



## Manganese coordination compounds: synthesis, chemistry and applications

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### ABSTRACT

Coordination compounds have rich diversity which provide not only stimulating structural chemistry but also exciting therapeutic properties. This paper consists the literature survey on the coordination compounds of Mn(II) ion with different Schiff bases having bidentate nature. These coordination compounds have gained increasing attention in antimicrobial activities, and all the Manganese coordination compounds are hypothesized to exhibit higher activity against microbial agents than the corresponding ligands. In addition, the coordination compounds have been characterized on the basis of elemental analyses, molecular weight, molar conductance, spectral (IR, reflectance, <sup>1</sup>H NMR, ESR) and magnetic susceptibility measurements and their possible structures are discussed and outlined.

*Keywords: Coordination compounds, antimicrobial studies, Schiff base and spectral studies*

### INTRODUCTION

A metal complex or more accurately known as the coordination compound is the aggregate of Lewis acid (electron pair acceptor like central metal atom or metal ion) and Lewis base(s) (electron pair donor).

Major emphasis on the syntheses, structural characterization and the applications of the coordination compounds has been given in the last few decades. A perusal of the Literature reveals that the coordination compounds have found versatile uses in our life as antiinflammatory,<sup>1</sup> scavenging,<sup>2</sup> analgesic,<sup>3</sup> antibiotic,<sup>4</sup> antioxidative,<sup>5,6</sup> antifungal,<sup>7-12</sup> antibacterial,<sup>13-20</sup> antiviral,<sup>21</sup> antifertility,<sup>22</sup> enzymatic,<sup>23</sup> antitoxic against insects,<sup>24</sup> antiulcer,<sup>25</sup> anti-HIV,<sup>26</sup> antituberculosis,<sup>27</sup> antitumor,<sup>28-33</sup> and stimulating agents towards the central and peripheral nervous systems,<sup>34</sup> in resin and polymer industries,<sup>35,36</sup> coating materials,<sup>37</sup> initiators of emulsion polymerization and copolymerization of diene and vinyl monomers,<sup>38</sup> as catalysts in polymerization, oxidation, decomposition, hydrolysis and electro-reduction,<sup>39-44</sup> heat resisting fibers and foams,<sup>45</sup> antidegradants for rubber,<sup>46</sup> for increasing the weather-resistance of polymers,<sup>47</sup> heat resistant adhesives,<sup>48</sup> hardner for polymers,<sup>49</sup> electric insulating materials,<sup>50</sup> corrosion

inhibitors,<sup>51</sup> dyeing and pigment industries,<sup>52</sup> pigments,<sup>53,54</sup> photoconducting polymers,<sup>55,56</sup> electrophotographic materials,<sup>57</sup> photographic developers,<sup>58</sup> detergents in lubricating oils,<sup>59</sup> ashless detergents in lubricating oils,<sup>60</sup> plant growth regulators,<sup>61-63</sup> for transport and storage of oxygen,<sup>64,65</sup> as models for molecules to absorb and release molecular oxygen reversibly similar to natural oxygen carriers like hemoglobin, hemocyanin and non-heme proteins<sup>66-68</sup> etc.

### COORDINATION COMPOUNDS OF MANGANESE(II) IONS

The ability of Mn(II) ions to form the coordination compounds with a wide range of ligands has been reported. These ligands are coordinated to Mn(II) ions in a mono-, bi-, tri-, tetra-, penta- and hexadentate fashions. We present here a brief survey of the Chemistry of coordination compounds of Mn(II) ions in which ligands are coordinated to Mn(II) ions in a bidentate manner.

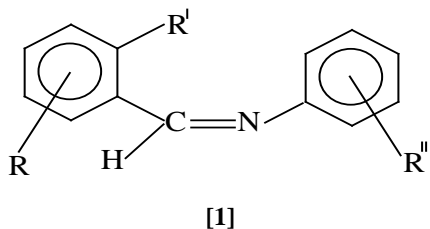
A reddish-brown, non-electrolyte ( $\Lambda_M = 10.5 \text{ mho cm}^2 \text{ mol}^{-1}$ ), four-coordinate compound,  $[\text{Mn}(\text{OAc})\text{L}(\text{H}_2\text{O})]$  (where  $\text{LH} = \mathbf{1}$ ;  $\text{R} = 3\text{-OMe}$ ,  $\text{R}' = \text{OH}$ ,  $\text{R}'' = \text{H}$ ) is obtained<sup>69</sup> by refluxing a mixture of an EtOH solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and a DMF solution of LH in 1:1 molar ratio for 4 h. The compound decomposes at 260 °C. It is soluble in DMF and DMSO. LH behaves as a monobasic bidentate ON donor ligand coordinating through its phenolic O and azomethine N atoms. The acetato ligand is coordinated in a monodentate fashion. The  $\nu(\text{Mn}-\text{O})$  and the  $\nu(\text{Mn}-\text{N})$  vibrations occur at 510 and 435  $\text{cm}^{-1}$ , respectively. The effective magnetic moment of the compound is 5.94 B.M.

