

## Synthesis, Cyclic Voltammetry and Chronoamperometry Studies of Cobalt(II) Complexes with Tridentate Schiff Base Ligands

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Tridentate Schiff base ligands were prepared by the condensation reaction of anthranilic acid with salicylaldehyde, furfural, thiophen-2-carboxaldehyde and pyridine-2-carboxaldehyde in ethanol. Cobalt(II) complexes of related Schiff base ligands were prepared by the reaction of the respective ligand with cobalt(II) acetate. The prepared ligands and oxalato-bridged cobalt complexes have been characterized by UV-vis, IR and <sup>1</sup>H NMR spectral data and elemental analysis. In all the cobalt(II) complexes it is supposed that the central metal has five coordination number and coordinated by a tridentate Schiff base ligand and two oxygen atoms of the oxalate ligand. The electrochemical properties of four Schiff base complexes have been investigated in the presence of tetrabutyl ammonium perchlorate as supporting electrolyte and by using a glassy carbon (GC) electrode. It has been found that all the cobalt complexes shows Co(II) oxidation process irreversibility. Cyclic voltammetry studies indicated that these processes are diffusion-controlled reactions. The obtained data from cyclic voltammetry and chronoamperometry studies showed that, the total limiting current of each of the studied compounds corresponds to one-electron transfer process.

**Key Words:** Synthesis, Cyclic voltammetry, Chronoamperometry, Cobalt(II) Complexes, Tridentate Schiff base ligands.

### INTRODUCTION

Compounds with the structure of >C=N- are known as Schiff bases, which are usually synthesized from the condensation of a primary amines and active carbonyl groups<sup>1,2</sup>. A large number of Schiff bases compounds are often used as ligands in coordination chemistry by considering their metal binding ability. The transition metal complexes having oxygen, nitrogen and sulfur donor Schiff bases possess unusual configuration, structural lability and are sensitive to molecular environment<sup>3</sup>. The environment around the metal center as coordination geometry, number of coordinated ligands and their donor group is key factor for metalloprotein to

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carry out a specific physiological function<sup>4,5</sup>. Schiff base with donors (N, O, S, *etc.*) have structural similarities with natural biological systems and imports in elucidating the mechanism of transformation and racemination reaction in biological systems physiological and pharmacological activities associated with them<sup>11-13</sup>. A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins and complexing ability towards some toxic metals, furthermore complexes of Schiff bases showed promising applications in biological activity and biological modeling application<sup>14-19</sup>. A plethora of references describing the metal complexes of Schiff bases have appeared in the literature during the past few decades. However, little is known on the detailed electrochemical studies of such complexes. In view this, we report here the preparation, characterization and electrochemical behaviour of the acetate complexes of cobalt(II) with the Schiff base derived from the condensation reaction of anthranilic acid with salicylaldehyde, furfural, thiophene-2-carboxaldehyde and pyridine-2-carboxaldehyde in ethanol.

## EXPERIMENTAL

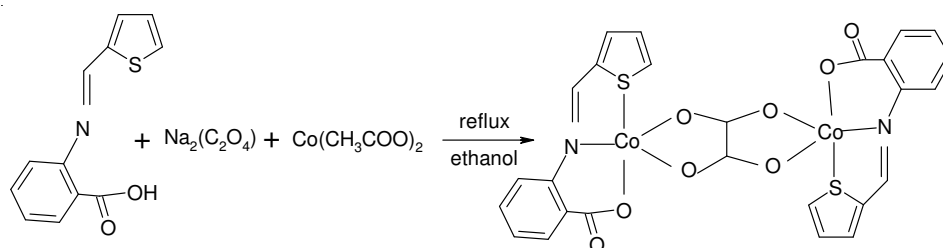
All chemicals used were of highest available purity. They include anthranilic acid, furfural, thiophene-2-carboxaldehyde, pyridine-2-carboxaldehyde, sodium oxalate and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ . The elemental analysis was made using Heareus CHN-O-RAPID analyzer. IR spectra were recorded on a Shimadzu model FTIR-prestige 21 spectrophotometer using KBr discs. <sup>1</sup>H NMR spectra were recorded using Bruker-SPEXTRSPIN Avanc 400 Ultra Shield. Electronic spectra of solutions of both ligands in DMF and the solid reflectance spectra of their metal complexes were recorded on UV-1700 Pharmaspec. UV-vis spectrophotometer Shimadzu. The conductivity measurements were carried out in DMF in room temperature using a Jenway 4510 conductometer instrument. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system which PGSTAT12 boards (Eco Chemie, Utrecht and The Netherlands). The system was run on a PC using GPES 4.9 softwares. A saturated Ag/AgCl electrode and Pt wire was a reference and counter electrodes, respectively. All potentials were measured with respect to the Ag/AgCl which was positional as close to the working electrode as possible by means of a Luggin capillary. Voltammetric measurements were performed at room temperature in DMF solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

