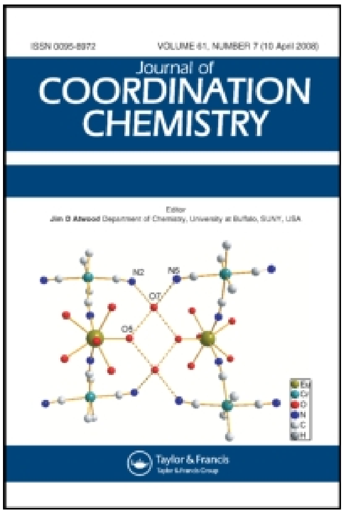

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Dinaphthotetraaza[14]annulene copper(II) complexes in the electrocatalytic reduction of carbon dioxide and bisulfite anion

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A modified synthetic route for the complexes [Cu(II)5,7,12,14-tetramethyldinaphtho [b,i][1,4,8,11]tetraaza[14]annulene], [Cu(II)tmdnTAA], and [Cu(II) 5,7,12,14-tetramethyl-6,13-dichloro-dinaphtho[b,i][1,4,8,11]tetraaza[14]annulene], [Cu(II)dCltmdnTAA], is presented in this work. The electrochemical characterization of both complexes and their precursors, [*bis*(2,4-pentanedionato)copper(II)], [Cu(II)(acac)$_2$] and [*bis*(3-chloro-2,4-pentanedionato)copper(II)], [Cu(II)(3-Cl-acac)$_2$], respectively, under nitrogen and carbon dioxide is also presented. The voltammetric response of [Cu(II)(acac)$_2$] and [Cu(II)(3-Cl-acac)$_2$] are different compared to [Cu(II)tmdnTAA] and [Cu(II)dCltmdnTAA] under nitrogen. Precursors show the reduction of Cu(I) to Cu(0) and the tetraazadinaphtho[14]annulene complexes do not. The chlorine substituted complex has a lower reduction potential than the unsubstituted homologue under nitrogen atmosphere. However, the contrary response is obtained in the presence of carbon dioxide: the unsubstituted complex is more catalytic in terms of potential because the current discharge appears 270 mV shifted to the anodic region. These facts can be explained in terms of electronic and steric effects. The modified electrode obtained by oxidative electropolymerization of [Cu(II)tmdnTAA] over glassy carbon electrode presented a suitable amperometric response for the sulfite reduction in acidic medium (pH = 2.7). A linear correlation was observed for the catalytic current and sulfite concentration between 0.6–6.0 mM range.

Keywords: Copper(II)tetraazadinaphtho[14]annulene; Copper(II)acetylacetone; Carbon dioxide reduction; Sulfite reduction

1. Introduction

There is growing interest in the synthesis of new macrocyclic ligands and transition metal complexes because they present electronic and structural characteristics that resemble some biological processes where the macrocyclic ligand plays an important role (see figure 1). One example is the macrocyclic ligand [(5,7,12,14)tetramethyldibenzo[b,i](1,4,8,11)tetra-aza[14]anuleno] (see figure 1b) [1, 2]. This fourteen-member macrocycle has four planar nitrogen atoms, where two of them can coordinate a cationic metal by losing two protons and becoming a dianion. The charge is localized in the 2,4-pentanediiminato backbone. In the neutral form, the dibenzo is an anti-aromatic system (4n), with a saddle-shaped structure. Also, the

