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Spectral and cyclic voltammetry studies of chloro-salicyliden aniline and some of its complexes with Co(II) and Mn(II)

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Abstract. The qualitative information about the interaction between 2-[[p-chlorophenylimino]methyl]phenol as attracting chelating Schiff base ligand (HL) with cobalt(II) and manganese(II) ions have been discussed by using the data of spectroscopy (IR, UV-Visible) and ¹H NMR resonance techniques. The electrochemical properties of these species have been carried out by using cyclic voltammetry studies to see the differences in the potential and activity behavior during and after the electron transfer process. The cyclic voltammetry behavior of ligand exhibited an irreversible one-electron transfer and redox diffusion-controlled process due to the linearity relationship between redox peaks current and square root of scan rates. The cyclic sweep for CoL and CoL₂ complexes appeared two irreversible oxidation peaks but with different values and positions, while the cyclic sweep of MnL and MnL₂ complexes appeared several redox peaks, which related to the formation of various manganese redox species. All complexes had a deviation of current and potential to more anodic values when the cyclic sweep was applied at different scan rates. A positive shift was observed for CoL₂ and MnL₂ complexes may be to the electron-donating and electron-withdrawing properties of phenyl substituted group.

Keywords. Schiff base, Bidentate salicylaldimine ligand, Neutral bidentate ligand, Cobalt (II) complex, Manganese (II) complex, Cyclic voltammetry

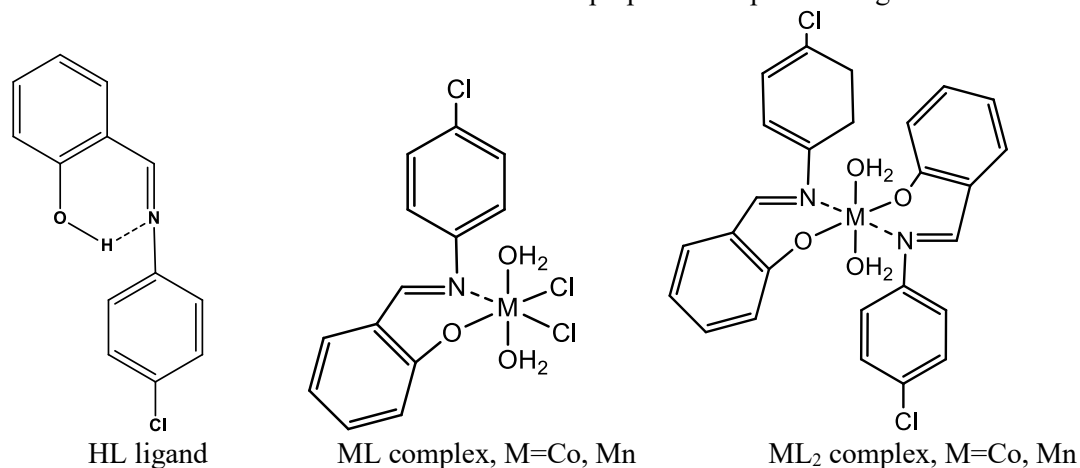
1. Introduction

Schiff bases as attracting chelating ligands with various transition metal ions were widely developed in coordination chemistry for their easy synthesis, moderate stability, diverse oxidation-reduction conditions, biological activities and other extensive applications [1, 2, 3, 4, 5, 6, 7, 8], and due to their containing of donor atoms like nitrogen and oxygen, they have been used as specific catalysts for oxidation, reduction, and other electronic transformations process in different organic and inorganic reactions [9, 10, 11]. Schiff base complexes of cobalt and manganese ions have been reported as effective complexes in many electrocatalytic processes due to the ability of their metal center for reduction to different oxidation states [12, 13, 14]. Moreover, the possible reduction of the ligand is useful to reduce the catalyst or abandon it in certain cases [15].