**Synthesis of Schiff base ligands:** The four Schiff base ligands, HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup> and HL<sup>4</sup> were prepared by refluxing of a solution of salicylaldehyde (2 mmol) or thiophene-2-carboxaldehyde (2 mmol) or furfural (2 mmol) or pyridine-2-carboxaldehyde (2 mmol), respectively, with anthranilic acid (2 mmol) in ethanol (10 mL), then allowed to cool to room temperature. The product was filtered off, recrystallized from ethanol and dried in desiccators over anhydrous  $\text{CaCl}_2$ . The physical data of corresponded compounds are collected in Table-1.

**Preparation of metal complexes:** The ethanolic solution of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (2 mmol) was added to a stirred solution of the above ligands, followed by the addition of an ethanolic solution of sodium oxalate (1 mmol). The resulting mixture was stirred under reflux for 1 h where upon the metal complexes were precipitated. The precipitated solid complexes were filtered, recrystallized and dried in vacuum desiccator over anhydrous  $\text{CaCl}_2$ . These complexes are stable in air, soluble in DMF and DMSO, insoluble in most organic solvents. The electronic spectra and their elemental analysis are presented in Table-1. The cobalt complexes of  $\text{HL}^1$ ,  $\text{HL}^2$ ,  $\text{HL}^3$  and  $\text{HL}^4$  are shown **1**, **2**, **3** and **4**, respectively.

## RESULTS AND DISCUSSION

Condensation of the aldehydes with amine readily gives rise to the corresponding Schiff base ligands,  $\text{HL}^1$ ,  $\text{HL}^2$ ,  $\text{HL}^3$  and  $\text{HL}^4$ . Their reaction with the  $\text{Co}(\text{II})$  ion afford the metal complexes (**1-4**) (Scheme-I). The Schiff bases are prepared as described in the experimental part, dried under vacuum and subjected to elemental analyses. The results of elemental analyses (C, H, N) with molecular formulae are presented in Table-1. The results obtained are in good agreement with those calculated for the suggested formulae.



Scheme-I

TABLE-1  
PHYSICA DATA FOR SCHIFF BASE LIGANDS AND THEIR COBALT COMPLEXES

Compd.	m.f. (m.w.)	Elemental analysis (%): found (calcd.)			m.p. (°C)
		C	H	N	
$\text{HL}^1$	$\text{C}_{14}\text{H}_{11}\text{NO}_3$ (241.3)	69.68 (69.69)	4.50 (4.59)	5.72 (5.80)	196
<b>1</b>	$\text{C}_{30}\text{H}_{18}\text{N}_2\text{O}_{10}\text{Co}_2$ (684.34)	49.25 (52.65)	2.43 (2.65)	3.74 (4.09)	300 decomposed
$\text{HL}^2$	$\text{C}_{12}\text{H}_9\text{NO}_2\text{S}$ (231.87)	62.40 (62.16)	3.77 (3.91)	6.39 (6.04)	125
<b>2</b>	$\text{C}_{26}\text{H}_{16}\text{N}_2\text{S}_2\text{O}_8\text{Co}_2$ (667.6)	46.88 (46.78)	2.39 (2.42)	4.22 (4.20)	330 decomposed
$\text{HL}^3$	$\text{C}_{12}\text{H}_9\text{NO}_3$ (215.21)	66.82 (66.97)	4.10 (4.21)	6.40 (6.51)	227
<b>3</b>	$\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_{10}\text{Co}_2$ (634.28)	49.12 (49.23)	2.49 (2.54)	4.41 (4.42)	357
$\text{HL}^4$	$\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ (226.24)	69.33 (69.02)	4.23 (4.45)	12.43 (12.38)	220
<b>4</b>	$\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_8\text{Co}_2$ (656.33)	51.32 (51.24)	2.69 (2.76)	8.43 (8.54)	293

