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Microwave synthesis of Tris-(1,10-phenanthroline)Manganese(II) complex and its electrochemical sensing property of catechol

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Abstract: Tris-1,10-phenanthroline manganese(II) complex was synthesized by microwave irradiation. The synthesized complex was characterized by UV-visible and FT-IR spectroscopy. Its electrochemical behaviour was examined by cyclic voltammetry (CV). The tris-1,10-phenanthroline manganese(II) complex was used for the electrochemical sensing of catechol. The manganese ion gets reduced as the oxidation of catechol proceeds, in this process the hydroxyl group is converted to keto group. This redox behaviour was the reason for electrochemical sensing of catechol by the tris-1,10-phenanthroline manganese(II) complex modified glassy carbon electrode. This GCE is having good sensing capability when compared with bare GCE electrode.
Key words: 1,10-phenanthroline, Manganese, electrochemical sensing, catechol.

1. Introduction & Experimental:

The transition-metal complexes with organic ligands like Schiff base, 1,10-phenthroline(Phen), bipyridine etc., has been developed in last decades. The transition metal complexes with Phen show good chemical and physical properties, due to its fascinating p-conjugated character and strong chelating abilities. The ternary complexes of Phen with transition metal is having considerable interest in the antifungal, anti-mycoplasma, antiviral and good redox behaviour[1].The manganese(II)complex was synthesized by microwave irradiation in this work. There are several methods for the deduction of phenolic compounds, including gas chromatography and spectrophotometry, but in the electrochemical sensing method we can detection nano molar level. The manganese ion gets reduced as the oxidation of catechol proceeds, in this process the hydroxyl group is converted to keto group. This redox behaviour was the reason for electrochemical sensing of catechol by the tris(1,10-phenanthroline) manganese(II) complex modified GCE[2].

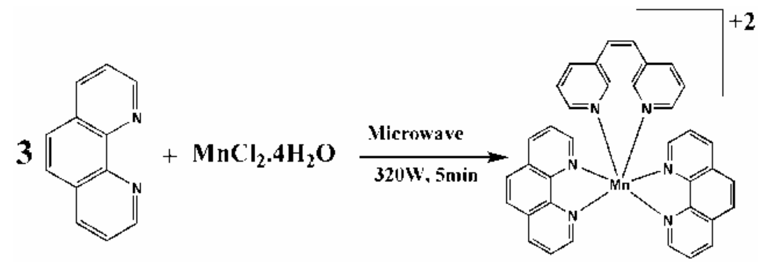
Reagents and apparatus:

1,10-phenanthroline,Manganese chloride tetrahydrate [MnCl2.4H_2O]and catechol were Purchased from AlfaAesar. The solvents and reagents were obtained commercially and were used without further purification. IR spectra were recorded on a PerkinElmer FT-IR 8300, Electronic spectral studies were carried out on a

PerkinElmer 320 spectrophotometer, and cyclic voltammograms were obtained on a CHI-1103A electrochemical analyzer using a three-electrode cell in which a bare and modified GCE were the working electrode.

Synthesis of tris(1,10-phenanthroline)manganese(III)complex:

An absolute methanol solution of 1,10-phenanthroline(0.541 g,3 mmol) was added drop wise with the stirred methanol solution of manganese chloride salt($MnCl_2.4H_2O$, 0.198g, 1 mmol) pale yellow color solution was obtained. It was stirred about 30 min. The solution was kept in microwave for 5min, 320W. On cooling to room temperature a pale yellow colour precipitate was obtained. The precipitate was filter and washed with hexane, it was recrystallized by methanol.



Scheme-1

2. Results and Discussion:

2.1. FT-IR analysis & Electronic spectral analysis

FT-IR spectrum of tris(1,10-phenanthroline) manganese(II) complex was shown in **Fig-1a.**The stretching frequency of C=N in complex appeared at 1601 cm^{-1} [3]. In the IR spectrum a strong band at the 1522cm^{-1} is due to the presence of aromatic C=C. Medium intensity band appearing in the region 3430 cm^{-1}corresponds to aromatic C – C. A band exhibits at 627 cm^{-1} shows the Mn-N binding frequency.

In the electronic spectra of $[Mn(C_{12}H_8N_2)_3]^{+2}$ complex (**Fig-1b),** the band at 275 nm is due to the n→π* transition in Phen (C=N) and shoulder around 404nm due to d-d transition of the central metal ion. The peak at 310nm is due to the π→π* transition of (C=N) in Phen. [4].