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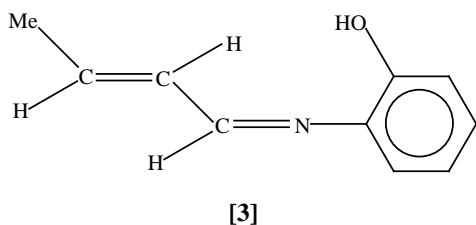
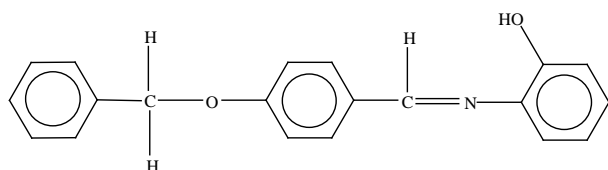
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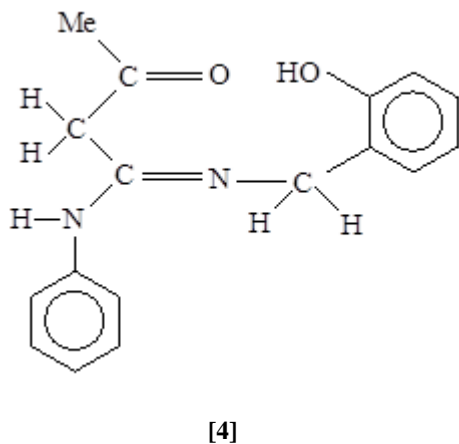


Howalader *et al.*<sup>70</sup> have synthesized a six-coordinate, orange-yellow compound,  $[\text{MnL}_2(\text{H}_2\text{O})_2]$  and another brown compound,  $[\text{MnL}'_2(\text{H}_2\text{O})_2]$  (here LH and L'H = **2** and **3**, respectively) by template method. The compounds melt at 180 and 200 °C, respectively. The appearance of two bands one at 16667, 16393  $\text{cm}^{-1}$  and another at 20704, 20000  $\text{cm}^{-1}$ , respectively and the

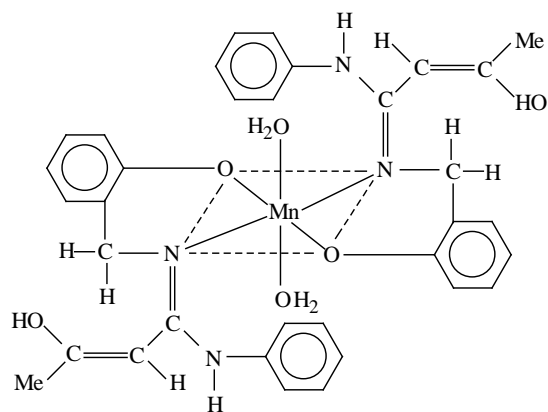


values of effective magnetic moments (5.94 and 5.78 B.M., respectively), correspond to high-spin octahedral symmetries of the compounds. The compounds are more active against *S. dysenteria*, *E. coli*, *P. aeruginosa*, *B. subtilis*, *S. lutea* and *S. aureus* than 2-aminophenol.

