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Cyclic and Square Wave Voltametric Studies of Mn(II) and Co(II) Dithiocarbamate Complexes

Fartisincha P. Andrew and Peter A. Ajibade[*]

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville,
Pietermaritzburg, 3209, South Africa
[*]E-mail: ajibadep@ukzn.ac.za

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The cyclic and square wave voltammetry of Mn(II) and Co(II) dithiocarbamate complexes have been investigated. The data obtained indicated one or two redox couple(s), with each redox couple associated with a sequential single electron transfer corresponding to metal center quasi-reversible redox processes. The Manganese(II) complexes (1 and 3) exhibited two redox couples in the range -0.4 to 0.6 V, the two oxidations and the corresponding reductions are assigned to Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV} redox processes. The cobalt(II) complexes (2 and 4) showed a single redox couple in the range 0.52 to 1.12 V, assigned to metal center one-electron quasi-reversible Co(II)/(III) and Co(III)/(II) oxidation and reduction respectively. The linear relationship of the plot of $I_{p,\,a}$ vs $\nu^{1/2}$ (Randles-Sevcik plot) suggested a diffusion controlled behaviour of all the complexes.

Keywords: Electrochemistry, Dithiocarbamates, Cyclic voltammetry, Manganese(II), Cobalt(II)

1. INTRODUCTION

The ability of dithiocarbamate ligands to stabilize metal ions in high or unusual oxidation states accounts for their rich electrochemistry [1, 2]. Metal complexes of dithiocarbamate exist in different oxidation states and their redox chemistry give rise to fascinating electronic and structural changes responsible for properties that make them useful as precursors for novel nanomaterials and chemotherapeutic agents [3, 4]. Dithiocarbamates that are coordinated to heavy metals at higher oxidation states are not stable due to the ease with which the metal center can be reduced that result in simultaneous oxidation of the dithiocarbamate ligand to thiuram disulfide [5]. Although the chemistry of metal complexes of dithiocarbamate have received tremendous attention [6-14], however, only few reports are available on the electrochemistry of cobalt and manganese dithiocarbamate complexes.

About two decades ago, Bond *et al.*, [15, 16] and in 2012, Hogarth [5] reported extensive review on the electrochemistry and redox behaviour of transition metal dithiocarbamate complexes with few reports on cobalt, manganese and ruthenium complexes. They established that metal dithiocarbamates undergo sequential one electron redox process that is in most cases metal center while others involve both ligand and metal center redox processes. They reported that Mn(II) undergo oxidation to Mn(III) vice versa and Mn(II) complexes, $Mn(R_2NCS_2)_3$ undergo oxidation to Mn(IV) and vice versa.

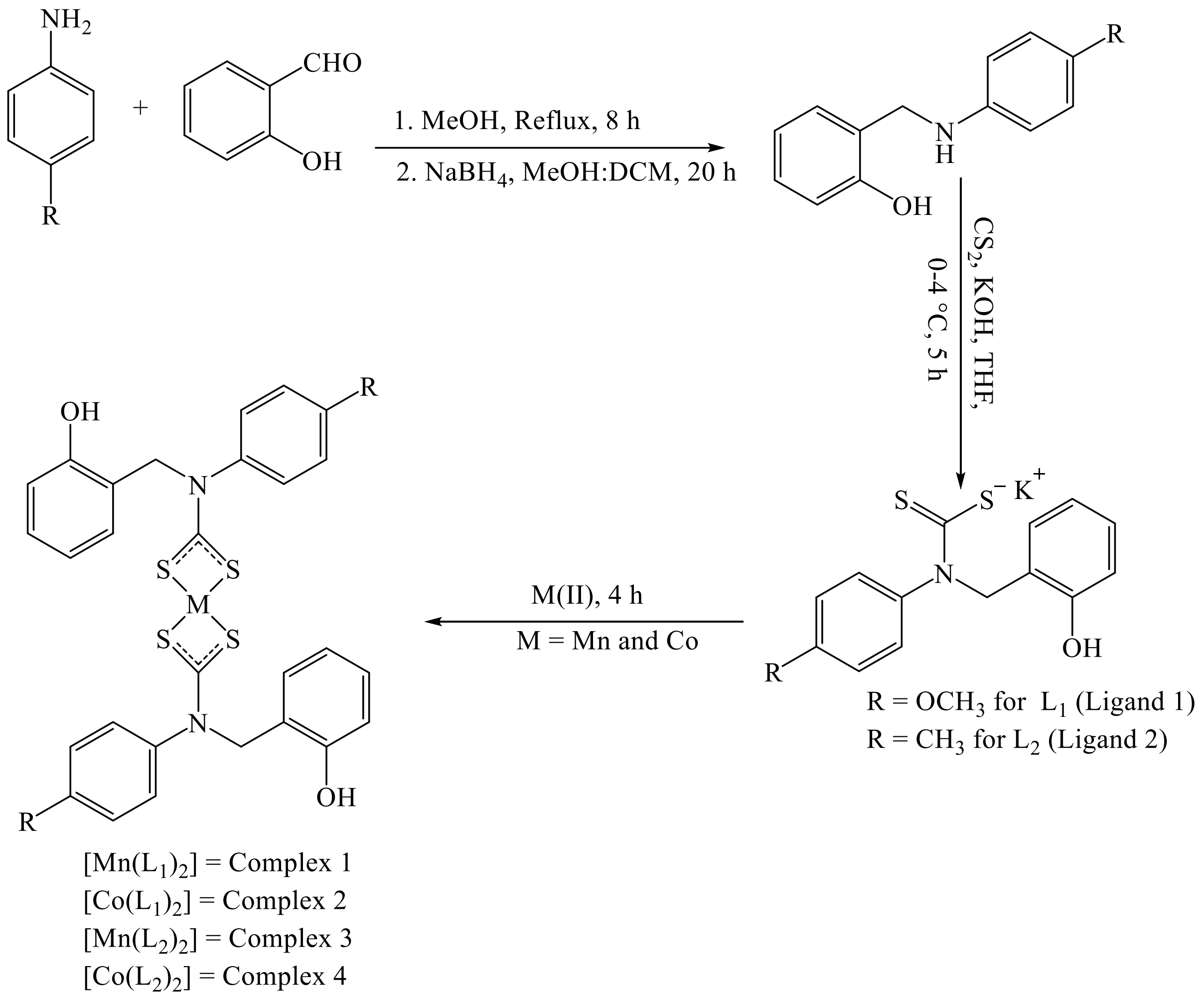
In other studies, the electrochemistry of manganese, cobalt and ruthenium dithiocarbamate complexes exhibited metal center sequential electron transfer process [17-19]. Hoa *et al.*, [20] established that Co(III) dithiocarbamate undergo reduction at mercury electrode in two successive diffusion controlled steps in DMSO, with the first step consisting of one-electron quasi-reversible and the second step involved two-electron irreversible step. The study concluded that the complexes dissociated before reduction with the release of the ligand and substituent dependent adsorption was also observed.