**Infrared spectra:** The IR data of the Schiff base ligands and their Co(II) complexes are listed in Table-2. The IR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may involved in chelation. The position and/or the intensities of these peaks are expected to be changed upon chelation<sup>20</sup>. These key peaks are listed in Table-2. The spectra of the free ligands show strong bands at 1625-1605 cm<sup>-1</sup> characteristics of the  $\nu(\text{C}=\text{N})$  (azomethine) stretching mode<sup>12,20</sup>. These bands are shifted to frequency in the 1615-1593 cm<sup>-1</sup> range indicating the coordination of the azomethine nitrogen atom to the central metal ions<sup>12</sup>. The  $\nu(\text{OH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  stretching vibrations are observed at 3450, 1668, 1589 and 1343 cm<sup>-1</sup> for HL<sup>1</sup> ligand. The participation of the carboxylate O atom in the complexes formation was evidenced from the shift in position of these bands to 3380, 1679, 1582 and 1404 cm<sup>-1</sup> for HL<sup>1</sup>-metal complexes<sup>12,13,20</sup>. The  $\nu(\text{OH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  stretching vibrations are observed at 3484, 1706, 1578 and 1422 cm<sup>-1</sup> for HL<sub>2</sub> ligand. The participation of the carboxylate O atom in the complexes formation was evidenced from the shift in position of these bands to 3306, 1720, 1569 and 1408 cm<sup>-1</sup> for HL<sup>2</sup>-metal complexes<sup>12,13,20,21</sup>. Similar results were achieved for other related compounds (Table-2), therefore, from the IR spectra, it is concluded that Schiff base ligands binds to the cobalt ion as tridentate ligands through related donor atoms.

TABLE-2  
INFRARED SPECTRAL DATA OF SCHIFF BASE  
LIGANDS AND THEIR COMPLEXES (cm<sup>-1</sup>)

Compound	$\nu(\text{OH})$	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$
HL <sup>1</sup>	3450	1582	1414	1708	1625
<b>1</b>	3380	1589	1404	1719	1593
HL <sup>2</sup>	3484	1578	1422	1705	1605
<b>2</b>	3306	1569	1408	1731	1615
HL <sup>3</sup>	3445	1588	1419	1711	1612
<b>3</b>	3362	1580	1398	1730	1604
HL <sup>4</sup>	3403	1580	1417	1701	1622
<b>4</b>	3350	1569	1401	1734	1610

<sup>1</sup>H NMR spectroscopic studies were carried out for the ligands in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectra of the ligands, displayed signals corresponding to the various protons. The observed chemical shifts along with spectral assignments are given in Table-3. The carboxylic acid proton appeared as a singlet at  $\delta$  9.87-9.95<sup>20</sup>. The imine protons appeared as a singlet<sup>20</sup> at  $\delta$  8.12, 8.20 and 8.23 for HL<sup>2</sup>, HL<sup>4</sup> and HL<sup>3</sup>, respectively and at  $\delta$  12 for HL<sup>1</sup>.

#### Electrochemical studies

**Cyclic voltammetry:** Fig. 1A illustrates cyclic voltammograms of 0.1 M tetrabutyl ammonium perchlorate in presence of the complex **1** using the glassy carbon electrode recorded at different potential sweep rates. Fig. 1B indicates anodic

TABLE-3  
<sup>1</sup>H NMR SPECTRAL DATA OF THE SCHIFF BASE LIGANDS HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup> AND HL<sup>4</sup>

