PREPARATION, SPECTRAL CHARACTERIZATION, THERMAL STABILITY AND BIOLOGICAL ACTIVITIES OF Mn (II) COMPLEX WITH 2- AMINOBENZONITRILE AND OCTANOATE

R. Govindharaju1, S. Balasubramaniyan1, L. Palanivelan1, K. Rajasekar1
& T. Ramachandramoorthy2

1Department of Chemistry, Govt. Arts College, Ariyalur-621 713, Tamil Nadu, India.
2PG & Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli- 620 017, Tamil Nadu, India.

ABSTRACT
Metal complex of Mn(II) with 2-aminobenzonitrile (ABN) and octanoate ion ligand was synthesized by using microwave irradiation and characterized by the elemental analysis, metal estimation, molar conductance, UV-Visible , IR and Far-IR spectra, non-electrolyte behaviour and monomeric nature of the complex asse from their low molar conductance value. The IR and UV-visible spectra suggest that the complex has Distorted octahedral geometry. The thermo gravimetric analysis of the complex shows the thermal stability of them. The antibacterial and antifungal activities of ligands 2-aminobenzonitrile and sodium octanoate and Mn(II) complex were studied against the following strains of microorganisms E-coli, Enterobacter, Klebsiella, Staphylococcus aureus, Streptococci, Salmonella typhi, P.aeruginosa, C. albicance, Aspergillus Flavus and Aspergillus niger by disc diffusion method. Mn(II) complex show enhanced activity compared with that of free ligand for Klebsiella, Streptococci and P.aeruginosa, organisms at 100µg/ml and at 50µg/ml.

KEY WORDS: Mn(II) complex, ABN, Octanoate, Antibacterial, Antifungal.

INTRODUCTION
Metal complexes have been receiving considerable attention for many years due to their interesting characteristics in the field of material science and biological system. On the other
hand aromatic nitriles have a wide range of applications in pharmaceuticals, pesticides and dye industries.\textsuperscript{[1-4]} Aromatic nitriles are useful in the manufacturing of protection coating, moulding resins, antioxidants and optical brighteners. In recent years, there has been increasing interest in synthesis of heterocyclic compounds by using nitriles that have biological and commercial importance. Microwaves are a form of electromagnetic radiation that is very similar to sun light and radio waves.\textsuperscript{[5-6]} Microwave irradiation having some advantage over the conventional heating viz., uniform heating, purity in final product, low operating cost, etc.,\textsuperscript{[7-8]} In this paper, we have described the microwave assisted synthesis, physico-chemical characterization, thermal stability and biological significance of Mn(II) complex with 2-aminobenzonitrile and octanoate ligands. The structure of the complex supported by micro analytical, spectral studies. The antimicrobial activities of the complex have also been evaluated.

**MATERIALS AND METHODS**

2-aminobenzonitrile and sodium octanoate were purchased from Sigma Aldrich. Manganese nitrate, DMSO, DMF, methanol, ethanol were of AnalaR grade, and used as such without further purification.

**INSTRUMENTS**

The elemental analysis of the complexes was carried out by using (Thermo Finnegan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The electrical conductivity measurements were conducted using $10^{-3}$ solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge 304 at 30°C. The UV-Visible spectra of Mn(II) complexes were recorded on Varian, Cary 5000 model UV Spectrophotometer. The IR spectra of the complexes were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in 4000-400 cm$^{-1}$ range with KBr pellet technique. The Far-IR Spectrum of the complexes was recorded by Bruker 3000, FT-IR Spectrometer. The TGA/DTA analysis of the complex was recorded on Perkin Elmer, Diamond TG/DTA instruments. The antimicrobial and antifungal studies of ligands 2-aminobenzonitrile, octanoate and its complexes were done by disc diffusion method.

**PREPARATION OF COMPLEXES**

(I) Preparation of Mn(II) Complex

0.91g (7.38 mmol) of ABN in ethanol and 1.33g (8.01 mmol) of sodium octanoate in ethanol to the manganese nitrate 1.00g (3.64 mmol) in methanol followed by microwave irradiation
for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The precipitated complex is pale yellow in colour with the yield were of 54.50%.

RESULTS AND DISCUSSION

Analytical Data
The elemental analysis and metal estimation indicates the stoichiometry of the complex. The complex is soluble in DMSO and DMF. It is pale yellow in colour. From the elemental analysis, metal estimation and molar conductance values are predicted that the complex may have the following stoichiometry \([\text{Mn(ABN)}_2(\text{OC})_2]\).