Giovagnini *et al*., [21] and Wheeler *et al*., [22] in separate studies reported the electrochemical behaviour of series of mono and bimetallic ruthenium N,N-dimethyl/diethyldithiocarbamate complexes in various solvents. The studies revealed that the redox process is solvent dependent, one-electron oxidation was observed in acetonitrile forming Ru(IV) whereas in dichloromethane two oxidations were observed with each characterized by single reversible process assigned to ligand and metal based process. They also undergo single electron reversible reduction to afford Ru(II). In this study, the electrochemical behaviour of Mn(II) and Co(II) dithiocarbamate complexes are presented.

2. EXPERIMENTAL

2.1. Materials and methods

The electrochemical behaviour were studied using autolab potentiostat (with Nova 1.7 software) equipped with three electrode system; a glassy carbon working electrode (GCWE), pseudo Ag/AgCl reference electrode (RE) and an auxiliary platinum counter electrode (CE). Fresh 2 mM solution of the complexes and the supporting electrolyte (0.1 M tetrabutylammonium hexafluorophosphate) was prepared in dichloromethane (DCM). All solutions were purged with nitrogen steam for about 10 min before every experiment. The glassy carbon working electrode is polished between each run with slurry of alumina and ultra-pure water on Buehler felt pad and rinsed thoroughly with ultra-pure water [23]. The compounds were prepared as reported [24] Figure 1.



Scheme 1. Schematic representation for the synthesis of the Mn(II) and Co(II) complexes

3. RESULTS AND DISCUSSION

3.1. CV and SW voltammetry of manganese(II) complexes

The cyclic voltammogram (CV) of ferrocene standard and overlay CVs of the manganese(II) complexes 1 and 3 measured at increasing scan rates are presented in Figures 2, 3 and 6. Cyclic voltametric data of the complexes at 100 mVs^{-1} scan rate and potential range of -0.5 to 1.2 V are presented in Table 1. All the complexes exhibited metal center electroactivity. Both the manganese complexes (1 and 3) showed two well defined redox couples, each of which is associated with a single electron process that is apparently quasi-reversible. The two oxidations and the corresponding reductions are assigned to Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV} redox processes (Eq. 1). [25, 26]. The separation of the peak potentials of the complexes (Table 1) approximately 90 mV vs Ag/AgCl for all the complexes at a scan rates of 100 mV/s are little above that of the diagnostic ferrocene (approximately 70 mV vs Ag/AgCl) reversible one electron process. This therefore suggest a quasi-reversible one electron transfer process and is a slow electron transfer kinetics [27].

$$[Mn^{II}(L)_2] \rightleftharpoons [Mn^{III}(L)_2] \rightleftharpoons [Mn^{IV}(L)_2] \text{ -------------- Eq. 1}$$

The Randles-Sevcik (Eq. 2), plot (a plot of cathodic peak currents (I_{pa}) versus square root of the scan rates $v^{1/2}$) for complexes 1 and 3 (Figures 5 and 8) showed ~~a~~ linear relationship, indicating free diffusion controlled reversible electron transfer process. The observed slight deviation from the linearity of the plot for complex 1 suggest either quasi-reversible electron transfer or the electron transfer occurs via surface absorbed species. However, the study of the behaviour of the peak-to-peak separations (Tables 2 and 3) which shifts with increased scan rate confirms that the process is electrochemically quasi-reversible electron transfer [28] for all the complexes.

$$I_{P,a} = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}} \text{ -- Eq. 2}$$

Where, $I_{p,a}$ = Anodic peak current, n = Number electron, F = Faraday's constant (96485 $Cmol^{-1-}$), A = Electrode area (cm^{-2}), D = Analyte diffusion coefficient cm^2s^{-1}, C = Concentration of complex.