Compound	δ (ppm)	Assignment
HL <sup>1</sup>	12	(s, 1H, azomethine)
	6.5-8	(m, 8H, 8ArH)
	9.9	(s, 1H, COOH)
HL <sup>2</sup>	9.95	(s, 1H, COOH)
	6.48-8.12	(m, 8H, 4ArH, 1-azomethine, 3-thiophene H)
HL <sup>3</sup>	9.93	(s, 1H, COOH)
	6.3-8.23	(m, 8H, 4ArH, 1-azomethine, 3-furan)
HL <sup>4</sup>	9.87	(s, 1H, COOH)
	6.4-8.2	(m, 9H, 4ArH, 1-azomethine, 4-pyridien)

peak currents increased linearly with the square root of the potential sweep rate, which indicates a mass transfer-controlling process of oxidation *via* diffusion. In addition the value of the electron-transfer coefficient for the reaction can be obtained from the following equation<sup>22</sup>:

$$E_p = \left( \frac{RT}{2\alpha F} \right) \ln v + \text{constant} \quad (5)$$

This is valid for a totally irreversible diffusion-controlled process. Using the dependency of anodic peak potential on the neperian logarithm of the potential sweep rate (Fig. 1C), the value of the electron-transfer coefficient was obtained as (0.39 ± 0.03). Tafel slope is (63.52 ± 0.03). On the basis of the slopes of the linear dependency of the anodic peak currents on the square root of the potential sweep rates (Fig. 1B) and the Randles-Sevcik equation<sup>23</sup>:

$$I_p = (2.99 \times 10^5) \alpha^{1/2} n^{3/2} AC^* D^{1/2} v^{1/2} \quad (6)$$

where  $I_p$  is the peak current,  $A$  is the electrode surface area,  $D$  is the diffusion coefficient and  $C^*$  is the bulk concentration of Schiff base, the diffusion coefficient for the complex **1** was calculated to be  $(5.27 \pm 0.03) \times 10^{-7} \text{ (cm}^2 \text{ s}^{-1}\text{)}$ .

Similar cyclic voltammograms were collected for other complexes. The values of  $D$  and  $\alpha$  obtained according to the method described in the above for these complex were reported in Table-4.

TABLE-4  
 CYCLIC VOLTAMMETRY DATA FOR Co(II) COMPLEXES IN DMF + 0.1 M  
 TETRABUTYLAMMONIUM PERCHLORATE

Compound	$E_{pa}$ (V)	$E_{pc}$ (V)	$I_{pa}$ (μA)	$I_{pc}$ (μA)	$D$ (cm <sup>2</sup> /s) × 10 <sup>-7</sup>	$\alpha$
<b>1</b>	1.192	-0.575	135	-103	5.27	0.39
<b>2</b>	1.142	-0.642	78	-88	4.64	0.45
<b>3</b>	1.216	-0.658	88	-113	6.73	0.53
<b>4</b>	0.933	-0.550	87	-102	5.24	0.38