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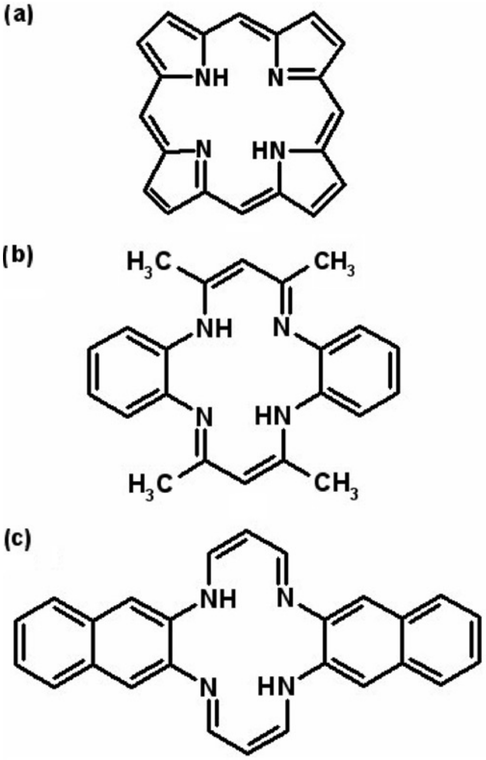

Figure 1. Molecular view of (a) porphyrin ring, (b) [(5,7,12,14)tetramethyldibenzo[b,i](1,4,8,11)tetra-aza[14]annulene], (H_2tmdbTAA), and (c) [dinaphtho[b,i](1,4,8,11)tetraaza[14]annulene], (H_2dnTAA).

molecular structure of (5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i](1,4,8,11)tetra-azacyclo-tetradecinate)copper(II) has been reported; the fourteen-member ring forms a saddle-like shape around the copper atom with the benzene rings and the diiminato chelate rings tilted on opposite sides of the "N_4" coordination plane [3a].

The synthesis and its experimental and theoretical characterization have been reported for a more unsaturated ligand, i.e. [dinaphtho[b,i][1,4,8,11]tetra-aza[14]annulene], where the molecular structure is similar to that reported for (5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i](1,4,8,11)tetraazacyclotetradecinate) copper(II) complex (see figure 1c) [3b]. Also, Costamagna *et al.* [4–8] have shown the synthesis, electrochemical, photochemical and photophysical properties of copper(II) and nickel(II) complexes with ligands derived from the ligand in figure 1(c). These complexes showed excited states with charge-separation, highly reactive excited states and luminescence from some states centered in the ligand backbone. These complexes also showed redox processes centered on the metal or on the ligand becoming good catalysts for the activation of molecular oxygen, carbon dioxide, sulfite [4, 5] and other small molecules.

Carbon dioxide and sulfur dioxide are small molecules of the utmost importance in environmental chemistry related issues such as the synthesis of ecologic fuels or the control of the greenhouse effect. Coordination compounds have shown electrocatalytic activity toward CO_2 and SO_2 and are promising because they allow rational optimization by designed modifications of their ligand or the central metal atom. On the basis of these precedents, we present the synthesis of two Cu(II)[dinaphtho[b,i][1,4,8,11]tetraaza[14]annulene] derivatives, their voltammetric responses under nitrogen and carbon dioxide in *N*,*N*-dimethylformamide solutions, and the electrocatalytic response of the modified electrode (CME) obtained by electropolymerization of [Cu(II)tmdnTAA] over glassy carbon for the sulfite reduction in aqueous solutions.

2. Experimental

2.1. *Materials and methods*

All reagents were of the highest grade available and used without further purification: 2,3-diaminonaphthalene, 99% (Sigma), copper(II)acetate, p.a. (Merck), 2,4-pentanodione (acetylacetone) (Merck), 3-chloro-2,4-pentanodione (3-chloro-acetylacetone) (Merck), methanol, p.a. (Merck), ethanol, p.a. (Merck), chloroform, p.a. (Merck), acetone, p.a. (Merck).

Elemental analysis of copper was performed in a Perkin Elmer 2380 AA spectrometer after an acid digestion (perchloric and nitric acid).

Melting points were measured with electrothermal IA9000 equipment.

IR-TF spectra were obtained in solid phase (KBr pellet) between 4000 and 400 cm^{-1} with a spectrophotometer Bruker IFS-66V.

UV-visible spectra were obtained in *N*,*N*-dimethylformamide (DMF) solutions using a Specord S100 along with Aspec Plus software.