Furthermore, the ratio of the anodic and cathodic peak current is approximately one which indicate that each redox process corresponds to one electron process. The square wave voltammograms (SWVs) of the complexes (Figures 4 and 7) showed the peak position that is consistent with the wave on the cyclic voltammograms.

Table 1. Selected CV parameters of ferrocene standard and Mn(II) and Co(II) complexes recorded at 100 mVs-1

Compound	**$E_{p,a}$ (V)**	**$E_{p,c}$ (V)**	**$E_{1/2}$ (V)**	**ΔE (mV)**
Ferrocene	0.451	0.383	0.417	68
$[Mn(L_1)_2]$	0.179	0.093	0.136	86
$[Mn(L_2)_2]$	0.213	0.122	0.168	91
$[Co(L_1)_2]$	0.868	0.782	0.825	86
$[Co(L_2)_2]$	0.872	0.776	0.824	96

$E_{1/2} = (E_{p,a} + E_{p,c})/2$, $\Delta E_p = E_{p,a} - E_{p,c}$,

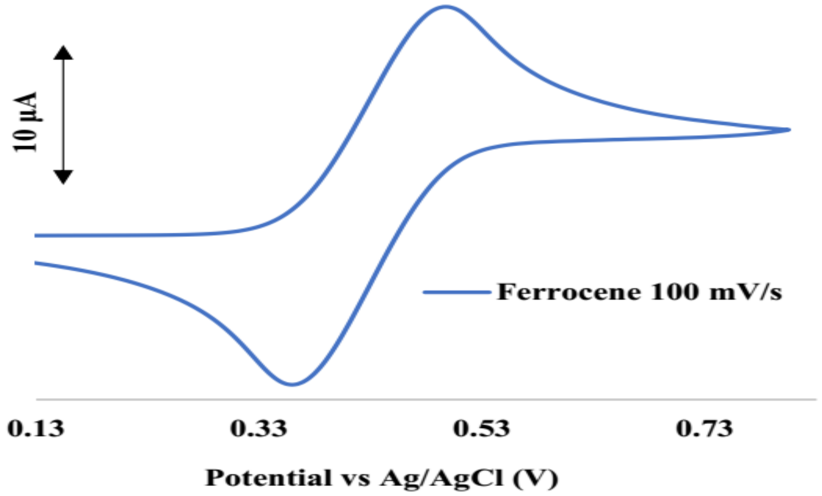


Figure 2. CV of ferrocene used as standard

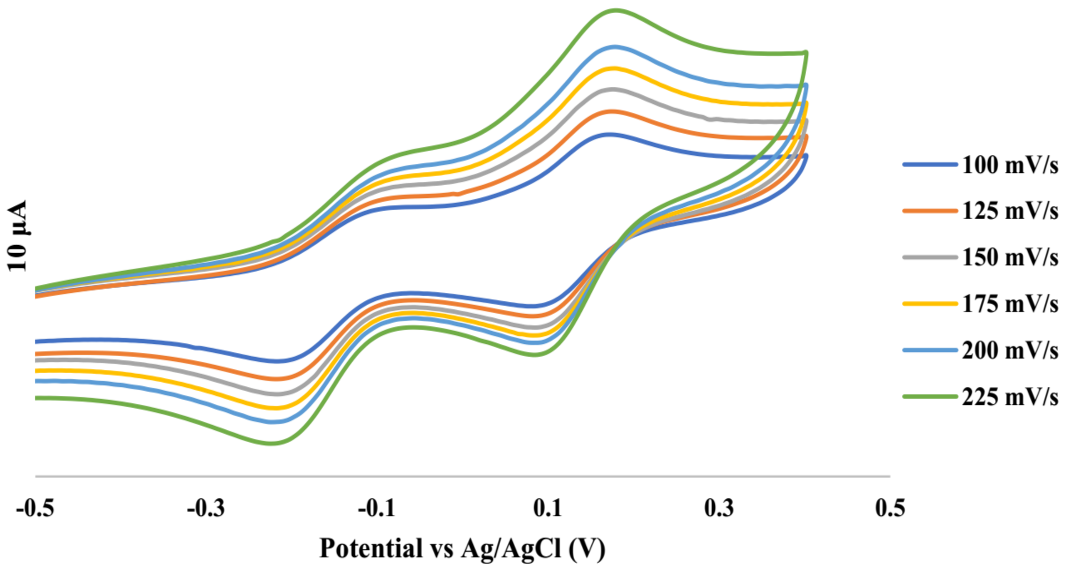


