

Synthesis, Characterization and Electrochemical Properties of μ -Oxalato Copper(II) and Nickel(II) Complexes of Anthranilic Acid Schiff Base Ligands

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Three copper(II) and three nickel(II) dinuclear oxalate-bridged compounds: $[\{\text{Cu}(\text{antrasal})\}_2\text{ox}]$ (**1**), $[\{\text{Cu}(\text{anrathio})\}_2\text{ox}]$ (**2**), $[\{\text{Cu}(\text{antrafur})\}_2\text{ox}]$ (**3**), $[\{\text{Ni}(\text{antrasal})\}_2\text{ox}]$ (**4**), $[\{\text{Ni}(\text{anrathio})\}_2\text{ox}]$ (**5**) and $[\{\text{Ni}(\text{antrafur})\}_2\text{ox}]$ (**6**) were prepared [antrasalH, anrathioH and antrafurH is the Schiff base formed by the condensation of anthranilic acid and salicylaldehyde, thiophene-2-carbaldehyde and furfural, respectively, ox = oxalate]. The oxalate-bridged binuclear metal complexes have been characterized by UV-Vis, IR and ^1H NMR spectra and elemental analysis. The electrochemical behaviour of metal(II) complexes with Schiff-base ligands has been investigated by cyclic voltammetry and chronoamperometry techniques. The obtained results allow to assign anodic peaks at 1.1, 1.719 and 1.258 V to oxidation of Cu(II) to Cu(III) for: $[\{\text{Cu}(\text{antrasal})\}_2\text{ox}]$, $[\{\text{Cu}(\text{anrathio})\}_2\text{ox}]$ and $[\{\text{Cu}(\text{antrafur})\}_2\text{ox}]$, respectively and peaks at 1.125, 0.983 and 1.208 V to oxidation of Ni(II) to Ni(III) for $[\{\text{Ni}(\text{antrasal})\}_2\text{ox}]$, $[\{\text{Ni}(\text{anrathio})\}_2\text{ox}]$ and $[\{\text{Ni}(\text{antrafur})\}_2\text{ox}]$, respectively. Coefficient and diffusion coefficients were determined for these complexes. The obtained results of cyclic voltammetry and chronoamperometry showed that the total limit current of each of the studied compounds corresponds to one-electron transfer process.

Key Words: Synthesis, Electrochemical properties, Copper(II), Nickel(II), Complexes, Tridentate Schiff bases.

INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, *e.g.*, their ability to reversibly bind oxygen and complexing ability towards some toxic metals¹.

Salen type complexes have been known since 1933 and are now the most important stereochemical models in main group and transition metal coordination chemistry²⁻⁴.

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For the last few decades the bi- and polynuclear metal complexes containing oxalate as bridging ligands have been widely studied due to their applications in various fields such as biology, chemistry, catalysis and photochemistry⁵⁻⁸. A number of studies have been carried out on the preparation and characterization of binuclear complexes of *d* and *f* metal ions with Schiff bases and ligands with different types of coordination sites⁹. It is established that the number and type of donor atoms bonded to a metal ion have a profound effect on the chemical and physical properties associated with the metal ions. It is well known that Schiff base ligands obtained from salicylaldehyde and mono- or polyamines with donor sets ON, O₂N₂, O₂N₃ and O₂N₄ give rise to nickel(II) and copper(II) complexes with coordination numbers 4, 5 and 6¹⁰. Schiff bases of salicylaldehyde with amino- and aminoalkylpyridines are structurally related to compounds participating in vitamin B₆ chemistry and are therefore attractive as model systems for the study of biological equilibria¹¹⁻¹⁴ and their copper(II) complexes have been under investigation for several years mainly due to the fact they are of interest to many fields of inorganic biochemistry¹⁵. In metal complexes of salen derivatives, the environment at the coordination center can be modified by attaching different substituents to the ligand, which provides a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity⁴. The binuclear copper(II) complexes with *bis*-bidentate bridging ligands in particular have been investigated, both experimentally and theoretically¹⁵⁻¹⁸. The influence of the different substituents on the superexchange mechanism of binuclear oxalate-bridged copper(II) complexes was studied^{19,20}. In the present paper we describe the synthesis, characterization and electrochemical behaviour of copper(II) and nickel(II) complexes of tridentate Schiff bases derived from the 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, Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·6H₂O. The elemental analysis was made using Heareus CHN-O-RAPID analyzer. FTIR spectra were recorded on a Shimadzu model Prestije 21 spectrophotometer using KBr discs. Electronic spectra of the metal complexes were recorded on UV-1700 Pharmaspec UV-vis spectrophotometer Shimadzu. Cyclic voltammetry experiments were performed using an AUTOLAB potentiostat/galvanostat model PGSTAT30. Cyclic voltammograms (CVs) were obtained using an Autolab modular electrochemical system (Eco chimie, Ulterecht, The Netherlands) equipped with a PGSTAT 20 module and driven by GPES (Eco chimie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/Ag Cl (Saturated KCl)/3 M KCl reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode, (Metrohm 0.0314 cm²) were employed for the electrochemical studies. 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 ligands were prepared according to literature methods as follow: The three Schiff base ligands antrasalH, antrathioH and antrafurH were prepared by refluxing a solution of salicylaldehyde (2.09 mL, 20 mmol) or thiophene-2-carboxaldehyde (1.84 mL, 20 mmol) or furfural (1.65 mL, 20 mmol) with anthranilic acid (2.74 g, 20 mmol) in ethanol (25 mL) respectively, then allowed to cool to room temperature. The product was filtered off, recrystallized from ethanol and dried in a desiccator over anhydrous CaCl₂.