The voltammetric characterization was performed using a VoltaLab PGZ 100 potentioscan along with Voltamaster 4 software. All the voltammetric measurements were performed in a conventional three compartment pyrex cell. The working electrode was a glassy carbon disk of 0.07 cm^2 area. The counter electrode was a Pt coil of high area and Ag/AgCl electrode was used as reference. In order to avoid contamination of the reference electrode, it was maintained in a hermetic tube with KCl solution, where the Luggin capillary was a Pt wire.

The modified electrode (CME) was obtained by oxidative electropolymerization onto glassy carbon electrode from dry acetonitrile solutions containing 1 mM [Cu(II)tmdnTAA] and 0.1 M $(C_2H_5)_4NClO_4$. The conducting polymer film increases the current intensity in each potential cycle between −0.1 and 1.1 V *versus* Ag/AgCl. The mechanism of the electropolymerization is similar to that observed by Deronzier and Marques [9] for oxidative electropolymerization of Ni(II) (and Cu(II))-dibenzo-14-annulene complexes, and Villagrán *et. al.* [10] for the oxidative electropolymerization of [Ni(II)tmdnTAA].

2.2. *Synthesis of the complexes*

Two general methods have been reported to synthesize [Cu(II) dinaphthotetraaza[14]-annulene] complexes [3, 4], namely (a) by reaction of the free ligand with $Cu(CH_3COO)_2 \cdot H_2O$ dissolved in *N*,*N*-dimethylformamide and (b) by reaction of 2,3-diaminonaphthalene with $Cu(CH_3COO)_2 \cdot H_2O$ to form an intermediate

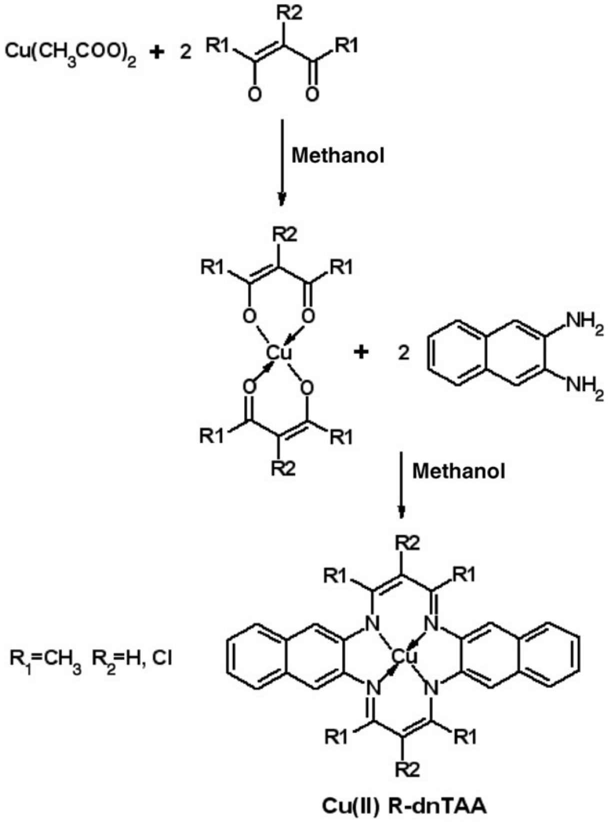

Figure 2. Scheme of synthesis for [Cu(II)tmdnTAA] and [Cu(II)dCltmdnTAA] macrocyclic complexes.

Cu(II)-(diaminonaphthalene)$_2$ and subsequent reaction with the corresponding diketone [4].

A modified (b) method has been used in this work, consisting of reaction of the diketone with $Cu(CH_3COO)_2 \cdot H_2O$ to form [Cu(II)(acac)$_2$] which is isolated and characterized. Then, this complex reacts with 2,3-diaminonaphthalene to obtain the tetraazamacrocycle, as shown in figure 2.