Figure 3. An overlay CVs of [Mn(L_1)$_2$] (Complex 1) with increased scan rate

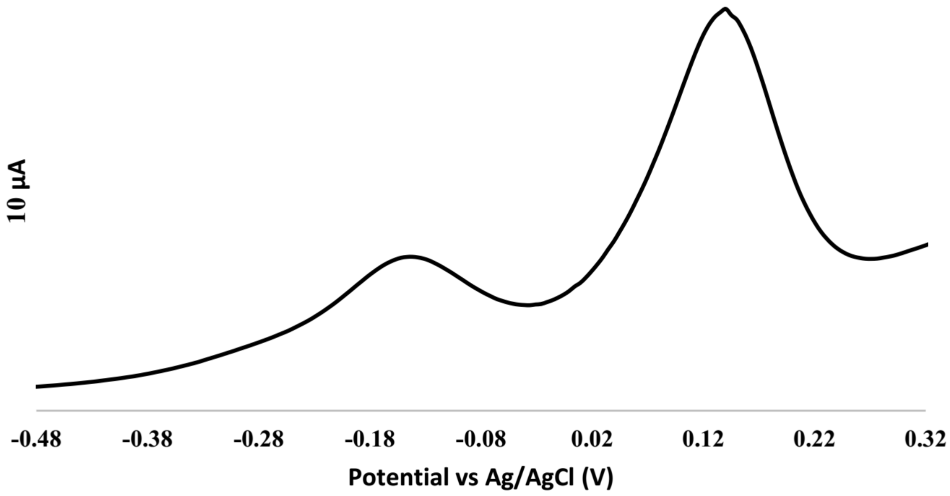


Figure 4. SWV of [Mn(L_1)$_2$] (Complex 1)

Table 2. CV data [Mn(L_1)$_2$] (Complex 1) at increasing scan rates

Scan rate (ν) /mVs^{-1}	ν$^{1/2}$ (mVs^{-1})$^{1/2}$	$E_{p,a}$/V	$E_{p,c}$/V	$E_{1/2}$ /V	ΔE_p/mV	$I_{p,a}$/10^{-6} (µA)
100 1st Redox	10.00	0.179	0.093	0.136	86	3.14
125	11.18	0.179	0.091	0.135	88	3.81
150	12.24	0.182	0.091	0.137	90	4.45
175	13.22	0.179	0.092	0.136	87	5.07
200	14.14	0.182	0.093	0.138	89	5.69
225	15.00	0.184	0.093	0.139	91	6.76
100 2nd Redox	10.00	-0.071	-0.217	-0.144	146	1.03
125	11.18	-0.081	-0.221	-0.151	140	1.31
150	12.24	-0.101	-0.220	-0.161	119	1.54
175	13.22	-0.106	-0.221	-0.164	115	1.75
200	14.14	-0.081	-0.218	-0.150	137	2.09
225	15.00	-0.091	-0.220	-0.155	129	2.45