In the present study, chloro-salicyliden aniline Schiff base and its complexes with Co(II) and Mn(II) have been synthesized and their structures were determined using the ¹H NMR method and characterized with spectroscopic techniques. The ligands' electrochemical and their complexes are being



by the cyclic voltammetry method by using DY 2300 series Potentiostat/ Bipotentiostat, which gave good information about the effect of electron-withdrawing and electron-donating groups on the electrical properties. The structures of Schiff base molecule and the prepared complexes are given in Scheme 1.



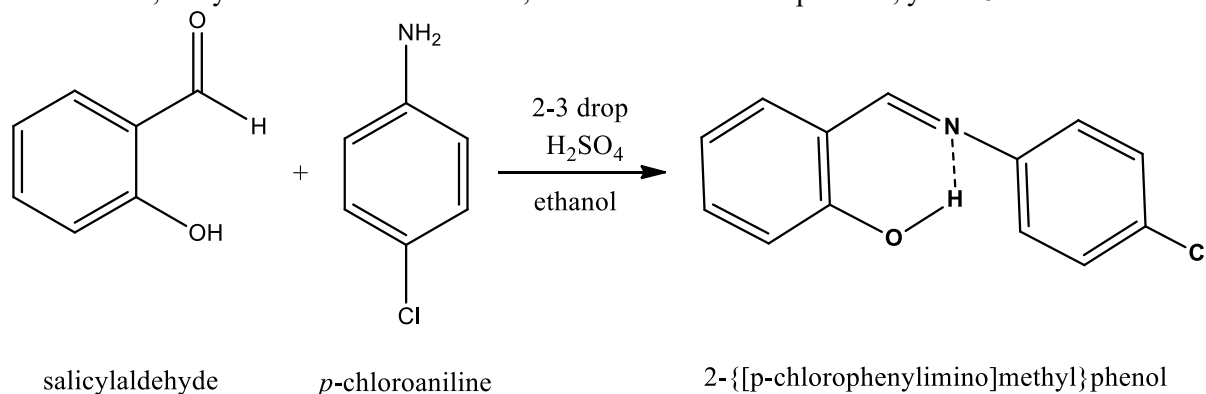
Scheme 1. The structures of Schiff base molecule and complexes.

2. Materials and Methods

The used chemicals and solvents were of analytical reagent grade and were supplied by Merck and BDH companies and used without further purification.

2.1. Ligand preparation

The Schiff base $C_{13}H_{10}NOCl$; HL ligand is prepared according to a previous procedure [16, 17], by dissolving 1.1 g; (1 mmol) of salicylaldehyde in 10 ml of ethanol and adding an equimolar quantity of *p*-chloroaniline to the ethanolic solution, magnetically stirring with adding of 2-3 drops of concentrated sulfuric acid, refluxing for 2 h and left overnight at room temperature. The product was filtered, washed with ethanol, recrystallized with hot ethanol, and dried at room temperature, yield: 82%.



Scheme 2.

2.2. CoL and CoL₂ complexes preparation

The cobalt complexes were prepared according to a previous procedure [18], by drop-wise addition of a hot solution of 1mmol of $Co(Ac)_2 \cdot 4H_2O$ in 10 ml of ethanol with stirring to a hot solution of 1 and 2 mmol of Schiff base ligand and refluxed on a water bath for 2 h. The product complexes were cooled, washed with ethanol and diethyl ether and dried overnight at 50 °C, yield: 66%, 56%, respectively.

2.3. MnL and MnL₂ complexes preparation

In the identical procedure [19], by drop-wise addition of a hot solution of 1 mmol of $MnCl_2 \cdot H_2O$ in 10 ml of ethanol with stirring to a hot solution of (1 and 2 mmol) of Schiff base ligand. The mixture was

refluxed on a water bath for 2 h, then 2 mmol of sodium acetate was added and the reflux was continued for 2 h. The obtained MnL and MnL_2 complexes were filtered, washed with ethanol and diethyl ether, and dried in vacuum at room temperature, yield: 52%, 49%, respectively.