(1) [Cu(II)(acac)$_2$]. This precursor was prepared by the literature method [11]. $Cu(CH_3COO)_2 \cdot H_2O$ (500 mg, 5.0 mmol) was heated under reflux in 20 mL methanol and a methanol solution (10 mL) of 2,4-pentanedione (0.5 mL, 2.5 mmol) was slowly added. After the solution was cooled to room temperature a blue precipitate was removed by filtration.

(2) [Cu(II)(3-Cl-acac)$_2$]. This precursor was prepared by the same method as for [Cu(II)(acac)$_2$], but using 3-cloro-2,4-pentanedione.

(3) [Cu(II)5,7,12,14-tetramethyldinaphtho[b,i][1,4,8,11]tetraaza[14]annulene], [Cu(II) tmdnTAA]. A mixture of [Cu(II)(acac)$_2$] (265 mg, 0.95 mmol) and 2,3-diaminonaphthalene (300 mg, 1.90 mmol) was heated under reflux in 20 mL methanol for 20 h. After the solution was cooled to room temperature a dark brown precipitate was removed by filtration. Yield 30%, melting point >300°C; UV-visible spectrum, nm, in DMF ($\varepsilon \times 10^{-3}\,\mathrm{cm}^{-1}\,\mathrm{M}^{-1}$): 260(11.9), 294(9.7), 346(4.6), 420(2.0). Infrared spectrum, cm^{-1} (mode): 2921 ($\nu_{\mathrm{C–H}}$), 1628 ($\nu_{\mathrm{C=N}}$), 1578 ($\nu_{\mathrm{C–C}}$), 454 ($\nu_{\mathrm{Cu–N}}$).

(4) [Cu(II)5,7,12,14-tetramethyl-6,13-Cl-dinaphtho[b,i][1,4,8,11]tetraaza14]annulene], [Cu(II)dCltmdnTAA] was prepared by the same method as for [Cu(II)tmdnTAA] but using [Cu(II)(3-Cl-acac)$_2$] precursor (300 mg, 0.9 mmol) and 2,3-diaminonaphthalene (285 mg, 1.8 mmol). It was obtained in 42% yield as a dark brown amorphous powder. Melting point >300°C; UV-visible spectrum, nm, in DMF ($\varepsilon \times 10^{-3}\,\mathrm{cm}^{-1}\,\mathrm{M}^{-1}$)]: 263(13.3), 300(7.3), 347(5.0), 419(0.9). Infrared spectrum, cm^{-1} (mode): 3054 ($\nu_{\mathrm{C–H}}$), 1624 ($\nu_{\mathrm{C=N}}$), 1575 ($\nu_{\mathrm{C–C}}$), 750 ($\nu_{\mathrm{C–Cl}}$), 474 ($\nu_{\mathrm{Cu–N}}$).

3. Results and discussion

Figure 3 shows the voltammetric responses for [Cu(II)(acac)$_2$] and [Cu(II)tmdnTAA] under nitrogen. [Cu(II)(acac)$_2$] shows one wave in the anodic part (Ia) and a corresponding wave in the cathodic part (IVa). The difference between this anodic (E_{pa}) potential value and any corresponding cathodic wave (E_{pc}) is very large, suggesting an irreversible redox process.

Additionally, at potentials more positive than 0 V, there are two waves (IIa and IIIa) that correspond to irreversible processes (see table 1). The anodic peak IIa is attributed to the oxidation of Cu(0) to Cu(I). The occurrence of the second reduction wave in Cu(II)(acac)$_2$ implies that the $[\mathrm{Cu(0)(acac)_2}]^{2-}$ species are unstable and ligand loss readily occurs. The free copper(I) ion is quickly solvated before its final reduction to elemental copper, as it has been mentioned [12–14]. A similar voltammetric behavior is observed for the [Cu(II)(3-Cl-acac)$_2$] precursor. Taking into account these features, the overall reaction scheme for Cu(II)(acac)$_2$ may be expressed by the following equations (1) to (3):

$$\mathrm{Cu(II)(acac)} + 2\mathrm{e}^- \rightleftarrows \left[\mathrm{Cu(0)(acac)_2}\right]^{2-} \tag{1}$$

$$\left[\mathrm{Cu(0)(acac)_2}\right]^{2-} \rightarrow \mathrm{Cu(0)} + 2(\mathrm{acac})_2^{2-} \tag{2}$$

$$\mathrm{Cu(0)} \rightleftarrows \left[\mathrm{Cu^{+}(I)(s)}\right] + \mathrm{e}^- \tag{3}$$