Electrical Conductance
The metal complex was dissolved in acetonitrile and the molar conductance of their \(10^{-3}\) solutions was measured at 30\(^\circ\)C. The low electrical conductance (71.58 ohm\(^{-1}\)cm\(^2\)mol\(^{-1}\)) value of the metal complex indicate that non-electrolyte nature (1:0 type electrolyte).\(^{[9]}\)

Table-1 Analytical and EC Values of the Complex

<table>
<thead>
<tr>
<th>Complex</th>
<th>EC (ohm(^{-1})cm(^2)mol(^{-1}))</th>
<th>%H</th>
<th>%C</th>
<th>%N</th>
<th>%M</th>
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<tr>
<td>([\text{Mn(ABN)}_2(\text{OC})_2])</td>
<td>71.58</td>
<td>7.32</td>
<td>62.38</td>
<td>9.69</td>
<td>9.51</td>
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IR Spectra
In the IR spectrum of free 2-aminobenzonitrile exhibit strong bands at 3453cm\(^{-1}\) and 3366 cm\(^{-1}\) respectively, indicating the asymmetric and symmetric stretching frequencies of NH\(_2\) group. These bands are broadened in the complex (3367cm\(^{-1}\)) which indicates the amino nitrogen atom as one of the coordinating groups. The \(v\) (C≡N) stretching frequency at 2206 cm\(^{-1}\) in free ABN gets shifted to higher wave numbers, 2212 cm\(^{-1}\) in complex which indicate that the nitrogen atom of the (-C≡N) is another coordinating group to the metal ions. In free octanoate the \(v\) (C=O) stretching at 1409 cm\(^{-1}\) get shifted to the higher frequencies 1454 cm\(^{-1}\) in complex which indicate the monodentate coordination of the octanoate ion through oxygen atom. All above observations confirmed the entry of both 2- aminobenzonitrile and octanoate ion in to the coordination sphere of the metal ions.\(^{[10-11]}\)
Fig. 1 IR spectra of ABN, Octanoate and [Mn(ABN)$_2$(OC)$_2$]

Far-IR Spectrum
From far-IR spectrum, the metal-ligating atom linkage may be assigned. In Mn(II) complex, the bands at 230 cm$^{-1}$, 510 cm$^{-1}$ and 455 cm$^{-1}$ correspond to δ(M-CN), δ(M-N) and δ(M-O) coordination respectively which indicates the bidentate nature of 2-aminobenzonitrile and the monodentate nature of octanoate ion.$^{[12]}$

Fig. 2 Far-IR spectrum of Mn(II) complex

UV-Visible spectrum of Mn(II) complex
The d$^5$ configuration of Mn(II) complex have the ground state term symbol is $^6$S, $\Delta_O$ for Mn(II) is 7500 cm$^{-1}$. The distorted octahedral Mn(II) complex show three transition at 38461 cm$^{-1}$ ($^4$A$_{2g}$ (F)) 31250 cm$^{-1}$ ($^4$E$_g$ (D) ) and 17241 cm$^{-1}$ ($^4$A$_{2g}$ ) lowest energy C-T band (n-$\pi^*$).$^{[13]}$
Thermo gravimetric (TG) and differential thermal (DTA) analysis used to describe the thermal behaviour of the Mn(II) complex. The TGA curve showed four mass loss steps. The first step occurred in the temperature range 89-187°C, the second step occurred in the temperature range 187-361°C, the third step between 361-420°C and the last step occurred in 420-470°C. The DTA curve showed Endothermic peaks at 420°C. [14]

Antimicrobial Activity
The antibacterial and antifungal activities of the compounds 2-aminobenzonitrile, sodium octanoate and the Mn(II) complex were determined by disc diffusion method using following microorganisms viz., E.coli, Enterobacter, Klebsiella, Staphylococcus aureus, Streptococci, Salmonella typhi, P.aeruginosa, C.albicans, Aspergillus Flavus and Aspergillus niger. The complex has potent active as compared to the free ligands at various concentrations for all the tested microorganisms except Klebsiella, Streptococci, and P.aeruginosa such increase in activity may be due to the nature of ligands and structure of the complexes. [15-16]
CONCLUSION
In this paper, the microwave assisted synthesis of 2-aminobenzonitrile and octanoate ion complex of Mn(II) is given. The structural feature of the complex is confirmed by elemental analysis, metal estimation, electrical conductivity and spectral studies. The complex is thermally stable and non-electrolyte and the antibacterial and antifungal activities of the complex is slightly higher than those of the free ligands viz., 2-aminobenzonitrile and octanoate.

ACKNOWLEDGEMENT
The authors thank the Principal, Government Arts College, Ariyalur for the facilities provided to carry out the work; they also thank to the Head and Staff members of STIC, Cochin, SAIF Mumbai and Chennai and St. Joseph’s College, Tiruchirappalli for providing instrumental data.
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