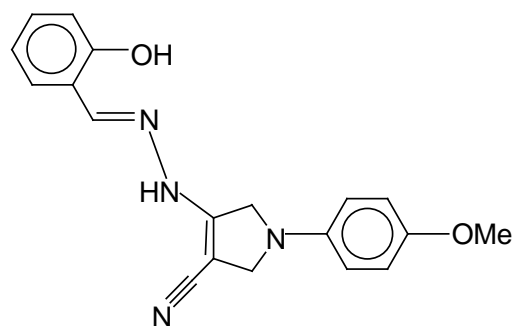
The synthesis of six-coordinate  $[\text{Mn}(\text{LH}_2)_2(\text{H}_2\text{O})_2]$  here  $\text{LH}_3 = \mathbf{4}$  has been reported<sup>71</sup>.  $\text{LH}_3$  acts as a monobasic bidentate ON donor ligand coordinating through its phenolic O and azomethine N atoms. The compound exhibit three absorption bands at 15500, 19250 and 24500  $\text{cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)(v_1)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(v_2)$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(v_3)$  transitions, respectively for octahedral



geometry. The effective magnetic moments of the compound is 5.90 BM. An octahedral structure(**5**) has been suggested for the compound.

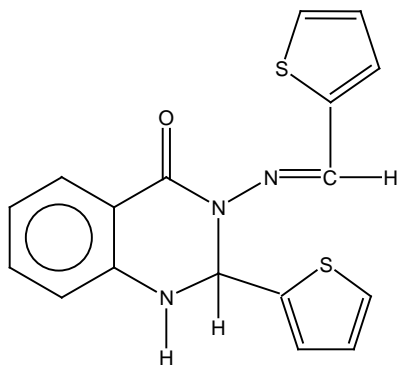


An air-stable, dimeric, six-coordinate, non-electrolyte ( $\Lambda_M = 15$  mho  $\text{cm}^2 \text{mol}^{-1}$  in DMF),  $[\text{Mn}_2(\text{OAc})_4(\text{LH}_2)(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  (where  $\text{LH}_2 = \mathbf{6}$ ) is obtained by refluxing an ETOH solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{LH}_2$  in 1:2 molar ratio<sup>72</sup>. The compound is



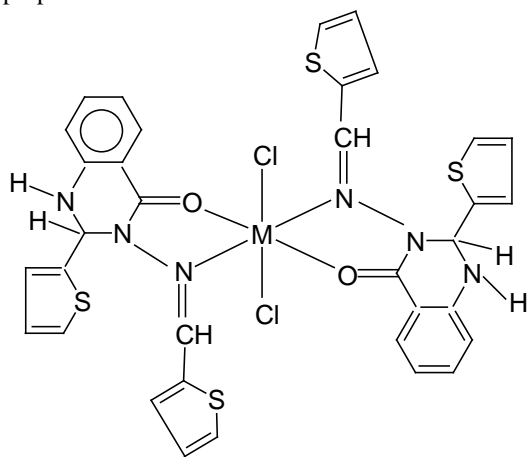
soluble in DMF and DMSO, but insoluble in water, EtOH and benzene. Although,  $\text{LH}_2$  is potentially a dibasic tetradentate ONNN donor ligand, but has been reported to act as neutral bidentate ON donor ligand to one of the Mn(II) ion and as a neutral bidentate NN donor ligand to another Mn(II) ion. The compound displays a band between 15384-16000  $\text{cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition which indicates its high-spin octahedral geometry. The lower value of effective magnetic moment (4.87 B.M.) of the compound indicates the presence of anti-ferromagnetic exchange between Mn(II) ions. The coordinated water molecules and acetato groups are lost at 125 °C and 281 °C, respectively. The compound shows strong inhibitory action against *B. subtilis*, *S. aureus*, *E. coli*, *A. faecalis*, *C. albicans* and *A. niger*.

A six-coordinate, non-electrolyte ( $\Lambda_M = 2.1$  mho  $\text{cm}^2 \text{mol}^{-1}$  in DMSO),  $[\text{MnCl}_2(\text{LH})_2]$  (where  $\text{LH} = \mathbf{7}$ ) is obtained<sup>73</sup> by refluxing a MeOH solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{LH}$  in 1:2 molar ratio for 1.5 h. The compound is soluble in MeOH, EtOH and DMSO, but insoluble in  $\text{Me}_2\text{CO}$ .  $\text{LH}$  acts as a neutral bidentate ON donor ligand coordinating through its carbonyl O and azomethine



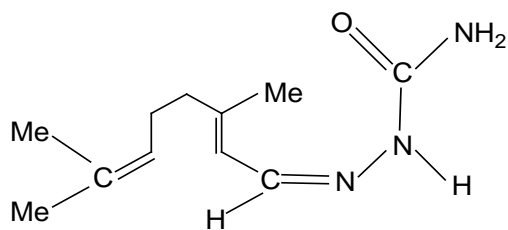
[7]

N atoms. The effective magnetic moment of the compound is 5.86 B.M. An octahedral structure (**8**, M = Mn) has been proposed.