The voltammetric response for [Cu(II)tmdnTAA] is very different: it shows one wave in the anodic part (Ib) and two corresponding waves in the cathodic part (VIb and VIIb). The difference between the potential value of the anodic (E_{pa}) and any corresponding cathodic wave (E_{pc}) is very large, which suggests an irreversible redox process. The cyclic voltammogram of this complex does not show the reduction of Cu(II) to Cu(0), and the demetalation process does not take place (see figure 3b) [14–16].

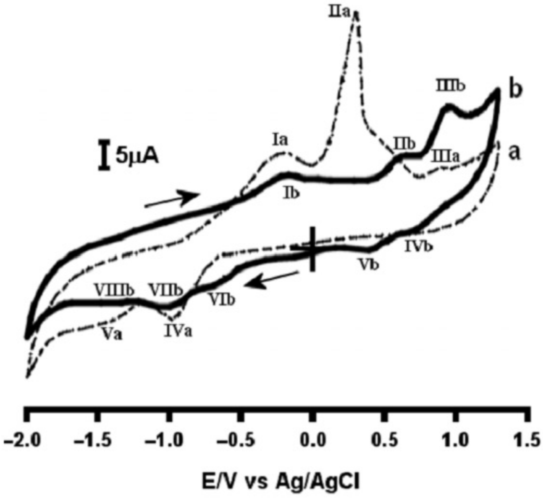

Figure 3. Cyclic voltammetry for (a): [Cu(II)(acac)$_2$] precursor (1×10^{-3} M) (------) and (b): [Cu(II)tmdnTAA] (1×10^{-3} M) (——) in DMF solution containing tetrethylammonium perchlorate (TEAP), scan rate 200 mV s^{-1} under nitrogen.

Table 1. Redox potentials for [Cu(II)(acac)$_2$] precursor and [Cu(II)tmdnTAA] and [Cu(II)dCltmdnTAA] macrocyclic complexes.

Compound	E_{pc} (V)	E_{pa} (V)	ΔE (V)	Peak
Cu(II)(acac)$_2$	–	0.20	–	Ia
	–	0.30	–	II
	–	0.87	–	IIIa
	−0.98	–	–	IVa
	−1.45	–	–	Va
Cu(II)tmdnTAA	−0.16	–	–	Ib
	0.40	0.60	0.20	Vb, IIb
	0.70	0.94	0.24	IVb, IIIb
	−0.70	–	–	VIb
	−1.03	–	–	VIIb
	−1.39	–	–	VIIIb
Cu(II)dCltmdnTAA	−0.18	–	–	Ic
	0.40	0.67	0.27	IIc, Vc
	0.75	0.93	0.18	IVc, IIIc
	−0.65	–	–	VIc
	−1.03	–	–	VIIc
	−1.40	–	–	VIIIc

[Cu(II)tmdnTAA] and [Cu(II)-CltmdnTAA] under nitrogen atmosphere. The [Cu(II)tmdnTAA] complex has reduction and oxidation processes associated to the macrocycle backbone and also redox processes metal centered (see figure 4). The quasi-reversible peak located at $E_{pa} = 0.60$ V and $E_{pc} = 0.40$ V (IIb and Vb respectively, figure 4) correspond to Cu(II)/Cu(III) couple, in agreement with the assignments reported by Bereman *et al.* for [Cu(II)5,7,12,14-tetraphenyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene] [15]. Furthermore, the irreversible process located at $E_{pa} = 0.94$ V (IIIb, figure 4)