2.4. Cyclic voltammetry

The electrochemical behavior of ligand and metal complexes was investigated by cyclic voltammetry for 10^{-3} M of a compound in acetonitrile containing 0.1 M of tetrabutylammonium tetrafluoroborate (TBATFB) as a supporting electrolyte at room temperature using Ag/AgCl as a reference electrode in a potential range of -1 to +2 V and a scan rate of 0.05 to 0.5 Vs^{-1} .

3. Result and Discussion

3.1. FT-IR spectra

FT-IR spectroscopy is a powerful tool for assigning geometry to the coordination chemistry. the operational classes and their FT-IR frequencies of Schiff base ligand and its Co(II) and Mn(II) complexes are listed in Table 1, Figures 1,2 and 3. They were recorded in wave number 4000-400 cm^{-1} by KBr pellets by using FT-IR 8400s Spectrophotometer model 2000 from Shimadzu, Japan.

The FT-IR spectrum of the ligand shows a high-intensity band at 1610 cm^{-1} assigned to ν (C=N) indicating the formation of azomethine group in the ligand [18]. This band was shifted to the longer frequency in the spectra of Co(II) and Mn(II) complexes, respectively, a suggestion the coordination of the metal ions with Schiff base ligand. The absence of phenolic -OH stretching frequency, at 3448 cm^{-1} of the ligand and appearance of new bands at (538-500) cm^{-1} in the spectra of the prepared complexes are assigned to ν (M-N) and ν (M-O), respectively [14] indicating the coordination of Schiff base through nitrogen atom of azomethine group and oxygen atom of the phenolic group [20]. The strong and sharp bands at 727-839 cm^{-1} confirm the presence of H_2O molecules in the coordination sphere of the complexes [21, 22].

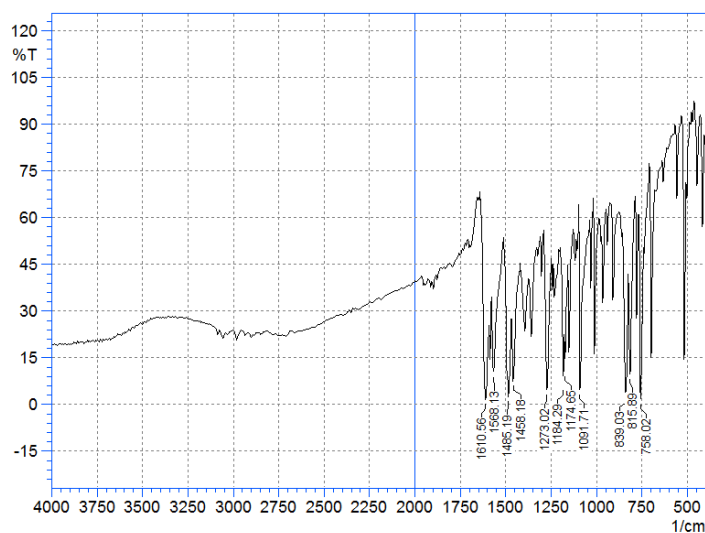


Figure 1. FT-IR spectrum of the Schiff base ligand.