The analytical and physical data of the ligands are: Compound: antrasalH- m.f.: C₁₄H₁₁NO₃, m.w.: 241.3 g mol⁻¹, m.p.: 196 °C, elemental analysis (%): C, 69.69; H, 4.59; N, 5.80. Found: C, 69.68; H, 4.5; N, 5.72, ¹H NMR (ppm, CDCl₃): 11-12 (s, 1H, COOH), 6.5-8 (m, 8H, 8ArH), 9.9 (s, 1H, azomethine). IR (KBr, cm⁻¹): ν(OH) 3450, ν_{asym}(COO) 1584, ν_{sym}(COO) 1343, ν(C=O) 1668, ν(C=N) 1612.

Compound: antrathioH- m.f.: C₁₂H₉NO₂S, m.w.: 231.87 g mol⁻¹, m.p. = 125 °C, elemental analysis (%): C, 62.16; H, 3.91; N, 6.04. Found: C, 62.40; H, 3.77; N, 6.39, ¹H NMR (ppm, CDCl₃): 9.95 (s, 1H, COOH), 6.48-8.12 (m, 8H, 4ArH, 1-azomethine, 3-thiopheneH). IR (KBr, cm⁻¹): ν(OH) 3484, ν_{asym}(COO) 1589, ν_{sym}(COO) 1422, ν(C=O) 1706, ν(C=N) 1605.

Compound: antrafurH- m.f.: C₁₂H₉NO₃, m.w.: 215.21 g mol⁻¹, m.p. = 227 °C, elemental analysis (%): C, 66.97; H, 4.21; N, 6.51. Found: C, 66.82; H, 4.1; N, 6.4, ¹H NMR (ppm, CDCl₃): 9.93 (s, 1H, COOH), 6.3-8.23 (m, 8H, 4ArH, 1-azomethine, 3-furan). IR (KBr, cm⁻¹): ν(OH) 3317, ν_{asym}(COO) 1577, ν_{sym}(COO) 1373, ν(C=O) 1732, ν(C=N) 1617.

Synthesis of metal complexes: The ethanolic solution of Cu(NO₃)₂·3H₂O (20 mmol, 4.83 g) or Ni(NO₃)₂·6H₂O (20 mmol, 5.82 g) was added to a stirred solution of the respective ligand, followed by the addition of an ethanolic solution of sodium oxalate (10 mmol). The resulting mixture was stirred under reflux for 1 h whereupon the metal complexes were precipitated. The precipitated solid complexes were filtered, recrystallized and dried in vacuum desiccator over anhydrous CaCl₂. These complexes are stable in air, soluble in DMF and DMSO, insoluble in most organic solvents. The copper and nickel complexes of antrasalH, antrathioH and antrafurH is shown [Cu(antrasal)₂ox] (1), [Cu(antrathio)₂ox] (2), [Cu(antrafur)₂ox] (3), [Ni(antrasal)₂ox] (4), [Ni(antrathio)₂ox] (5), [Ni(antrafur)₂ox] (6), respectively.

