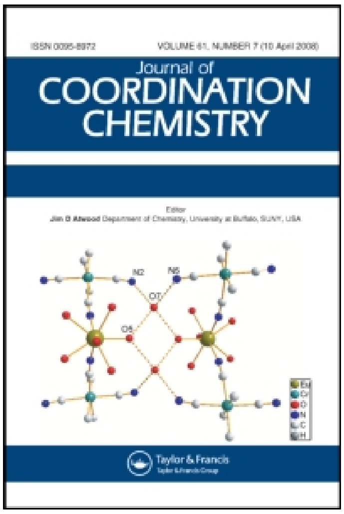

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CONTRIBUTION OF THE LIGAND TO THE ELECTROREDUCTION OF CO_2 CATALYZED BY A COBALT(II) MACROCYCLIC COMPLEX

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The electrochemical reduction of carbon dioxide using hexa-aza-macrocycles derived from the condensation of 1,10-phenanthroline and its Co(II) complex as an electrocatalyst dissolved in dimethylformamide has been studied by cyclic voltammetry and UV-visible spectroscopy. The ligand does not show catalytic activity and only generates hydrogen when it is reduced under carbon dioxide. The cobalt complex shows electrocatalytic activity toward the reduction of carbon dioxide, generating carbon monoxide and formic acid. Cyclic voltammetry and UV-visible spectroscopy show that the active site for the reduction is the metal center in oxidation state (I), although the reduced cobalt center alone is not enough to promote reduction of the carbon dioxide. Electrolysis at controlled potential shows that only at potentials corresponding to reduction of the ligand (second reduction) does carbon dioxide reduction occur. Cobalt(I) probably reacts with CO_2 forming a non-isolated intermediate which, when reduced, gives CO and formic acid. The second reduction that takes place on the ligand regenerates the catalyst and gives products, thus becoming the rate-determining step of the reaction.

Keywords: Carbon dioxide; Electroreduction; Hexaazacyclophane; Cobalt macrocyclic complexes

INTRODUCTION

The use of fossil fuels in the past century has generated a continuous increase in the carbon dioxide atmospheric concentration, creating the "greenhouse effect", which produces undesirable changes in the global climate [1].

Electrochemical reduction of carbon dioxide is one way to exploit this raw material, converting it to other chemicals of major value such as methanol and formic acid [2]. This reaction has been studied using metallic cathodes, semiconductors and different kinds of carbon as substrates [3]. Macrocyclic complexes containing transition metals have been used in the electrocatalytic reduction of carbon dioxide [4]. In this field, $Ni(Cyclam)^{+2}$ is the complex most extensively studied [5]. Moreover, other macrocycles

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such as porphyrins, phthalocyanines and hexa-aza-macrocycles show electrocatalytic activity for this reaction [6–8]. In previous work we have shown that hexa-aza-macrocycles substantially decrease the overpotential of reduction of carbon dioxide using glassy carbon electrodes [9]. In general, the reduction of CO_2 involves the formation of intermediate species between the reduced metal center and carbon dioxide. Flash photolysis and pulse radiolysis studies have shown that carbon dioxide forms short-lived intermediates with radicals derived from these macrocycles [8]. In some cases, cobalt complexes form isolated or detectable adducts between CO and the metal [10–12]. On the other hand, semi-empirical calculations have revealed that the catalytic activity of transition metal hexa-aza-macrocycles involves the metal center and the ligand [13,14].

The aim of this work is to present new results for the electrocatalytic reduction of carbon dioxide mediated by a hexa-aza-macrocycle derived from condensation of 1,10-phenanthroline. This study includes a spectroscopic characterization of the electrolyzed species in solution and a comparison between the activities of the free ligand and the Co(II) complex, in order to elucidate the role of the metal center and the ligand in the electrocatalysis.