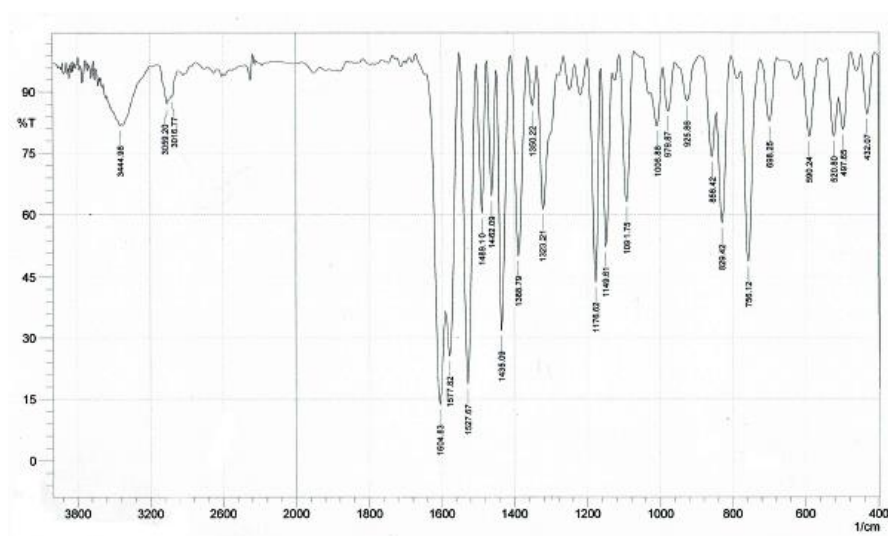


Figure 2. FT-IR spectrum of CoL complex.

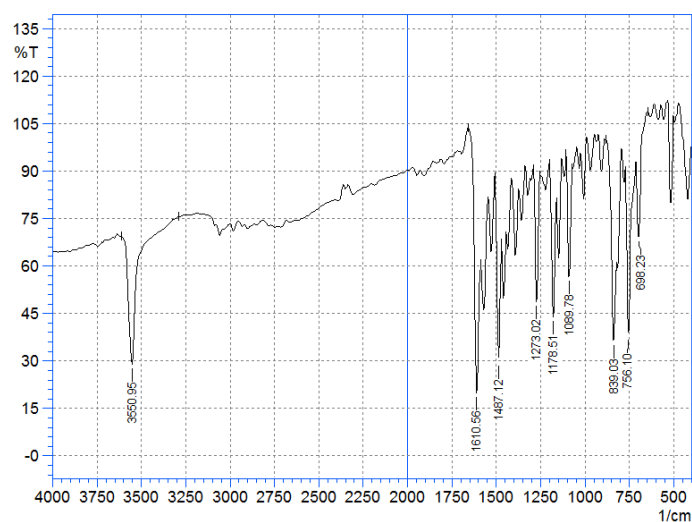


Figure 3. FT-IR spectrum of CoL₂ complex.

Table 1. Selected FT-IR bands (cm⁻¹) of ligand and its complexes.

Compound	ν Ar-CH	ν CH=N	ν C-O	ν C=C
HL	3050	1610	1273	1568
CoL	3016	1604	1248	1489
CoL ₂	3075	1610	1273	1487
MnL	2978	1612	1230	1531
MnL ₂	3059	1612	1273	1566

3.2. Electronic spectra

The electronic spectrum of Schiff base ligand; HL shows three main bands (Fig. 4). The first absorption band at 272 nm attributed to π - π^* transition for the aromatic system, while the second absorption band attributed to π - π^* transition of imine group which appeared at 322 nm [23]. This band was not

significantly affected by chelating. The third absorption band showed at 344 nm assigned to $n-\pi^*$ transition which was shifted to a shorter wavelength (blue shift) upon formation of the complex [24]. This shift may be attributed to the donation of lone pairs of O/N (p orbital) \rightarrow metal ion charge transfer (LMCT) suggesting the coordination of Co(II) and Mn(II) ions by the donor atoms of the ligand [25].