Compound (1): [Cu(antrasal)₂ox]- m.f.: C₃₀H₁₈N₂O₁₀Cu₂, m.w.: 693.57 g mol⁻¹, m.p. = 243 °C. Elemental analysis (%): C, 51.95; H, 2.62; N, 4.04. Found: C, 48.10; H, 2.59; N, 5.55. UV-Vis in DMF λ_{max} = 259, 284, > 400 nm. IR (KBr, cm⁻¹): ν(OH) 3439, ν_{asym}(COO) 1570, ν_{sym}(COO) 1383, ν(C=O) 1619, ν(C=N) 1592, ν_{asym}(CO) 1637, ν_{sym}(CO) 1316 and δ(CO) 753.

Compound (2): [Cu(antrathio)₂ox]- m.f.: C₂₆H₁₆N₂S₂O₈Cu₂, m.w.: 676.83 g mol⁻¹, m.p = 293 decomposed. elemental analysis (%): C, 46.14; H, 2.38; N, 4.55. Found: C, 46.10; H, 2.31; N, 4.14. UV-Vis in DMF λ_{max} = 270, 335, 422 nm. IR

(KBr, cm^{-1}): $\nu(\text{OH})$ 3286, $\nu_{\text{asym}}(\text{COO})$ 1570, $\nu_{\text{sym}}(\text{COO})$ 1383, $\nu(\text{C=O})$ 1619, $\nu(\text{C=N})$ 1600, $\nu_{\text{asym}}(\text{CO})$ 1641, $\nu_{\text{sym}}(\text{CO})$ 1328 and $\delta(\text{CO})$ 765.

Compound (3): [$\{\text{Cu}(\text{antrafur})\}_2\text{ox}$]- m.f.: $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_{10}\text{Cu}_2$, m.w.: 643.51 g mol^{-1} , m.p. = 284 °C. Elemental analysis (%): C, 48.53; H, 2.51; N, 4.35. Found: C, 48.47; H, 2.40; N, 4.31. UV-Vis in DMF $\lambda_{\text{max}} = 263, 335, 400$ nm. IR (KBr, cm^{-1}): $\nu(\text{OH})$ 3275, $\nu_{\text{asym}}(\text{COO})$ 1530, $\nu_{\text{sym}}(\text{COO})$ 1389, $\nu(\text{C=O})$ 1624, $\nu(\text{C=N})$ 1604, $\nu_{\text{asym}}(\text{CO})$ 1639, $\nu_{\text{sym}}(\text{CO})$ 1323 and $\delta(\text{CO})$ 762.

Compound (4): [$\{\text{Ni}(\text{antrasal})\}_2\text{ox}$]- m.f.: $\text{C}_{30}\text{H}_{18}\text{N}_2\text{O}_{10}\text{Ni}_2$, m.w.: 683.87 g mol^{-1} , m.p. = 257 °C decompose. Elemental analysis (%): C, 52.69; H, 2.65; N, 4.09. Found: C, 51.09; H, 2.52; N, 5.53. UV-Vis in DMF $\lambda_{\text{max}} = 268, 323, 421$ nm. IR (KBr, cm^{-1}): $\nu(\text{OH})$ 3442, $\nu_{\text{asym}}(\text{COO})$ 1571, $\nu_{\text{sym}}(\text{COO})$ 1335, $\nu(\text{C=O})$ 1614, $\nu(\text{C=N})$ 1586, $\nu_{\text{asym}}(\text{CO})$ 1639, $\nu_{\text{sym}}(\text{CO})$ 1319 and $\delta(\text{CO})$ 758.

Compound (5): [$\{\text{Ni}(\text{anrathio})\}_2\text{ox}$]- m.f.: $\text{C}_{26}\text{H}_{16}\text{N}_2\text{S}_2\text{O}_8\text{Ni}_2$, m.w.: 667.12 g mol^{-1} , m.p. = 273 °C decomposed. Elemental analysis (%): C, 46.81; H, 2.42; N, 4.2. Found: C, 46.78; H, 2.37; N, 4.22. UV-Vis in DMF $\lambda_{\text{max}} = 263, 336, > 400$ nm. IR (KBr, cm^{-1}): $\nu(\text{OH})$ 3308, $\nu_{\text{asym}}(\text{COO})$ 1578, $\nu_{\text{sym}}(\text{COO})$ 1408, $\nu(\text{C=O})$ 1617, $\nu(\text{C=N})$ 1593, $\nu_{\text{asym}}(\text{CO})$ 1644, $\nu_{\text{sym}}(\text{CO})$ 1316 and $\delta(\text{CO})$ 791.