EXPERIMENTAL

Synthesis and characterization of the hexa-aza-macrocycle ligand (HAM-H_2) and the Co(II) complex (HAM-Co(II)) have been previously reported [15]. Voltammetric studies were performed in a hermetic three-compartment cell, where the reference electrode compartment was connected to the working electrode by a modified Pt-bridge lugging capillary, to avoid contact of the working electrode solution with the aqueous electrolyte of the reference electrode. The working electrode was a glassy carbon disc (3 mmϕ Radiometer-Copenhagen); the counter electrode was a Pt wire of large area (Aldrich) and an Ag/AgCl electrode (Bioanalytical Systems) was used as reference. All the potentials quoted in this work are referred to this potential. The cyclic voltammetric measurements were carried out in an AFCBP1 Pine bipotentiostat, connected to a rotating disk unit. Potential-controlled electrolysis was performed with a Universal Programmer 175 connected to a digital coulometer 174 PAR. For electrolysis measurements an H-type cell and a reticulated glassy carbon working electrode were used. The solvent, *N*,*N*-dimethylformamide (DMF) (Merck, p.a.) and the supporting electrolyte, tetrabutylammonium perchlorate (TBAP) (Baker, p.a.), were dried before using, following the procedures reported [16–21]. Analysis of the products was performed by gas chromatography. A Varian 3400 gas chromatograph equipped with capillary columns of molecular sieves and DB1 for TCD and FID detectors, respectively, was used in determination of gas products. A spectroscopic method was used to determine formaldehyde and formic acid [22]. When electrolysis experiments were performed with a dry solvent, the electroreduction of CO_2 mediated by the macrocycles was very slow. But when $10^{-2}\,cm^2$ of water was added to $18\,cm^3$ of solution containing the free ligand or the Co complex, the catalysis was enhanced. However, the voltammograms recorded with or without added water are practically the same [17–19]. In order to obtain significant quantities of products, the electrolysis was carried out with $10^{-2}\,cm^3$ of water/$18\,cm^3$ of solution. UV-visible spectra were recorded on a CARY 1-E spectrophotometer. All measurements were carried out using air-free techniques [20,21].

RESULTS AND DISCUSSION

Electrochemical Characterization

Figure 1 shows the ligand used in this study. Figure 2 depicts the potentiodynamic profile of HAM-H_2 under N_2 and CO_2 atmospheres. In N_2 two irreversible peaks at −0.74 and −1.54 V have a diffusional behavior, i.e., the graph Ip *vs.* the square root of the scan rate gives straight lines (not shown). In CO_2 the voltammogram does not show dramatic changes: the main difference is a cathodic wave that starts at *ca.* −0.25 V, centered at *ca.* −0.65 V, and a current discharge that reaches 12.5 μA at the negative limit of potential. The increase in current is very low in terms of electrocatalysis. However, this small increment in current indicates an interaction between the free ligand and CO_2. This interaction could be explained in terms of acid–base behavior between the bridged nitrogens of the macrocycle and the CO_2, where the nitrogens are nucleophiles and the carbon of CO_2 acts as an electrophile. UV-visible spectroscopic studies have demonstrated that these nitrogens are easily protonated [8, 13], and indicate that acid–base interactions between the macrocycle and CO_2 are feasible. An interaction of this kind between the ligand and CO_2 will decrease electronic density on the

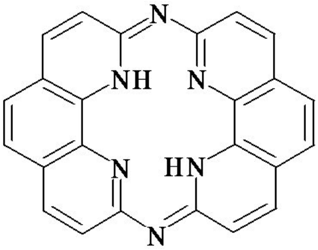

FIGURE 1 Structure of the ligand hexa-aza-macrocycle, HAM-H_2. The replacement of the internal hydrogen atoms by Co gives rise to the complex HAM-Co(II).

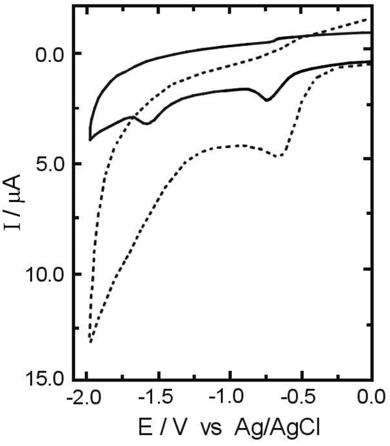

FIGURE 2 Cyclic voltammogram of HAM-H_2 under N_2 (——), under CO_2 (- - -). [HAM-H_2] ≈ 5×10^{-4} M/DMF/[PTBA] = 0.1 M; potential scan rate = 20 mVs^{-1}.