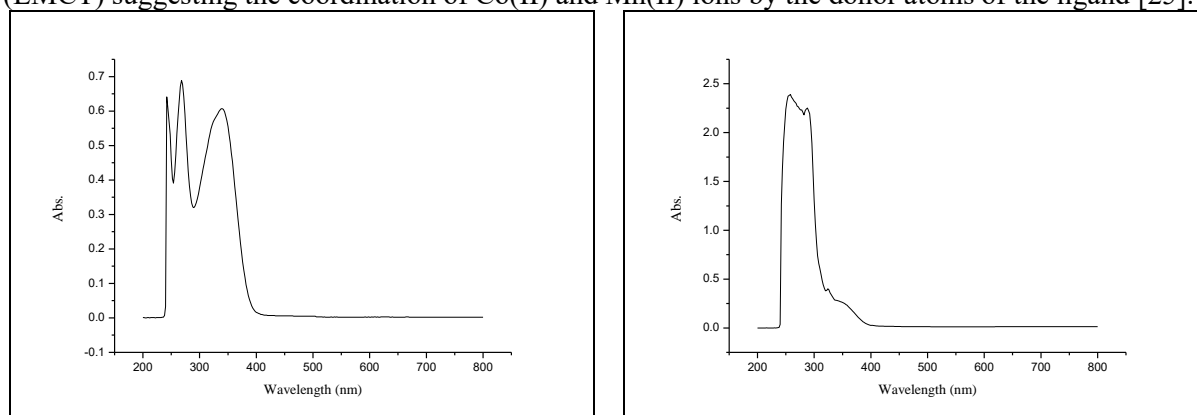


Figure 4. The electronic spectra of Schiff base ligand and MnL_2 complex, respectively.

3.3. Electrochemical studies

The cyclic voltammetry behavior of HL exhibited three irreversible redox peaks of one-electron transfer which may be to the formation of anions and cations species due to a reduction and oxidation process corresponding to an irreversible electron transfer [31, 32, 33]. By using different scan rates, the deviation in current was observed and various potential anodic values were measured which may be related to the increase of the scan rates, see Fig. 7. The linearity relationship as shown in Fig. 8, derived from redox peaks current with the square root of scan rates illustrates that the redox is a diffusion-controlled process [34]. The electrochemical data of the ligand and prepared complexes are summarized in Table 2.

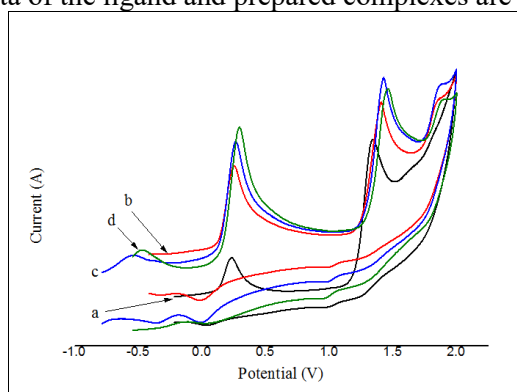


Figure 5. The cyclic voltammograms of the Schiff base ligand at different scan rates; a (0.05 Vs^{-1}), b (0.1 Vs^{-1}), c (0.2 Vs^{-1}) and d (0.5 Vs^{-1}).

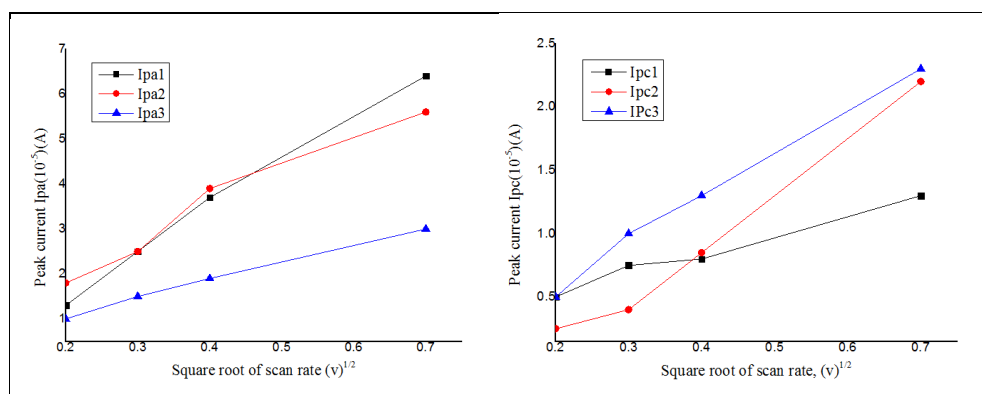


Figure 6. The plot of peak current against square root of scan rate of ligand.

Table 2. The oxidation and reduction potential values of the ligand and its complexes at scan rate 0.2 Vs^{-1} .