[8]

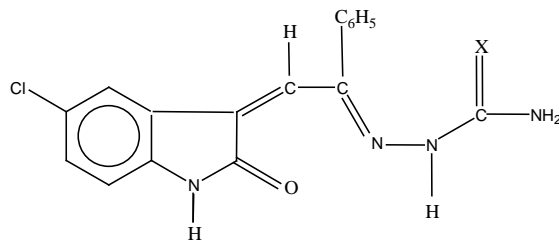
Sharma *et al.*<sup>74</sup> have synthesized a brown, air-stable, non-hygroscopic, six-coordinate, non-electrolyte ( $\Lambda_M = 1.87 \text{ mho cm}^2 \text{ mol}^{-1}$  in DMF),  $[\text{MnCl}_2(\text{LH})_2]$  (where LH = **9**) by refluxing an EtOH solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and LH in 1:2 molar ratio for 6-8 h. The compound is readily soluble in DMSO and DMF, but insoluble in water. LH acts as a neutral bidentate ON donor ligand coordinating through its carbonyl O and azomethine N atoms. The compound displays four bands at 18200, 24800, 29700, 31900  $\text{cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)(v_1)$ ,  ${}^6A_{1g} \rightarrow {}^4E_g ({}^4G)(v_2)$ ,  ${}^6A_{1g} \rightarrow {}^4E_g ({}^4D)(v_3)$  and  ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4P)(v_4)$  transitions, respectively. The effective magnetic moment of the



[9]

compound is 5.87 B.M. The compound shows strong inhibitory action against *S. aureus* and *E. coli*.

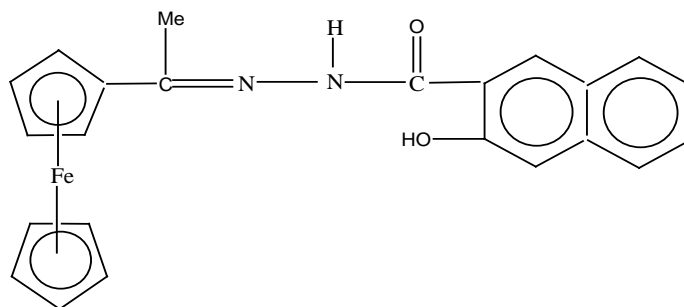
Garg *et al.*<sup>75</sup> have synthesized two yellow coloured, four-coordinate, monomeric, non-electrolytes ( $\Lambda_M = 10\text{-}15 \text{ mho cm}^2 \text{ mol}^{-1}$ ),  $[\text{MnCl}(\text{H}_2\text{O})]$  and  $[\text{MnL}_2]$  (here LH = **10**; X = O, S) by refluxing  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and LH in 1:1 and 1:2 molar ratios, respectively for 10-12 h in dry MeOH. The compounds are soluble



[10]

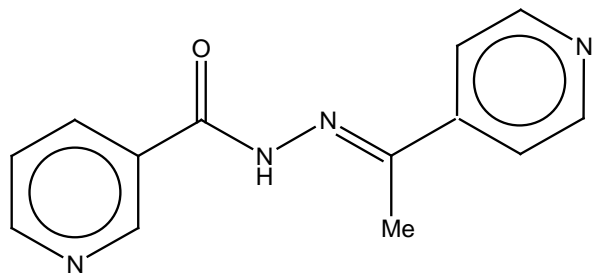
in MeOH, DMF, DMSO and THF. Their effective magnetic moments are 5.85 and 6.13 B.M., respectively, suggesting a high-spin state in these compounds. LH acts as a monobasic bidentate ON or SN donor ligand in the respective coordination compound coordinating through its enolic O or thioenolic S and azomethine N atoms. The *g* values for the compounds lie between 1.933-1.987, suggesting a tetrahedral geometry for them. The compounds have fungitoxic nature which is increased due to the direct attachment of halogen atom to metal in  $[\text{MnCl}(\text{H}_2\text{O})]$ . The ligand containing sulphur and its coordination compounds are more active against fungi and bacteria than their oxygen analogues.