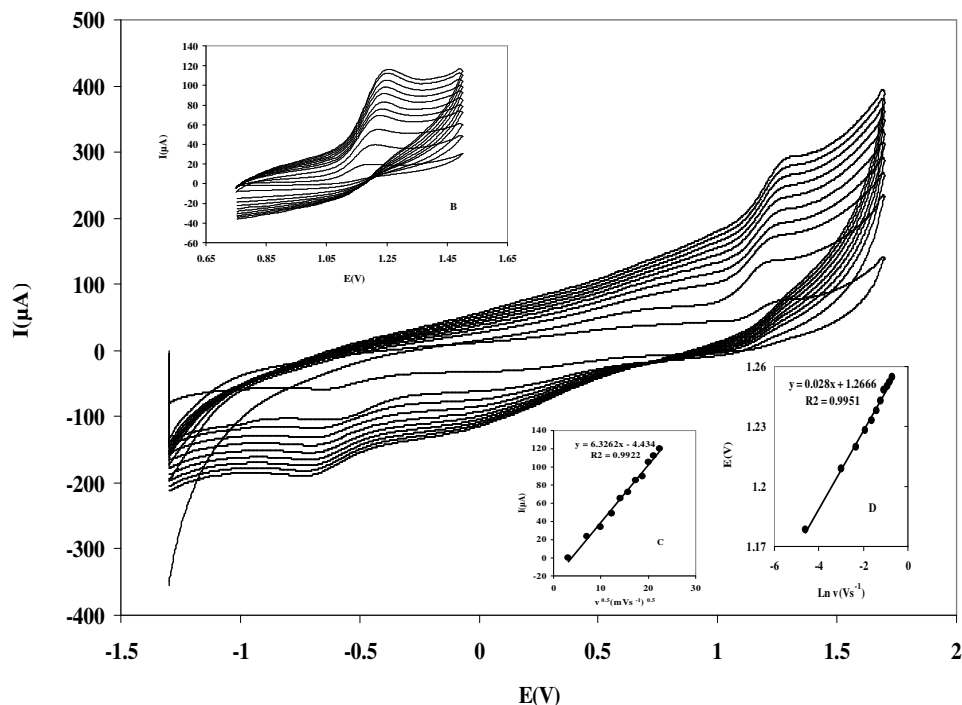


Fig. 1. A: Cyclic voltammograms of the GC electrode in 0.1 M tetrabutylammonium perchlorate solution in the presence of 0.1 M the complex **1** at various potential sweep rates of 10, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600 ( $\text{mV s}^{-1}$ ). B: typical cyclic voltammograms in the oxidation range of the GC electrode in 0.1 M tetrabutylammonium perchlorate solution. B: Dependence of anodic peak current during the forward sweep on the square roots of potential sweep rate. C: Dependence of the peak potential on  $\log v$  for the oxidation of the complex **1** at GC electrode obtained from the data of panel (A)

**Chronoamperometry:** Chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the rate constant on the GC surface. Fig. 2A shows chronoamperograms for the GC electrode in the absence (a) and presence: 0.01 (b), 0.03 (c), 0.05 (d), 0.07M (e), 0.09 (f), 0.1 (g) 0.15 (h) and 0.2M (i) of the complex **1** over a concentration range of 0.001-0.2 (M). The applied potential steps were 560 mV. The plot of net current *versus*  $t^{-0.5}/\text{s}^{-0.5}$  which has been obtained by removing the background current by the point-by-point subtraction method gives a straight line, Fig. 2B. This indicates that the transient current must be controlled by a diffusion process. The transient current is due to oxidation of the complex **1** and the current increases as its concentration is raised. We can obtain the diffusion coefficients of the complex **1** according to the Cottrell equation<sup>23</sup>:

$$I = nFAD^{1/2}C^* \pi^{-1/2}t^{-1/2} \quad (1)$$

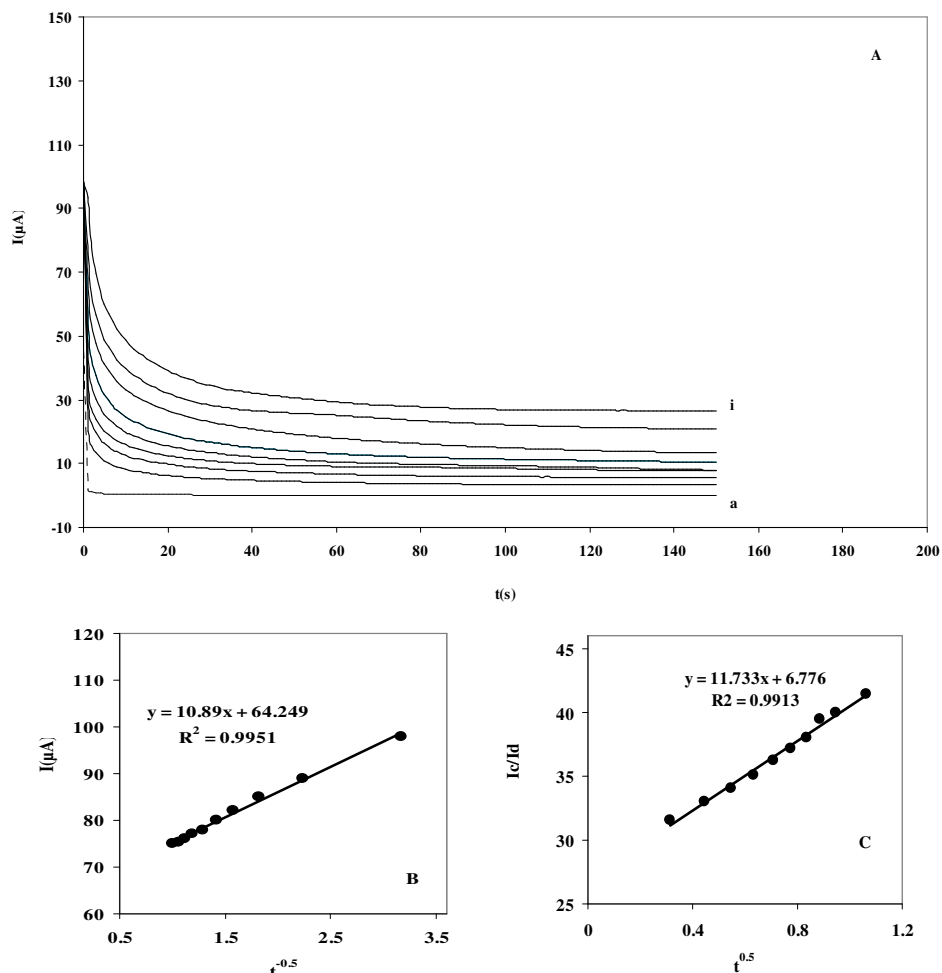


Fig. 2. A: chronoamperograms of GC electrode in 0.1 M tetrabutylammonium perchlorate solution containing the complex **1** with different concentrations of 0 (a), 0.01 (b), 0.03 (c), 0.05 (d), 0.07 M (e), 0.09 (f), 0.1 (g), 0.15 (h) and 0.2 M (i) respectively. Potential steps were 1.3 V. B: The plot of net current of chronoamperogram of GC electrode in 0.15 M the complex **1** (obtained by subtracting the background current using the point-by-point subtracting method) vs.  $t^{-0.5}$ . C: Dependence of  $I_c/I_d$  on  $t^{0.5}$  derived from the data of chronoamperograms of a and i in part A

where  $D$  is the diffusion coefficient and  $C^*$  is the bulk concentration. The mean value of the diffusion coefficients of the complex **1** was founded to be  $(6.11 \pm 0.02) \times 10^{-7} \text{ (cm}^2 \text{ s}^{-1}\text{)}$ . These values are in agreement with those obtained using cyclic voltammetry (Fig. 1).

The rate constants of the reactions of the complex **1** and the ensued intermediates with the redox sites of the GC electrode can be derived from the chronoamperograms according to previous report<sup>14</sup>:

$$\frac{I_c}{I_d} = \lambda^{1/2} \left[ \pi^{1/2} \operatorname{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}} \right] \quad (2)$$

where  $I_c$  is the catalytic current in the presence of the complex **1**,  $I_d$  the limiting current in the absence of the complex **1** and  $\lambda = kCt$  ( $k$ ,  $C$  and  $t$  are the catalytic rate constant, bulk concentration of the complex **1** and the elapsed time, respectively) is the argument of the error function. For  $\lambda > 1.5$ ,  $\operatorname{erf}(\lambda^{1/2})$  almost equals unity and equation (11) reduces to:

$$\frac{I_c}{I_d} = \lambda^{1/2} \pi^{1/2} = \pi^{1/2} (kCt)^{1/2} \quad (3)$$

From the slope of the  $I_c/I_d$  plot the value of  $k$  at a given concentration of the complex **1** is derived. The mean value of  $k$  in the concentration range of 0.01-0.2 (M) was found to be  $(8.55 \pm 0.03) \times 10^{+4}$  ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ).

Similar chronoamperograms were collected for other complexes. The values of  $D$  and  $k$  obtained according to the method described in the above for these carbohydrates were reported in Table-5.

TABLE-5  
VALUES OF THE REACTION RATE CONSTANTS (K) AND THE  
DIFFUSION COEFFICIENTS (D) FOR Co(II) COMPLEXES IN  
DMF 0.1 M TETRABUTYLAMMONIUM

Compound	D ( $\text{cm}^2/\text{s}$ ) $\times 10^{-7}$	k ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) $\times 10^4$
<b>1</b>	6.11	8.55
<b>2</b>	6.42	6.24
<b>3</b>	9.33	0.94
<b>4</b>	2.11	4.71

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