Comp.	Oxidation steps					Reduction steps				
	$E_{pa1}(\text{V})$	$E_{pa2}(\text{V})$	$E_{pa3}(\text{V})$	$E_{pa4}(\text{V})$	$E_{pa5}(\text{V})$	$E_{pc1}(\text{V})$	$E_{pc2}(\text{V})$	$E_{pc3}(\text{V})$	$E_{pc4}(\text{V})$	$E_{pc5}(\text{V})$
HL	0.3	1.42	1.9	---	---	-0.25	0.01	1	---	---
CoL	0.25	1.25	---	---	---	---	---	---	---	---
CoL ₂	0.4	1.4	1.8	---	---	---	---	---	---	---
MnL	0.25	1.125	1.37	1.84	---	1.37	1	0	-0.28	---
MnL ₂	0.27	1.125	1.375	1.62	1.87	1.75	1.37	1.04	0.03	-0.25

The cyclic sweep for CoL and CoL₂ complexes appeared two irreversible oxidation peaks, but with different values and positions as shown in Figure 9, caused by one-electron transfer, the first peak attributed to the formation of Co(II) π cation radical and the second for Co(III) [35]. Another weak oxidation peak for CoL₂ complex was noticed clearly at 1.8 V with a scan rate 0.1 and 0.2 Vs^{-1} , maybe due to the presence of the phenolic hydroxyl group of the ligand excess, which acts as a proton donor [36]. Moreover, the same deviation of current and potential to more anodic values for ligand were observed when the cyclic sweep was done for CoL and CoL₂ complexes at the different scan rates (Figure 10).

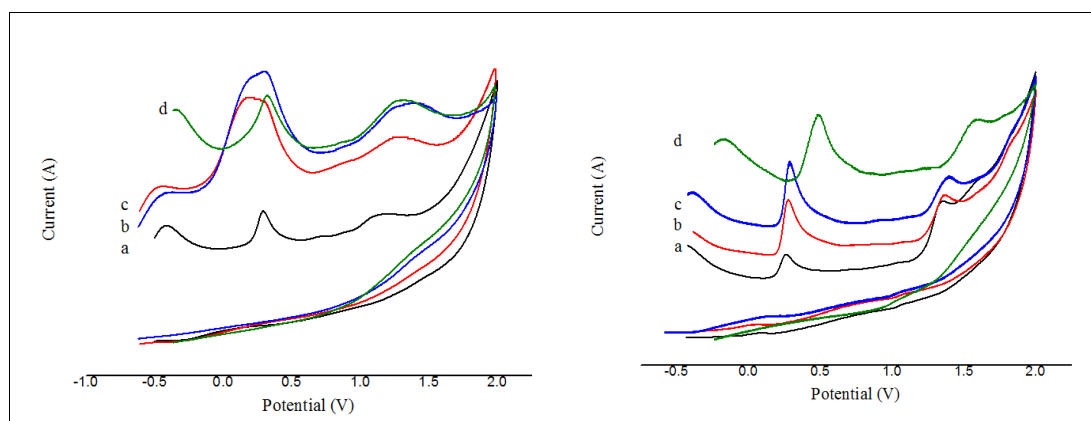


Figure 7. The cyclic voltammograms of CoL and CoL₂ complexes, respectively at different scan rates; a (0.05 Vs^{-1}), b (0.1 Vs^{-1}), c (0.2 Vs^{-1}) and d (0.5 Vs^{-1}).