Compound (6): [$\{\text{Ni}(\text{antrafur})\}_2\text{ox}$]- m.f.: $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_{10}\text{Ni}_2$, m.w.: 633.80 g mol^{-1} , m.p. = 264 °C decompose. Elemental analysis (%): C, 49.27; H, 2.54; N, 4.42. Found: C, 49.23; H, 2.57; N, 4.46. UV-Vis in DMF $\lambda_{\text{max}} = 269, 340, 400$ nm. IR (KBr, cm^{-1}): $\nu(\text{OH})$ 3305, $\nu_{\text{asym}}(\text{COO})$ 1543, $\nu_{\text{sym}}(\text{COO})$ 1408, $\nu(\text{C=O})$ 1616, $\nu(\text{C=N})$ 1589, $\nu_{\text{asym}}(\text{CO})$ 1649, $\nu_{\text{sym}}(\text{CO})$ 1372 and $\delta(\text{CO})$ 781.

RESULTS AND DISCUSSION

The elemental analyses and UV-Vis spectral data of the complexes are given. The obtained results are in good agreement with those calculated for the suggested formulae. The complexes are soluble in DMF and DMSO and are insoluble in some common organic solvents.

The mode of binding of Schiff base ligands to the metal ion was elucidated by recording the IR spectra of the complexes as compared with the spectra of the free ligands. The spectra of two free ligands show two strong bands at 1612, 1605 and 1617 cm^{-1} characteristics of the $\nu(\text{C=N})$ (azomethine) stretching mode for (antrasalH), (anrathioH) and (antrafurH) respectively^{21,22}. These bands are shifted to lower frequency in the 1592, 1600 and 1589-1604 cm^{-1} range indicating the coordination of the azomethine nitrogen atom to the central metal ions²⁰. The $\nu(\text{OH})$, $\nu(\text{C=O})$, $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ stretching vibrations are observed at 3450, 1668, 1584 and 1343 cm^{-1} for (antrasalH) ligand. The participation of the carboxylate O atom in the complexes formation was evidenced from the shift in position of these bands to 3442-3439, 1619-1614, 1571-1570 and 1383-1335 cm^{-1} for antrasalH-metal complexes^{21,22}. The $\nu(\text{OH})$, $\nu(\text{C=O})$, $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ stretching vibrations are observed at 3484, 1706, 1589 and 1422 cm^{-1} for (anrathioH) ligand. The participation of the carboxylate O atom in the complexes formation was

evidenced from the shift in position of these bands to 3308-3286, 1619-1617, 1578-1570 and 1408-1382 cm^{-1} for antrathioH-metal complexes^{21,22}. 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 3317, 1732, 1577 and 1373 cm^{-1} for (antrafurH) ligand. The participation of the carboxylate O atom in the complexes formation was evidenced from the shift in position of these bands to 3305-3275, 1624-1616, 1543-1530 and 1408-1389 cm^{-1} for antrafurH-metal complexes^{21,22}. The occurrence of tetradentate oxalate is clearly observed in the IR spectrum of the complexes: the $\nu_{\text{asym}}(\text{CO})$ 1649-1637, $\nu_{\text{sym}}(\text{CO})$ 1372-1316 and $\delta(\text{CO})$ 791-753 cm^{-1} bands agree very well with those reported for similar Ni and Cu complexes²³.

The absorption spectra were measured in DMF solution at λ ranging from 190 to 1000 nm. For Schiff base (antrasalH) shows sharp bands at 267 and 324 nm, these bands can be attributed to π - π^* and n - π^* transitions and the complexes (**1**, **4**) showed bands in the range 259, 284, 407 nm for (**1**) and 268, 323, 421 nm for (**4**). The d - d bands are not observed due to the low concentration (*ca.* 10^{-4} mol dm^{-3}) of the complex solution. These bands should be low in intensity in the region of 500-600 nm.