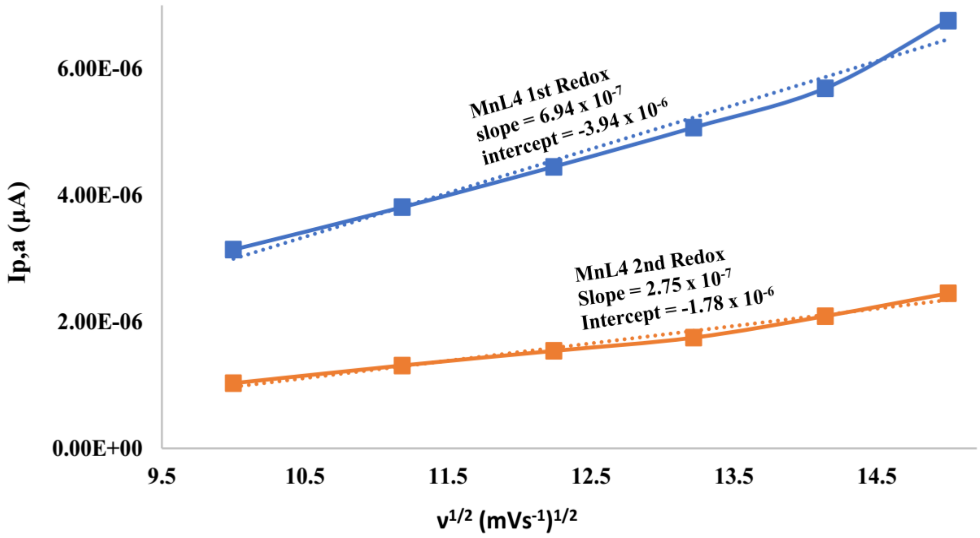


Figure 5. Randles-Sevcik plot for $[Mn(L_1)_2]$ (Complex 1) redox couple

Table 3. CV data $[Mn(L_2)_2]$ (Complex 3) with increased scan rate

Scan rate (ν) /mVs^{-1}	ν$^{1/2}$ (mVs^{-1})$^{1/2}$	$E_{p,a}$/V	$E_{p,c}$/V	$E_{1/2}$ /V	ΔE_p/mV	$I_{p,a}$/10^{-6} (μA)
100 1st Redox	10.00	0.213	0.122	0.168	91	3.14
125	11.18	0.220	0.124	0.172	96	3.81
150	12.24	0.220	0.126	0.173	94	4.45
175	13.22	0.221	0.126	0.174	95	5.07
200	14.14	0.220	0.122	0.171	98	5.69
225	15.00	0.225	0.120	0.173	105	6.76
100 2nd Redox	10.00	-0.073	-0.177	-0.125	104	1.03
125	11.18	-0.048	-0.182	-0.115	134	1.31
150	12.24	-0.058	-0.171	-0.115	113	1.54
175	13.22	-0.060	-0.171	-0.116	111	1.75
200	14.14	-0.060	-0.178	-0.119	118	2.09
225	15.00	-0.060	-0.178	-0.119	118	2.45

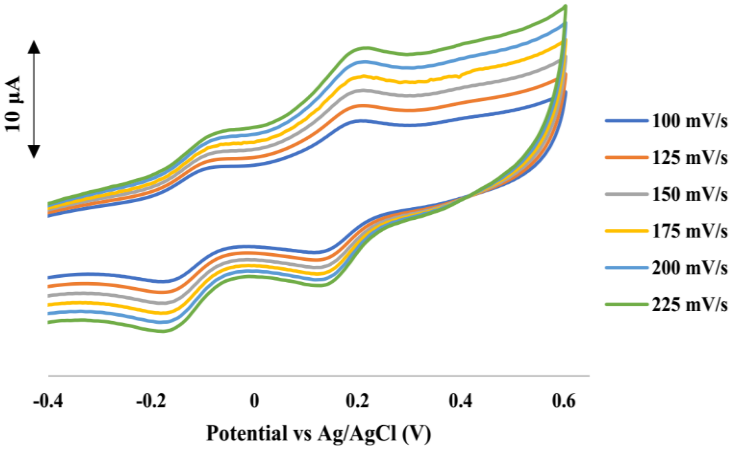


Figure 6. An overlay CVs of $[Mn(L_2)_2]$ (complex 3) with increased scan rate

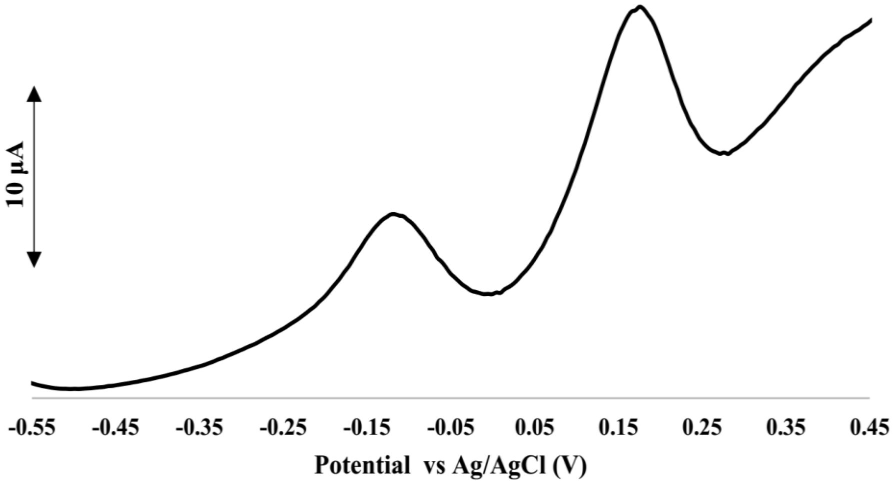


Figure 7. SWV of [Mn(L_2)$_2$] (complex 3)