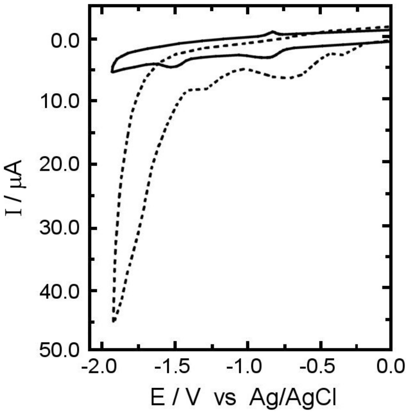

FIGURE 3 Cyclic voltammogram of HAM-Co(II) under N_2 (——), under CO_2 (- - -). [HAM-Co(II)] $\approx 5 \times 10^{-4}$ M/DMF/ [PTBA] = 0.1 M; potential scan rate = 20 mV s^{-1}.

macrocycle making it more easily reduced. When the HAM-H_2 was electrolyzed at −1.80 V *vs.* Ag/AgCl, the only product detected was hydrogen.

Figure 3 shows the voltammetric response of HAM Co(II), under N_2 and CO_2 atmospheres. The voltammogram in N_2 presents two peaks at −0.86 and −1.50 V. The peak at −0.86 V is *quasi*-reversible and could be assigned to the Co(II)/Co(I) redox process by comparison with other related macrocyclic complexes that have a Co(II)/Co(I) couple close to the potential observed here [23, 24]. The peak at −1.50 V could correspond to the same peak present in Fig. 2 for the free ligand and could be assigned to a redox process of the ligand. In the case of the cobalt complex, more drastic changes are observed when N_2 is replaced by CO_2, in comparison with the free ligand. In CO_2, a small change starts at −0.30 V like the peak that starts at −0.25 V in the case of the free ligand (see Fig. 2). This process can be assigned to a ligand response, because a shift in the potential due to the presence of the metal is feasible. A broad signal appears centered at −0.75 V. Beyond −1.41 V a large current discharge is observed. The broad peak at −0.75 V could be assigned to a first reduction that involves the metal center and where an intermediate between the reduced cobalt and the reactant molecule is formed. Indeed, the irreversibility of this wave under CO_2 atmosphere indicates an interaction between the Co(I) and the CO_2 that disappears when the Co is oxidized. This intermediate does not generate products, because electrolysis at this potential does not show formation of products. After formation of the intermediate, at potentials more negative than the metal and ligand reduction processes, a large current discharge appears. This indicates that not only is the reduced cobalt needed to promote the electroreduction of CO_2 but a second electron transfer process is also required. This second electron transfer process must involve the ligand because there is no metal redox couple at those negative potentials. The metal complex presents two relevant redox processes in CO_2: a peak at *ca.* −0.75 V (−0.86 V under N_2) assigned to the Co(II)/Co(I) redox couple responsible for the formation of a Co(I)–CO_2 intermediate and a second peak at *ca.* −1.41 V assigned to a ligand process. In other words, complete reduction of the cobalt complex (two-electron reduction) leads to the reduction of CO_2 and regeneration of the catalyst. The potential where the reduction of CO_2 takes place does not coincide with the ligand redox process. The reduction begins at more negative potential indicating an intramolecular electronic transfer between the reduced ligand and the intermediate. The electrolysis of HAM-Co(II) at -1.65 V under CO_2 gives CO as the main carbon product measured by gas chromatography. Also, using a DB1 column and an FID detector, formic acid was detected. Its presence was confirmed using the chromotropic method [22]. The formation of both products was expected because using HAM-M as catalysts for this reaction shows that production of CO and formic acid require similar energy [9].

UV-Visible Characterization of the Electrochemically Generated Species

For this kind of macrocycle, Gouterman's assignments of the bands that appear in the UV-visible spectrum [14, 24, 25] cannot be applied. For this reason, we label the bands arbitrarily: bands that appear below 350 nm will be called "α bands" and bands that appear above 350 nm will be called "β bands". To our knowledge, the spectrum in DMF for this macrocycle has not been recorded before. However, the features of the spectrum in Nujol [14] are similar to those of the spectra in this work.

Figure 4 shows the UV-visible spectra recorded under N_2 for HAM-H_2. The spectrum of the species is shown without application of potential, i.e., at open circuit potential (OCP) (spectrum 4.a). In spectrum 4.a the bands correspond to transitions from the ground state A_{1g} to the excited states $^1B_{xu}$ ($x = 1,2,3$) [25]. For this spectrum, α bands present a maximum at *ca.* 300 nm and β bands present a maximum at *ca.* 400 nm. The spectrum corresponding to the species electrolyzed shows an increment in the absorbance of the α bands without changes in the profile. Spectrum 4.b depicts the electronic transition behavior of the species at OCP under CO_2. The only difference from spectrum 4.a is an increase in the absorbance of the peak at *ca.* 400 nm, probably due to a change in the optical density of the solution. The spectra of the electrolyzed ligand (-0.80, -1.80 V) do not show any significant changes (not shown). Thus, there are no strong interactions between the reduced ligand and carbon dioxide that permit electronic transfer.