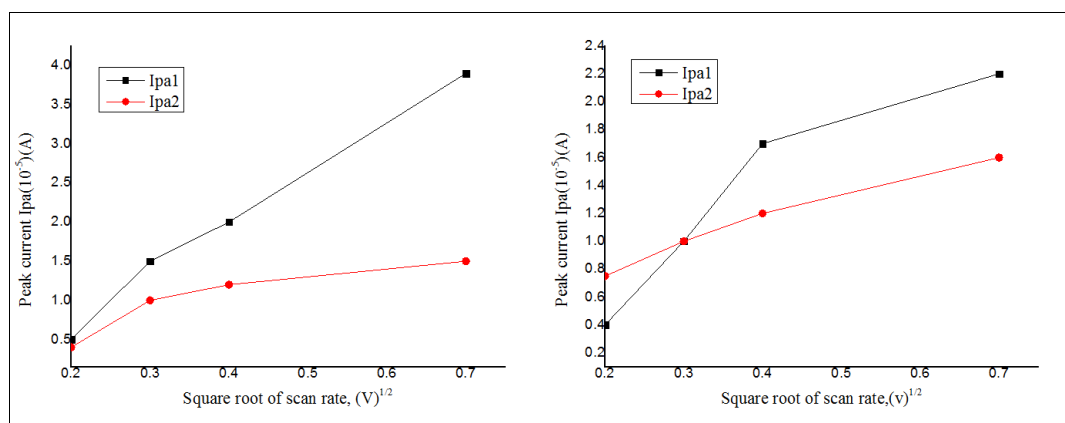


Figure 8. The plot of peak current against square root of scan rate of CoL and CoL₂, respectively.

The cyclic sweep for MnL and MnL₂ complexes appeared several redox peaks, which related to the formation of various manganese redox species [37] as shown in Figure 11. Two peaks are reversible redox couples $I_{pa}/I_{pc} = 0.9-1.0$ A, the first redox peaks couple are assumed to be the Mn(III)/Mn(II), while the second is assumed to be the Mn(IV)/Mn(III) with the one-electron transfer. Moreover, the scan for MnL₂ gave another reduction and oxidation peaks, related to the presence of an additional phenolic hydroxyl group of the ligand which acts as a proton donor [36]. Both MnL and MnL₂ complexes had a deviation of current and potential to more anodic values when the cyclic sweep was done at different scan rates as shown in Figures 12, 13, respectively.

By comparing the potential values for prepared complexes which summarized in Table 2, a positive shift was observed for CoL₂ and MnL₂ may be due to the electron-donating and electron-withdrawing properties of phenyl substituted group [38].

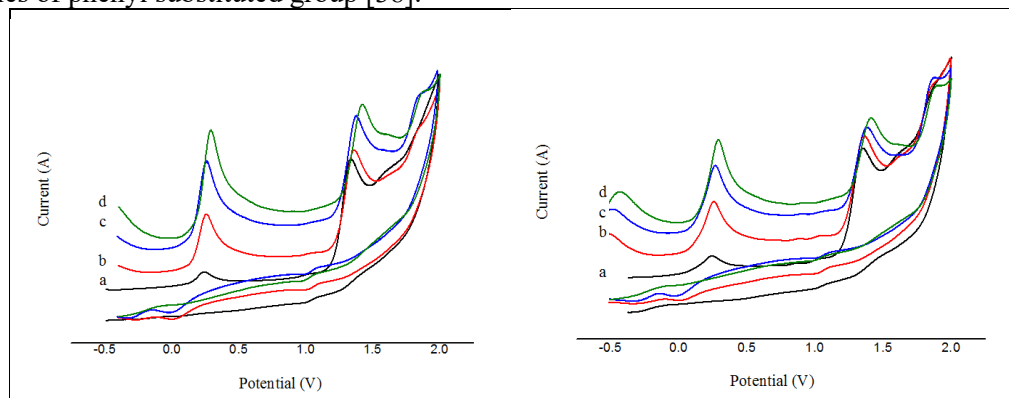


Figure 9. The cyclic voltammograms of the MnL and MnL₂ complexes, respectively at different scan rates; a (0.05 Vs⁻¹), b (0.1 Vs⁻¹), c (0.2 Vs⁻¹) and d (0.5 Vs⁻¹).