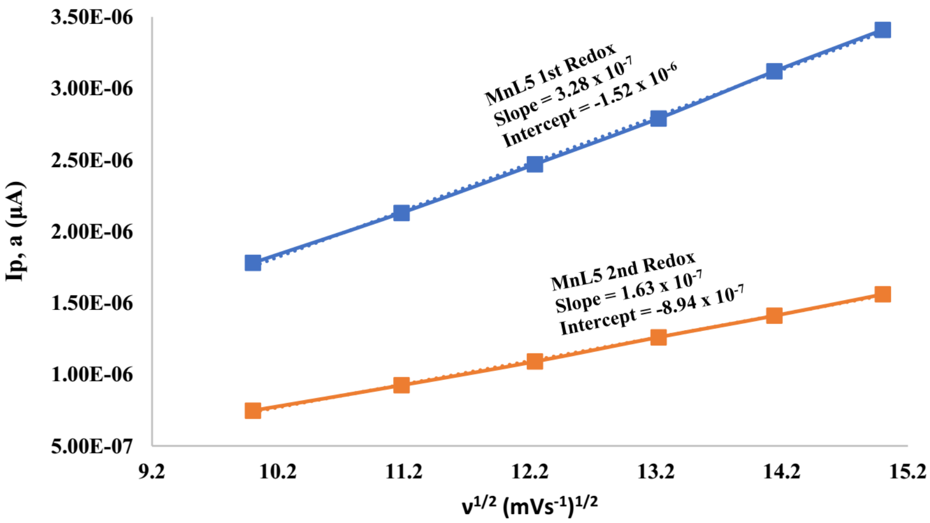


Figure 8. Randles-Sevcik plot for [Mn(L_2)$_2$] (complex 3) redox couple

3.2. CV and SW voltammetry of cobalt(II) complexes

The cyclic voltammetry data for the cobalt(II) complexes 2 and 4 are presented in Tables 4 and 5, the voltammograms are shown in Figures 9 and 12. Both complexes displayed one redox couple at positive potential range of 0.52–1.12 V vs Ag/AgCl that consist of one Co(II)/(III) oxidation and corresponding Co(III)/(II) reduction [29-31]. The Co(II)/(III) oxidation (Eq. 3) was observed at $E_{p,a}$ = 0.868 V Vs Ag/AgCl and Co(III)/(II) reduction (Eq. 4) was observed at $E_{p,c}$ = 0.782 V vs Ag/AgCl for complex 2. For complex 4, Co(II)/(III) oxidation was observed at $E_{p,a}$ = 0.872V Vs Ag/AgCl and Co(III)/(II) reduction was observed at 0.776 V Vs Ag/AgCl at 100 mV/s.

$$[Co^{II}(L)_2] \rightleftharpoons [Co^{1II}L)_2] + e^- \text{----------} (3) \quad \text{Oxidation}$$

$$[Co^{III}(L)_2] + e^- \rightleftharpoons [Co^{II}L)_2] \text{-----------} (4) \quad \text{Reduction}$$

Similarly, the peak separation (ΔE_p) of the oxidation and reduction process is approximately 90 mV. All the redox processes in the complexes are metal center one electron quasi-reversible redox process characterized by a peak separation (ΔE_p) greater than that of ferrocene standard (approximately 70 mV) and slightly increased with increased scan rate [32]. The approximately unit value of the ration of the anodic to cathodic peak current and square wave of the cobalt(II) complexes (Figures 10 and 13) further confirmed that it was one electron process [30]. The linear relationship observed in the plot (Figures 11 and 14) of square root of increased scan rate and cathodic peak current indicated a diffusion controlled behaviour of all the complexes [33, 34].

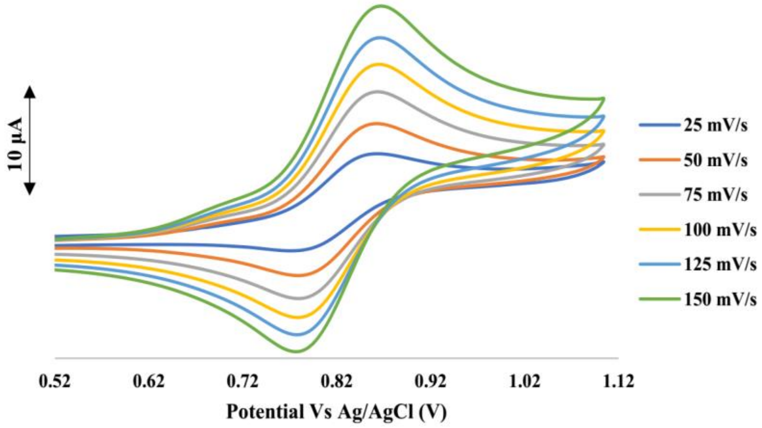


Figure 9. An overlay CVs of $[Co(L_1)_2]$ (complex 2) with increased scan rate

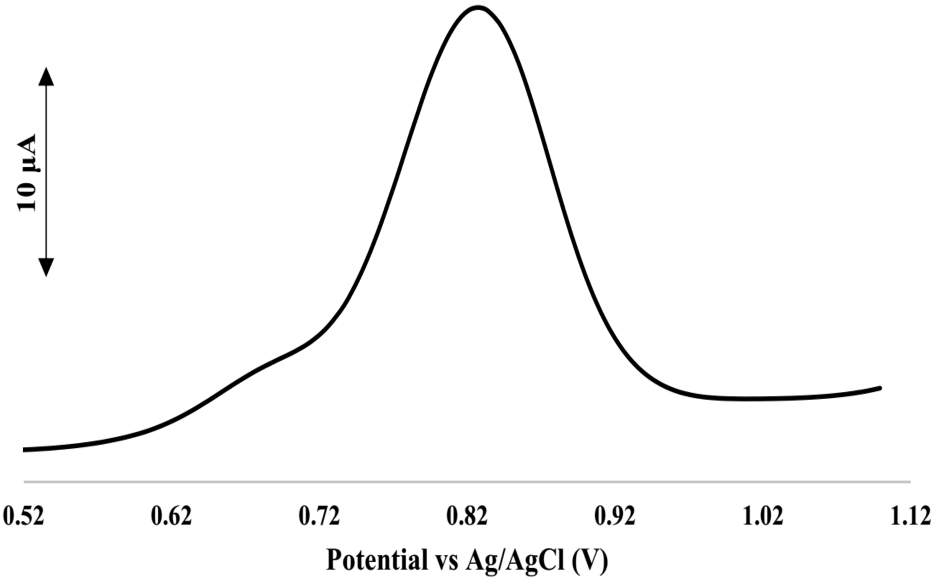


Figure 10. SW voltammogram of $[Co(L_1)_2]$ (complex 2)

