$(H$_2$O)$_4$	320	400	3400
Bd(SAH)$_2$	320	408	985
Mn$_2$-Bd(SA)$_2$(H$_2$O)$_4$	320	395	890
Bd(MAH)$_2$	320	410	2990
Mn$_2$-Bd(MA)$_2$(H$_2$O)$_4$	320	399	2380
PPD(PAH)$_2$	290	338	160
Mn$_2$-PPD(PA)$_2$(H$_2$O)$_4$	290	328	25
PPD(SAH)$_2$	290	340	800
Mn$_2$-PPD(SA)$_2$(H$_2$O)$_4$	290	330	260
PPD(MAH)$_2$	290	345	140
Mn$_2$-PPD(MA)$_2$(H$_2$O)$_4$	290	329	70

The excitation spectra of the ligand shows a maximum at 290, 320 and 350nm and shows an emission peak at 405,340 and 410nm. The spectral data of the compounds are given in Table.3 and Fig.5. Mn(II) complexes shows a decrease in intensity compared to its ligand .The emission observed in the complexes tentatively assigned to the π-π* transitions [31].
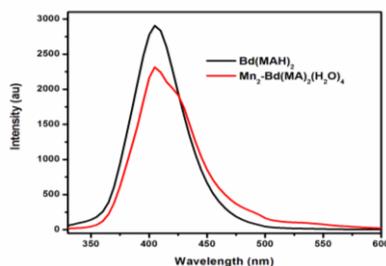

Fig.5 Fluorescence Spectra for Bd(MAH)$_2$ and Mn$_2$Bd(MA)$_2$(H$_2$O)$_4$

This is probably due to quenching effect of the transition metal which bound to the ligand during complexation whereby the charge transfer transition occurred between ligand and metal ion [32]. This can also be accounted for by the effect of oxygen available and therefore quenched the fluorescence intensity of the complexes [33]. The decrease in intensity of complexes may be explained by ligand to metal charge transfer.

3.6 Thermal studies

The Thermograms of the [Mn Bd(SA)$_2$]$_2$ and [Mn Bd(PA)$_2$]$_2$ Complexes shows the thermal decomposition takes place in stages. Thermograms of the [MnBd(SA)$_2$]$_2$ shows that below a temperature of 250^0C a slow weight loss is observed. Starting around 280^0C a major weight loss takes place. Between 400-450^{0}C and 700^{0}C negligible weight loss takes place. Beyond 700^{0}C it appears that all the sample evaporates. It has been reported by Brode et al [34] that the water molecules bind to the ligand through hydrogen bonding. In their study of complexes containing some azo ligands, water was found hydrogen bonded to the azo group. Deshpande and Shah [35] have attributed the weight loss at 120^{0}C to water molecule bound to the ligand. The loss of

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ligand in general has been found to take place in stages[36]. Analysis of the thermograms in the present study shows that the major decomposition takes place at least in two steps. This is indicated by the two peaks in the DTA curve for $[MnBd(SA)_2]_2$. The weight loss of 23.4% found in the thermograms of the complex corresponds to the loss of two succinic acid moieties, such a loss may be expected on thermolysis of the amide ligands. The thermogram of Ligand confirms such an expectation. An endothermic weight loss takes place starting at 150^0C and a further exothermic weight loss beyond 250^0C. The decomposition of the complex starts only at 290^0C thus showing that the ligand is thermally more stable in the complex. Similar thermal behavior is observed in the case $[MnBd(PA)_2]_2$.

Thermograms of the $[Mn\ Bd(PA)_2]_2$ shows the decomposition between 275^0C and $450^0\ C$ takes place in two steps is inferred from the shape of the TGA curve and the presence of two discernable peaks in the DTA curve. The stages of weight loss have been subjected to a kinetic analysis using the method of Coats and Redfern[37]. According to these authors a plot of either

$$Log\{[1-(1-\alpha)^{1-n}]/T^2(1-n)\} \text{ versus } 1/T,$$
or Where n=1,

$$Log\ [-log(1-\alpha)/T^2] \text{ versus } 1/T$$

Should be a straight line, the slope of which is equal to $-E/2.3R$. α in the above terms is the fraction of weight loss in the step and E is the energy of activation of the step. A linear regression of the values of the terms with n=0,1/2,2/3 and n=1 against 1/T was carried out. From the TG curves, the order n, activation energy E, and pre-exponential factor A, of the thermal decomposition were elucidated. In $[MnBd(PA)_2]_2$ complex the weight loss step from 275^0C-450^0C in the thermogram corresponds to a first order decomposition as indicated by the large correlation coefficient for the line involving n=1. For this step an energy of activation of $133 Jmol^{-1}$ has been calculated. Similar analysis of the weight loss step starting at 475^0C shows this step follows a zero order decay and an energy of activation of $46 Jmol^{-1}$.