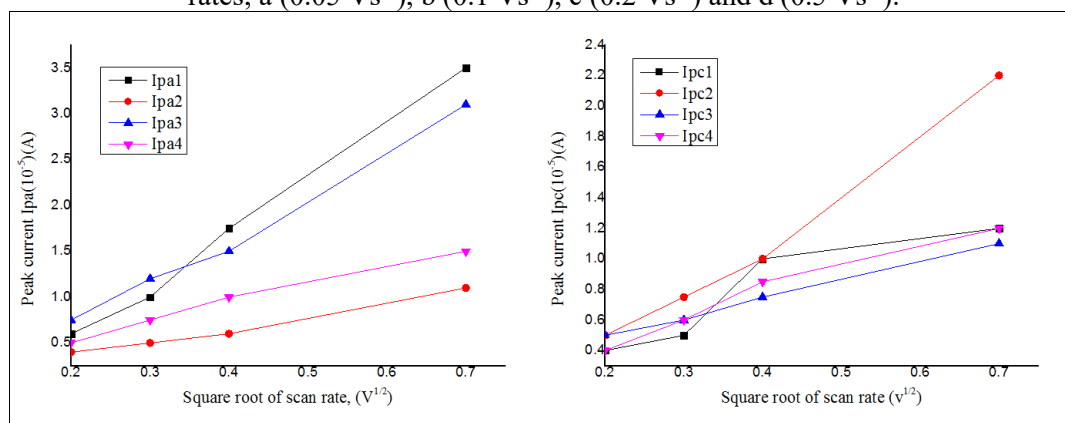


Figure 10. The peak current against the square root of scan rate of MnL complex.

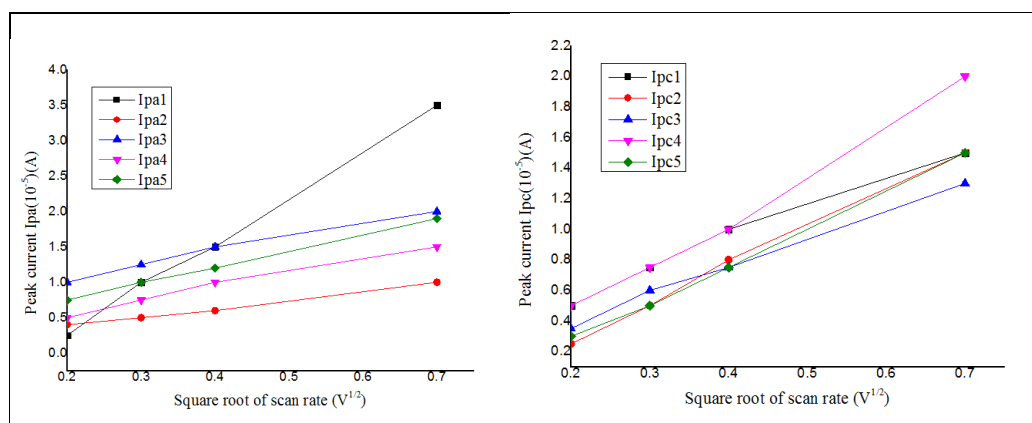


Figure 11. The plot of peak current against square root of scan rate MnL_2 complex.

4. Conclusion

The characteristic chelating properties of 2- $\{p$ -chlorophenylimino $\}$ methyl $\}$ phenol ligand (HL) with cobalt(II) and manganese(II) ions have been investigated by spectroscopic techniques and cyclic voltammetry studies. The infrared data conforming that, the coordination of metal ions with Schiff base ligand introduced via the nitrogen atom of azomethane and oxygen atom of the phenolic group. The electronic spectra observed that the coordination takes place via the donation of lone pairs of O/N (p -orbital) \rightarrow metal ion charge transfer (LMCT). While the differences in the number of peaks and 1H NMR chemical shift of the free ligand and its complexes confirm that the bonding between them occurs. The cyclic voltammetric behavior of the prepared complexes was studied during and after the electron transfer process. The ligand exhibited an irreversible one-electron transfer and redox diffusion-controlled process, the Co(II) complexes appeared two irreversible oxidation peaks but with different values and positions and Mn(II) complexes appeared many redox peaks, which related to the formation of various manganese redox species. All complexes had a deviation of current and potential to more anodic values when the cyclic sweep was done at different scan rates.

5. Acknowledgments

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