Table 4. CV data for $[Co(L_1)_2]$ (complex 2) with increased scan rate

Scan rate (ν) /mVs^{-1}	$ν^{1/2}$ $(mVs^{-1})^{1/2}$	$E_{p,a}$/V	$E_{p,c}$/V	$E_{1/2}$ /V	$ΔE_p$/mV	$I_{p,a}/10^{-6}$ (μA)
25	5.00	0.863	0.772	0.818	91	9.20
50	7.07	0.856	0.782	0.819	75	12.3
75	8.66	0.868	0.782	0.825	86	15.6
100	10.00	0.868	0.782	0.825	86	18.5
125	11.18	0.863	0.777	0.820	86	21.2
150	12.25	0.868	0.777	0.823	91	2.44

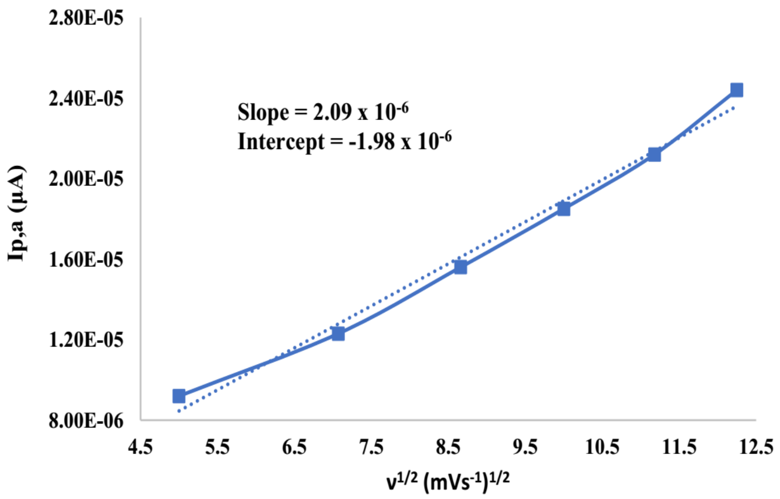


Figure 11. Randles-Sevcik plot for $[Co(L_1)_2]$ (complex 2) redox couple

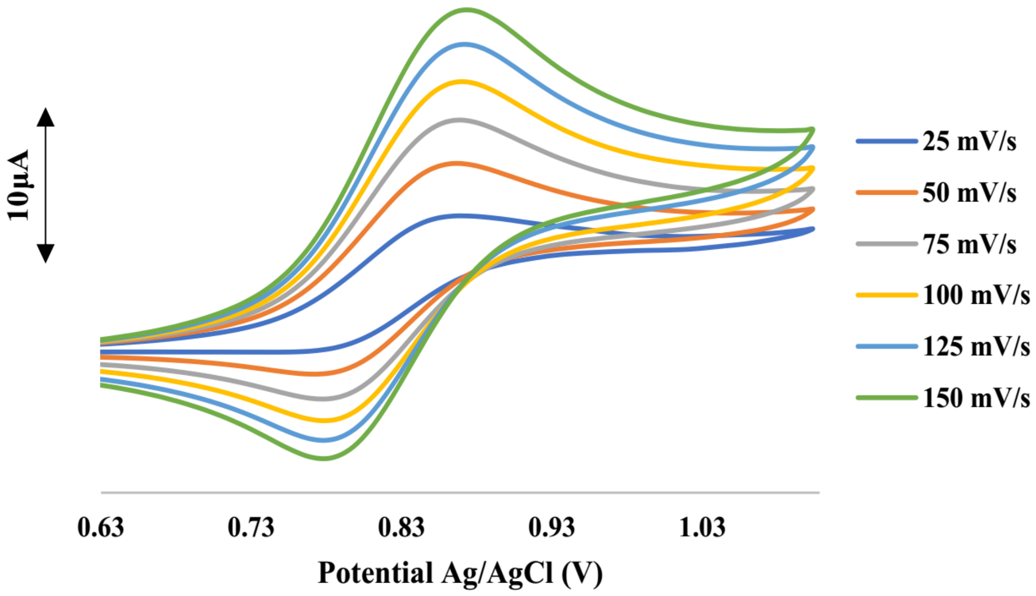


Figure 12. An overlay CVs of $[Co(L_2)_2]$ (complex 4) with increased scan rate

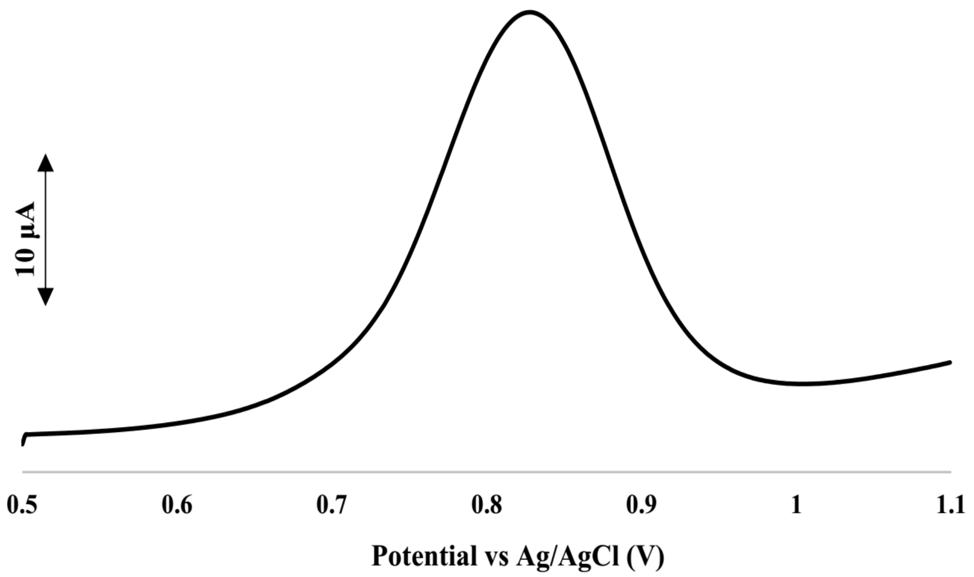


Figure 13. SW voltammogram of $[Co(L_2)_2]$ (complex 4)

Table 5. CV data for $[Co(L_2)_2]$ (complex 4) with increased scan rate

Scan rate (ν) /mVs^{-1}	$\nu^{1/2}$ (mVs^{-1})$^{1/2}$	$E_{p,a}$/V	$E_{p,c}$/V	$E_{1/2}$ /V	ΔE_p/mV	$I_{p,a}/10^{-6}$ (µA)
25	5.00	0.872	0.746	0.809	126	8.49
50	7.07	0.872	0.771	0.823	101	11.8
75	8.66	0.872	0.776	0.824	96	14.5
100	10.00	0.872	0.776	0.824	96	17.0