3.7 Antimicrobial studies

The antimicrobial activity was carried out. The *in vitro* antibacterial screening effects of the synthesized compounds were tested against four bacterial strains namely, Salmonella typhi, Escherichia coli, Enterobacter, shigella,and fungi namely Asperginia and Rhizopus.SP by disk diffusion method, using nutrient agar medium.

Table. 4 Antimicrobial activity of the ligands and their Manganese(II) complexes
(Zone of inhibition in mm)

Compound	Antibacterial activity			
	Salmonella typhi	**Escherichia coli**	**Enterobacter**	**Shigella**
$Bd(PAH)_2$	16	12	11	13
$Mn_2\text{-}Bd(PA)_{2(}H_2O)_4$	27	18	19	18
$Bd(SAH)_2$	12	11	12	14
$Mn_2\text{-}Bd(SA)_{2(}H_2O)_4$	16	15	19	18
$Bd(MAH)_2$	12	11	15	9
$Mn_2\text{-}Bd(MA)_{2(}H_2O)_4$	16	15	17	14
$PPD(PAH)_2$	10	12	13	11
$Mn_2\text{-}PPD(PA)_{2(}H_2O)_4$	15	16	17	15
$PPD(SAH)_2$	10	15	17	12
$Mn_2\text{-}PPD(SA)_{2(}H_2O)_4$	26	19	20	18
$PPD(MAH)_2$	10	10	9	11
$Mn_2\text{-}PPD(MA)_{2(}H_2O)_4$	19	14	15	16

The solution with different concentration (20 mg/mL, 30 mg/mL, 40 mg/mL, 50 mg/mL) was prepared by dissolving the compounds in DMSO.

The well was made on agar medium, inoculated with microorganisms. To this well, the test solution was added and the Petri dishes were incubated for 24 hrs

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for bacteria and 48hrs for fungi. During this period, the test solutions are diffused and the growth of the inoculated microorganisms was affected. The inhibition zone was developed, at which the concentration was noted and measured in mm. Results were compared with standards namely streptomycin[38-39]against bacteria and nystatin for

fungi at the same concentration. All the complexes showed remarkable biological activity against bacteria and inactivity against Fungi. The results were presented in Table.4 and Fig. 6.

Fig.6 Antibacterial Activity for $Bd(SAH)_2$ and $Mn_2\text{-}Bd(SA)_{2(}H_2O)_4$

4. CONCLUSION

Consideration of the experimental data, along with the binucleating nature of the ligands employed in the present study inferred that the ligand binds the metal through the amide carbonyl oxygen and acid carbonyl oxygen. The electronic and fluorescence data supports the ligand to metal charge transfer. From the

thermal studies the ligand are thermally stable in the complexes. The complexes found to have a good antibacterial activity and inactive in antifungal property. The possible structure is proposed based on elemental and spectral data. The structure shown in Fig.7.
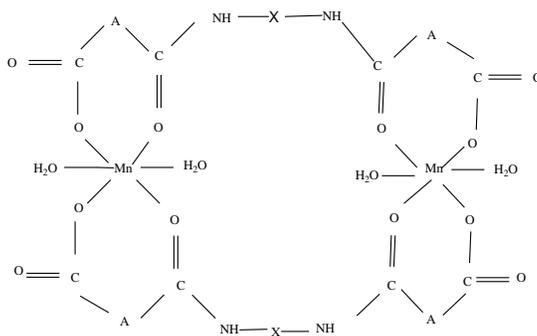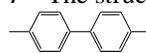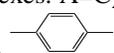

Fig. 7 – The structure of the Mn complexes: $A=C_2H_4$ or C_6H_4 or C_2H_2

X= ⬡⬡ for Bd complexes and ⬡ for PPD complexes

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