For Schiff base (antrathioH) shows sharp bands at 220, 280 and 320 nm, these bands can be attributed to π - π^* and n - π^* transitions and the complexes (**2**, **5**) showed bands in the range 270, 335, 422 nm for (**2**) and 263, 336, > 400 nm. The d - d bands are not observed due to the low concentration (*ca.* 10^{-4} mol dm^{-3}) of the complex solution. These bands should be low in intensity in the region of 500-600 nm.

The UV-Vis spectrum of complexes (**3**, **6**) showed bands at 263, 335, 400 nm for (**3**) and 269, 340, 400 nm for (**6**).

The cyclic-voltammetric behaviour of 0.001 M of Schiff base compounds (**1-6**) was investigated in alkaline solutions. The voltammograms of the studied compounds in alkaline solution at different scan rates ranging (100-500 mV/s) exhibit two well defined anodic peaks on alkaline solution (Fig. 1A). The extent of the anodic shift of the peak (E_p) as a function of the sweep rate, the difference between the potentials at half-peak ($E_{p/2}$) and at the peak (E_p), confirm the irreversible nature of the electrode process²⁴. So, the anodic peak potential (E_p) varies with the logarithm of the potential sweep rate according to the following equation²⁵:

$$E_p = -1.14 \left(\frac{RT}{\alpha n_a F} \right) + \left(\frac{RT}{\alpha n_a F} \right) \ln \left(\frac{k_{f,h}}{D^{1/2}} \right) - \left(\frac{RT}{2\alpha n_a F} \right) \ln(\alpha n_a v) \quad (1)$$

On the plotting E_p or $E_{p/2}$ for the investigated compound *vs.* $\log v$, linear correlations are obtained and the anodic symmetry coefficient (α) values were calculated from the slope of these plots. Values of the symmetry coefficient (α) were also determined from the difference of peak and half-peak anodic potentials by means of the following equation:

$$E_p - E_{p/2} = 1.875 \left(\frac{RT}{\alpha n_a F} \right) \quad (2)$$

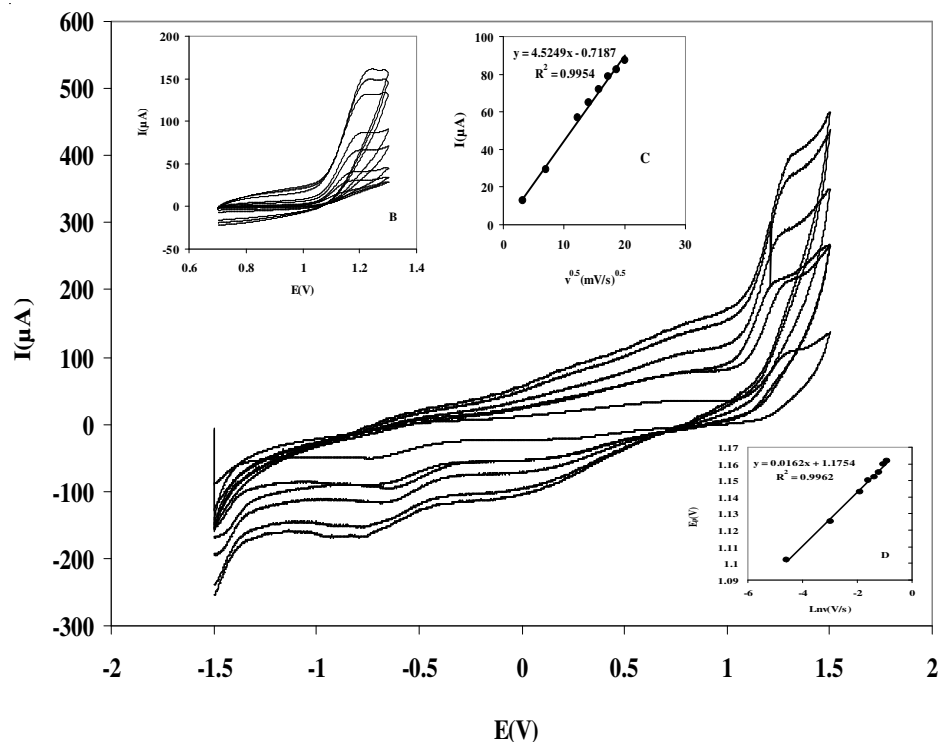


Fig. 1. A: Cyclic voltammograms of the glassy carbon electrode in 0.1 M tetrabutylammonium perchlorate solution in the presence of 0.1 M $[\text{Cu}(\text{antrasal})_2]\text{ox}$ at various potential sweep rates of 100, 200, 250, 300, 400 and 500 (mV s^{-1}). B: typical cyclic voltammograms in the oxidation range of the GC electrode in 0.1 M tetrabutylammonium perchlorate solution. C: Dependence of anodic peak current during the forward sweep on the square roots of potential sweep rate. D: Dependence of the peak potential on $\log v$ for the oxidation of $[\text{Cu}(\text{antrasal})_2]\text{ox}$ at glassy carbon electrode obtained from the data of panel (A)

And were found to be less than 0.5 when $n_a = 1$ (Table-1), confirming the irreversible nature of the oxidation process.

TABLE-1
DATA OF CYCLIC VOLTAMMETRY FOR COMPOUND
UNDER INVESTIGATION AT 25 °C, $v = 0.5$ V/s

Compound	$E_p - E_{p/2}$ (mV)	D ($\text{cm}^2/\text{s}) \times 10^{-7}$	α
$[\text{Cu}(\text{antrasal})_2]\text{ox}$	112	3.53	0.42
$[\text{Cu}(\text{antrafur})_2]\text{ox}$	115	5.94	0.41
$[\text{Cu}(\text{antrathio})_2]\text{ox}$	110	9.65	0.43
$[\text{Ni}(\text{antrasal})_2]\text{ox}$	120	10.06	0.40
$[\text{Ni}(\text{antrafur})_2]\text{ox}$	128	2.88	0.38
$[\text{Ni}(\text{antrathio})_2]\text{ox}$	132	4.50	0.38

For the irreversible charge transfer process²⁶, the peak current (I_{pirr}) can be expressed by the following equation:

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

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. On plotting I_{pirr} *vs.* $v^{1/2}$ straight lines with some slight deviation from the origin are obtained revealing the diffusion character of the current²⁷. The diffusion coefficient for $[Cu(\text{antrasal})_2\text{ox}]$ was calculated to be 3.53×10^{-7} ($\text{cm}^2 \text{s}^{-1}$). Similar cyclic voltammograms were collected for other complexes. The values of D and α obtained according to the method described in the above for these complexes were reported in Table-1.

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), 0.07 M (e), 0.09 (f), 0.1 (g) 0.15 (h) and 0.2M (i) of $[Cu(\text{antrasal})_2\text{ox}]$ over a concentration range of 0.001-0.2 (M). The applied potential steps were 1.27 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 $[Cu(\text{antrasal})_2\text{ox}]$ and the current increases as the $[Cu(\text{antrasal})_2\text{ox}]$ concentration is raised. We can obtain the diffusion coefficients of the (1) according to the Cottrell equation²⁷:

$$I = nFAD^{1/2}C^* \pi^{-1/2} t^{-1/2} \quad (4)$$

where D is the diffusion coefficient and C^* is the bulk concentration. The mean value of the diffusion coefficients of $[Cu(\text{antrasal})_2\text{ox}]$ was founded to be 4.61×10^{-7} ($\text{cm}^2 \text{s}^{-1}$). These value are in agreement with those obtained using cyclic voltammetry (Fig. 1).

The rate constants of the reactions of (1) and the ensued intermediates with the redox sites of the glassy carbon electrode can be derived from the chronoamperograms according to²⁷:

$$\frac{I_c}{I_d} = \lambda^{1/2} \left[\pi^{1/2} \text{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}} \right] \quad (5)$$

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

$$\frac{I_c}{I_d} = \lambda^{1/2} \pi^{1/2} = \pi^{1/2} (kCt)^{1/2} \quad (12)$$

From the slope of the I_c/I_d plot the value of k at a given concentration of (1) is derived. The mean value of k in the concentration range of 0.01-0.2 (M) was found to be 0.97×10^4 ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$).