125	11.18	0.872	0.776	0.824	96	19.3
150	12.25	0.872	0.776	0.824	96	21.5

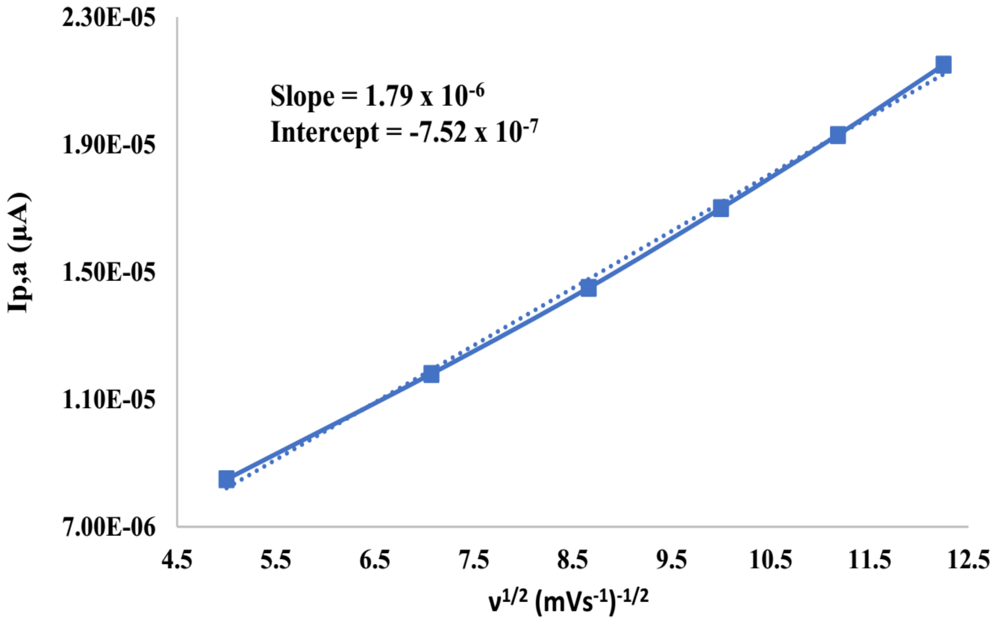


Figure 14. Randles-Sevcik plot for $[Co(L_2)_2]$ (complex 4) redox couple

4. CONCLUSION

The electrochemical behaviour of manganese(II) and cobalt(II) dithiocarbamate complexes were studied using cyclic and square wave voltammetry. The manganese(II) complexes 1 and 3 behaved in a similar way and showed two redox couples in their cyclic voltammograms. Each of the couples are associated with sequential single electron quasi-reversible process and overall metal center Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV} redox processes. Like the manganese(II) complexes, the cobalt(II) complexes 2 and 4 also exhibited metal center redox process comprising of one quasi-reversible electron process assigned to Co(II)/Co(III) and Co(III)/Co(II) redox process. Randles-Sevcik plots of anodic peak current versus the square root of the scan rate ($I_{p,\ a}$ vs $\nu^{1/2}$) for all the complexes revealed a diffusion controlled behaviour.

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