A brown coloured, four-coordinate, weak electrolyte ( $\Lambda_M = 23.3 \text{ mho cm}^2 \text{ mol}^{-1}$  in DMF),  $[\text{Mn}(\text{LH}_2)_2] \cdot 2\text{H}_2\text{O}$  (where  $\text{LH}_2 = \mathbf{11}$ ) is obtained<sup>76</sup> by refluxing an EtOH solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{LH}_2$  in 1:2 molar ratio for 6 h. The compound decomposes at 288 °C. It dissolves in DMF and DMSO.  $\text{LH}_2$  acts as a monobasic bidentate ON donor ligand coordinating through its enolic O and azomethine N atoms.



[11]

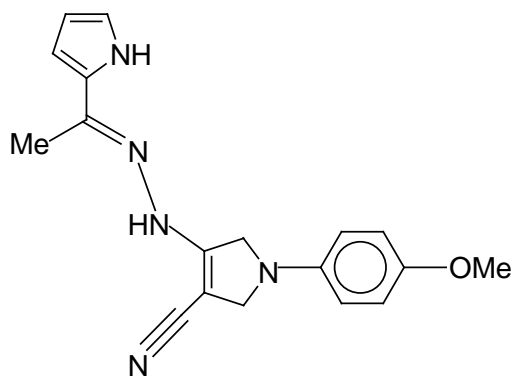
Hosny *et al.*<sup>77</sup> have synthesized a yellow coloured, air-stable, 1:2 electrolyte ( $\Lambda_M = 170 \text{ mho cm}^2 \text{ mol}^{-1}$ ),  $[\text{Mn}(\text{LH})(\text{H}_2\text{O})_2]\text{Cl}_2$  (where LH = **12**) by refluxing an EtOH solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and LH in 1:1 molar ratio for 2 h. The compound is soluble in water, DMF and DMSO. It melts at  $> 300 \text{ }^\circ\text{C}$ .



[12]

The chlorine molecules are lost between 345-437 °C. LH acts as a neutral bidentate ON donor ligand coordinating through its enolic O and azomethine N atoms. The compound displays three bands at 20408, 24390 and 29585  $\text{cm}^{-1}$  due to the  ${}^6A_1 \rightarrow {}^4T_1(G)$ ,  ${}^6A_1 \rightarrow {}^4T_2(G)$  and  ${}^6A_1 \rightarrow {}^4E$  transitions, indicating its tetrahedral geometry. The effective magnetic moment of the compound is 5.87 B.M.

An air-stable, dimeric, six-coordinate, non-electrolyte ( $\Lambda_M = 18 \text{ mho cm}^2 \text{ mol}^{-1}$  in DMF),  $[\text{Mn}_2(\text{OAc})_4(\text{LH}_2)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  (where  $\text{LH}_2 = \mathbf{13}$ ) has been obtained<sup>72</sup> by refluxing an EtOH solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{LH}_2$  in 1:2 molar ratio. The compound is soluble in DMF and DMSO, but insoluble in water, EtOH and  $\text{C}_6\text{H}_6$ . Although,  $\text{LH}_2$  is potentially a dibasic tetradentate NNNN donor ligand, but has been reported to act as neutral bidentate NN donor ligand to both the Mn(II) ions. The compound displays a band between 15384-16000  $\text{cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition which indicates its high-spin octahedral geometry. The lower value of effective magnetic moment (4.98



[13]

B.M.) of the compound is due to the presence of anti-ferromagnetic exchange between Mn(II) ions. The coordinated water molecules and acetate groups are lost at 126 °C and 325 °C, respectively. The compound shows strong inhibitory action against *B. subtilis*, *S. aureus*, *E. coli*, *A. faecalis*, *C. albicans* and *A. niger*.

## CONCLUSION

The synthesized ligands and their coordination compounds have been studied on the basis of their elemental analyses, molecular weight, molar conductance, spectral (IR, reflectance,  ${}^1\text{H}$  NMR, ESR) and magnetic susceptibility measurements. The antimicrobial studies suggest that all the coordination compounds show significant enhanced antimicrobial activities as compared to

the ligand. Some of the synthesized coordination compounds, have been found superior than the others in inhibiting the growth of bacteria, therefore, they may be used as antibacterial agents in pharmaceutical industry for mankind, after testing their cytotoxicity to human beings.

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