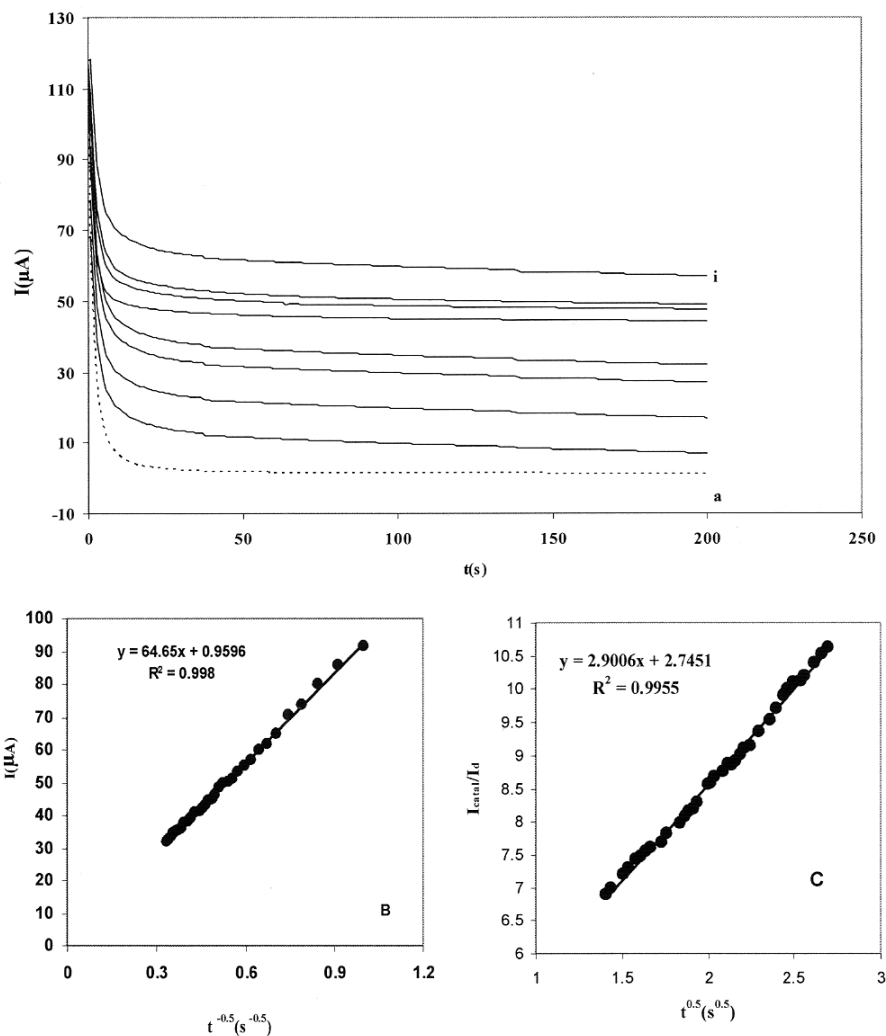


Fig. 2. A: chronoamperograms of GC electrode in 0.1 M tetrabutylammonium perchlorate solution containing $[\text{Cu}(\text{antrasal})_2\text{Ox}]$ with different concentrations of 0 (a), 0.01 (b), 0.03 (c), 0.05 (d), 0.07 M (e), 0.09 (f), 0.1 (g) 0.15 (h) and 0.2 M (i), respectively. Potential steps were 1.27 V. B: The plot of net current of chronoamperogram of GC electrode in 0.15 M $[\text{Cu}(\text{antrasal})_2\text{Ox}]$ (obtained by subtracting the background current using the point-by-point subtracting method) vs. $t^{-0.5}$. C: Dependence of I_{net}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of a and i in part A

Similar chronoamperograms were collected for other complexes. The values of D and k obtained according to the method described in the above for these complexes were reported in Table-2.

TABLE-2
VALUES OF THE REACTION RATE CONSTANTS (k) AND THE DIFFUSION
COEFFICIENTS (D) FOR Ni(II), Cu(II) COMPLEXES IN DMF 0.1 M
TETRABUTYL AMMONIUM

Compound	D (cm ² /s)×10 ⁻⁷	k (cm ³ mol ⁻¹ s ⁻¹) × 10 ⁴
[{Cu(antrasal)} ₂ ox]	4.61	0.97
[{Cu(antrafur)} ₂ ox]	8.80	1.11
[{Cu(antrathio)} ₂ ox]	3.26	2.44
[{Ni(antrasal)} ₂ ox]	4.98	0.89
[{Ni(antrafur)} ₂ ox]	4.32	8.62
[{Ni(antrathio)} ₂ ox]	8.44	2.59

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