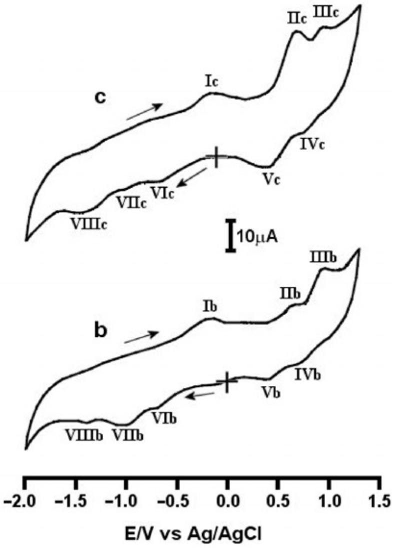

Figure 4. Cyclic voltammetry for (c): [Cu(II)dCltmdnTAA] (1×10^{-3} M) and (b): [Cu(II)tmdnTAA] (1×10^{-3} M) containing tetraethylammonium perchlorate (TEAP), scan rate 200 mV s^{-1} under nitrogen.

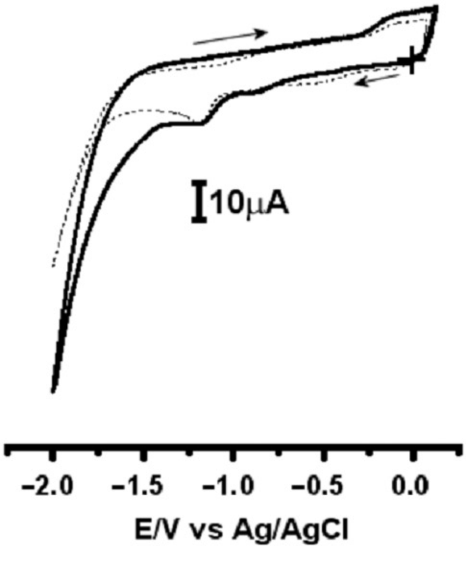

Figure 5. Cyclic voltammetry for [Cu(II)tmdnTAA] (——) and [Cu(II)dCltmdnTAA] (- - - - - -) (1×10^{-3} M) complexes containing tetraethylammonium perchlorate (TEAP) under carbon dioxide, scan rate 200 mV s^{-1}.

corresponds to an oxidation centered in the ligand, as described by Walsh *et al.* in electrochemical studies with macrocyclic complexes with tetraazannulene ligands [16]. In the cathodic region three quasi-reversible processes located at $E_{pc} = -0.70$ V, $E_{pc} = -1.03$ V, and $E_{pc} = -1.39$ V are observed (VIb, VIIb and VIIIb,