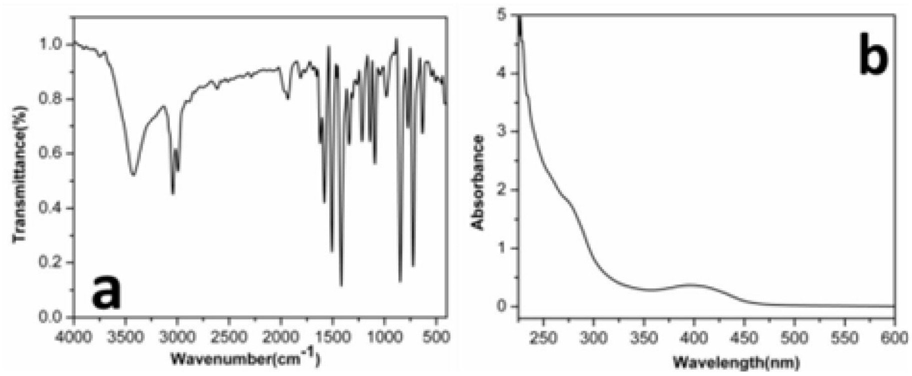


Fig. 1: **(a) FT-IR Spectrum $[Mn(C_{12}H_8N_2)_3]^{+2}$; (b) Electronic Spectrum of $[Mn(C_{12}H_8N_2)_3]^{+2}$.**

2.2. Electrochemistry of tris(1,10-phenanthroline)manganese(III)complex

The electrochemical behavior of tris(1,10-phenanthroline)manganese(II) complex was studied in acetonitrile containing 0.1 M TBAP at a glassy carbon working electrode, The cyclic voltammogram was shown in **Fig-2a.** It gives a broad oxidation peak around 0.58V but this complex shows two reduction peaks, it shows that the Mn(II)/Mn(V) one step oxidation and it will reduced at Mn(V)/Mn(III) one step then Mn(III)/Mn(II) another step. The electrochemical polymerization of $[Mn(C_{12}H_8N_2)_3]^{+2}$ shown in **Fig-2b**, the GCE was modified by electrochemical polymerization method for the sensing of catechol.

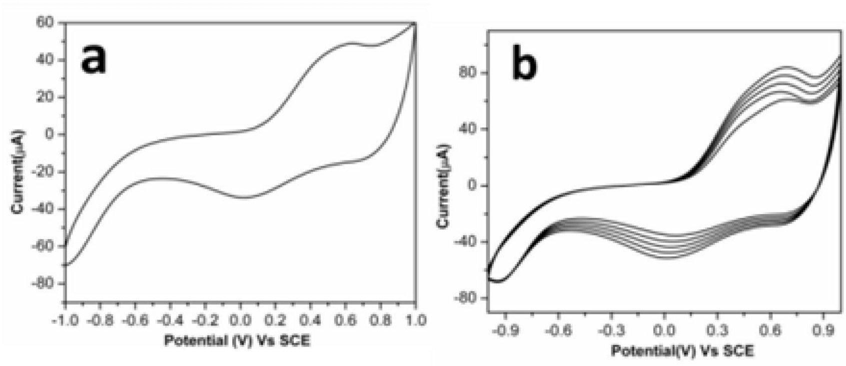


Fig. 2: (a)Cyclic voltammogram of $[Mn(C_{12}H_8N_2)_3]^{+2}$; (b) Electrochemical polymerization of $[Mn(C_{12}H_8N_2)_3]^{+2}$ at the scan rate of 50 mVs^{-1} in acetonitrile containing 0.1 M TBAP.

2.3. Electrochemical sensing of catechol

The **Fig-3a** shows shift in potential and enhanced peak current for the modified electrode when compared with the bare GCE. It explains the electrocatalytic sensing ability of the modified electrode. This electrocatalytic effect was enhancing due to the electron accepting nature of the central metal ion in the metal complexes on the modified GCE. Fig.3b shows differential pulse voltammograms of Catechol, 1μM to 150 μM under optimized experimental conditions. It clear that the tris(1,10-phenanthroline)mangasese(II) modified GCE can be successfully used for the electrochemical sensing of Catechol [5,6].

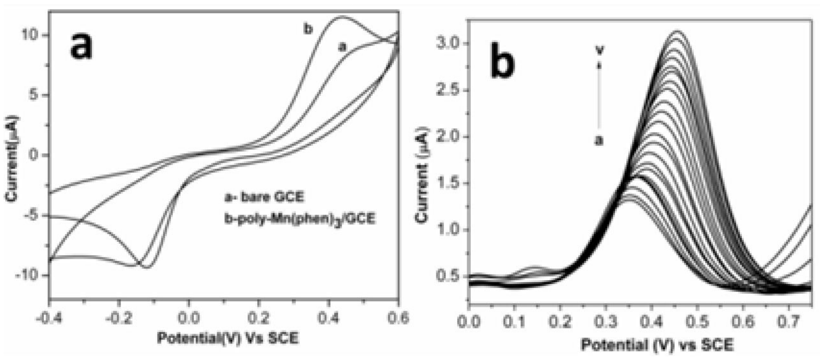


Fig.3: (a)Cyclic voltammetric response of 1 mM catechol at (a) bare GCE &(b) Modified GCE, and (b) DPV measurement of catechol.

3. Conclusion:

The tris(1,10-phenanthroline)manganese(II) complex was synthesized by microwave irradiation method and their coordination chemistry and electrochemical sensing property have been investigated by UV-visible, FT-IR spectroscopy techniques and CV. The synthesized manganese complex was used to modify GCE by electropolymerisation method for the sensing of catechol. From the electrochemical sensing experiment, it can be concluded that the tris(1,10-phenanthroline)manganese(II) complex has good sensing activity towards the catechol. Hence, the GCE modified with manganese (II) complex will be a good sensor for catechol.

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