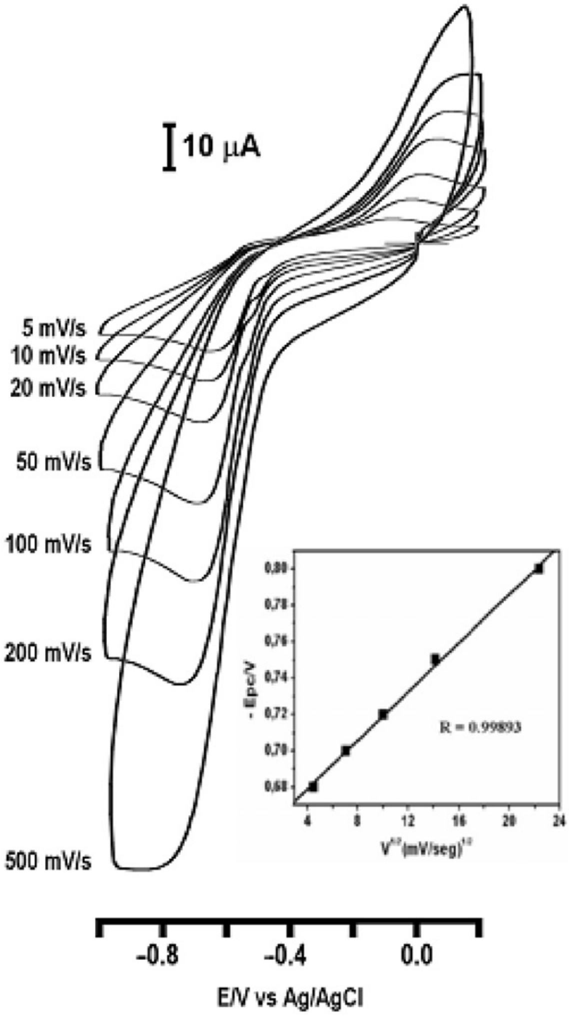

Figure 6. Cyclic voltammetry for bisulfite reduction over poly-[Cu-tmdnTAA]/glassy carbon electrode (in pH = 2.7 buffer) at different scan rates in $\mathrm{mV\,s^{-1}}$. The inset shows the plot of $-E_{pc}$ *vs.* $v^{1/2}$.

respectively, figure 4). It is not straightforward to assign which of these three cathodic peaks correspond to metal-centered or ligand-centered processes. The peak VIb, figure 4, could correspond to a metal-centered process and the other processes could correspond to the macrocycle, in analogy to similar studies reported for Cu(II) and Ni(II) macrocycle complexes with tetraazannulene ligands [4, 8].

The [Cu(II)dCltmdnTAA] complex presents similar voltammetric behavior to [Cu(II)tmdnTAA]. However, the chlorine subtituents in the 2,4-pentanediiminato backbone of the macrocycle shift the cathodic potential ca 50 mV to more positive values, under nitrogen atmosphere (see VIc, table 1, figure 4).

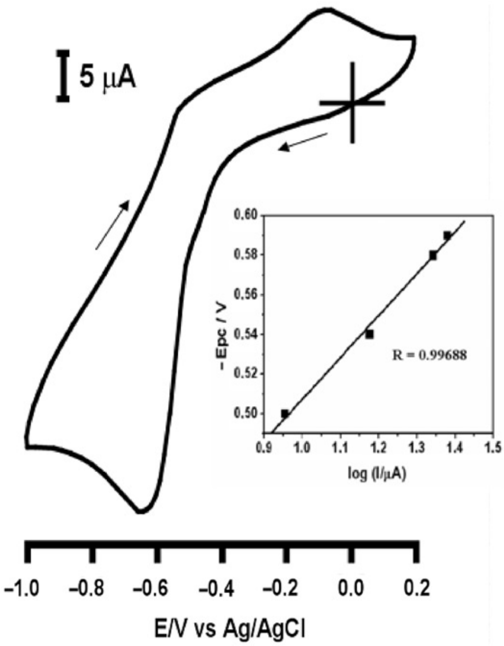

Figure 7. Cyclic voltammetry for the bisulfite reduction over poly-[Cu-tmdnTAA]/glassy carbon electrode (in pH = 2.7 buffer) at 5 mV s^{-1}. The inset shows the Tafel plot of $-E_{pc}$ *vs.* log IμA^{-1}.

[Cu(II)tmdnTAA] and [Cu(II)dCltmdnTAA] under carbon dioxide atmosphere. The [Cu(II)tmdnTAA] and [Cu(II)dCltmdnTAA] complexes show similar voltammetric behavior under carbon dioxide. However, [Cu(II)tmdnTAA] does reduce carbon dioxide (at $E_{pc} = -1.45$ V, 270 mV) at more positive potential than [Cu(II)dCltmdnTAA], $E_{pc} = -1.72$ V. The metal center in its lower oxiadtion state, i.e. Cu(I) is the active site, as shown by Costamagna *et al.* [17]. The metal center is oxidized in the presence of carbon dioxide with concomitant formation of an adduct. It would be difficult to stabilize this adduct in the case of [Cu(II)dCltmdnTAA] because the steric hindrance of the chlorine atoms. Therefore, the unsubstituted [Cu(II)tmdnTAA] complex is a better electrocatalyst for carbon dioxide activation (see figure 5). The electrocatalytic reduction of carbon dioxide needs water to proceed and the evolution of hydrogen is always a competitive reaction in the same potential region [8].

Poly-[Cu(II)-tmdnTAA]/glassy Carbon Modified Electrode(CME) in the electrocatalytic reduction of sulfite. In aqueous solution at pH = 2.7 the sulfite equilibrium is dominated by bisulfite species [18], as shown in equation (4).

$$SO_3^{2-} + H^+ = HSO_3^- \tag{4}$$

Figure 6 shows the voltammetric response of the modified electrode at different scan rates, which indicates an $-E_{pc}$ shift to negative values when the scan rate is increased,

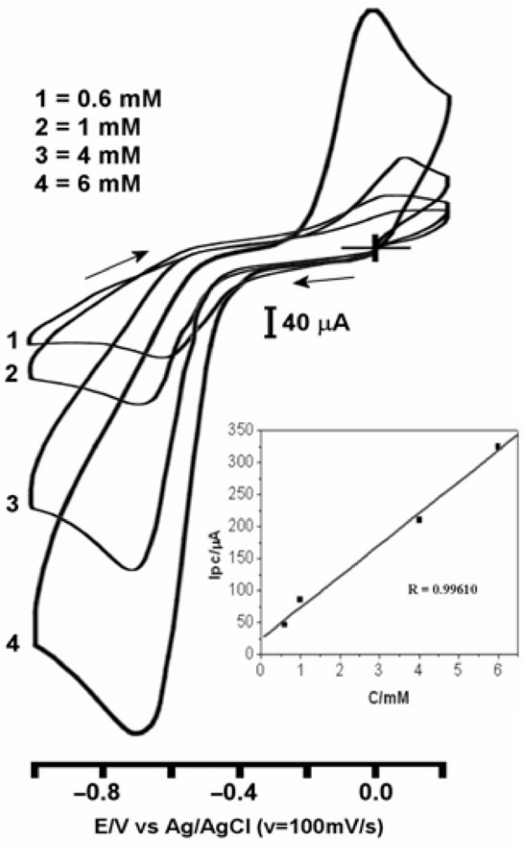

Figure 8. Cyclic voltammetry over poly-[Cu-tmdnTAA]/glassy carbon electrode at $pH = 2.7$ at $200\,mV\,s^{-1}$ for bisulfite at different concentrations. The inset shows the calibration curve, Ipc *vs*. bisulfite concentrations.

suggesting that the electron transfer is slow compared to the rate of the potential scan. The inset shows a plot of $-E_{pc}$ *versus* $v^{1/2}$; the linearity observed indicates a process controlled by diffusion of bisulfite from the bulk to the CME surface. In order to get information about the rate-determining step a Tafel plot, $-E_{pc}$ *versus* $\log I$ at a scan rate of $5\,mV\,s^{-1}$, is shown in figure 7. The slope of the Tafel plot, $n(1-\alpha)F/2.3RT = 211\,mV\,dec^{-1}$, indicates that one electron transfer process is rate limiting.

Figure 8 shows the calibration curve I_{pc} *versus* bisulfite concentration at $pH = 2.7$, which is linear in the range 0.6–6.0 mM. From the slope of the calibration curve it is possible to observe good sensitivity of the modified electrode for bisulfite reduction. The reduction process can be interpreted in terms of a single-electron, single-proton of HSO_3^- to yield the sulfur dioxide radical anion and water [18]. After this reaction, the electrogenerated radical anion dimerizes, generating dithionite anion, as shown in equations (5) and (6):

$$HSO_3^- + e^- + H^+ \rightarrow SO_2^{\cdot -} + H_2O \tag{5}$$

$$2SO_2^{\cdot -} = S_2O_4^{2-} \tag{6}$$

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