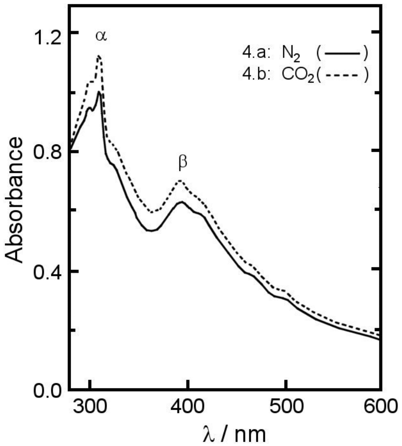

FIGURE 4 Electronic spectra of the ligand in DMF, (4.a) under N_2, (4.b) under CO_2. [HAM-H_2] $\approx 5 \times 10^{-5}$ M/[PTBA] = 0.01 M, registered at OPC.

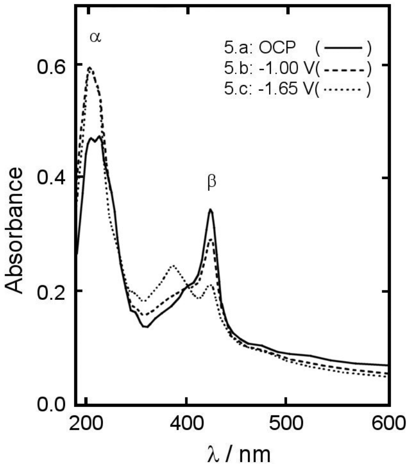

FIGURE 5 Electronic spectra of the complex in DMF under N_2. [HAM-Co(II)] $\approx 5\times10^{-5}$ M, [PTBA] = 0.01 M. Applied potentials: OCP (5.a); −1.00 V (5.b); −1.65 V (5.c).

Figure 5 depicts the spectra of HAM-Co (II), at different potentials under N_2. The potential values were chosen according to the different features of the voltammogram under N_2 atmosphere (see Fig. 3). At OCP (spectrum 5.a) the spectrum shows some differences with spectrum 4.a. For instance, the α bands that show a clear maximum at *ca.* 300 nm for the free ligand (see spectrum 4.a) in this case show two small peaks of similar intensity at 302 and 310 nm. In the case of the β bands there is a peak at 423 nm and a shoulder at *ca.* 400 nm. This spectrum shows how the metal changes the electronic energies of the ligand [14, 25]. On the other hand, the Co metal decreases the absorbance of the whole spectrum. Spectrum 5.b corresponds to a cobalt complex electrolyzed at −1.00 V. For the electrolyzed Co complex, a new band appears between 350 and 400 nm, with a shoulder at 380 nm. The β bands show a small peak at 402 nm and a decrease in intensity. Similar behavior has been observed when cobalt-phthalocyanines are electrolyzed at potentials close to the Co(II)/Co(I) redox couple [26–28]. The appearance of new bands in the β zone, near 400 nm can be attributed to metal–ligand charge transfer bands [29]. Another important feature in Fig. 5 is two "isosbestic" points, i.e., points that do not change their intensity when the applied potential changes, located at 402 and 335 nm. The presence of these points could be explained as an electrochemical transformation between two species, Co(II)L(−2)→ $\text{Co(I)L}(-2)^{-1}$; the reduced Co complex promotes a new band, a charge transfer band between the metal Co(I) and the ligand under N_2 atmosphere. Spectrum 5.c corresponds to the completely reduced complex at −1.65 V. The charge transfer band increases its intensity and shifts to the blue region whereas the β bands diminish in intensity. However, spectrum 5.c is very similar to spectrum 5.b because the isosbestic points do not move. If doubly reduced species were formed, then a new equilibrium should appear, with different isosbestic points. It is very surprising that the spectrum of the completely reduced species has isosbestic points that coincide with the spectrum of the "open circuit" species. Probably, spectrum 5.c corresponds to the singly reduced species. It is possible that the doubly reduced complex reacts with traces of water forming H_2 (non-detected in our experimental conditions) [17–19] or a fast decomposition

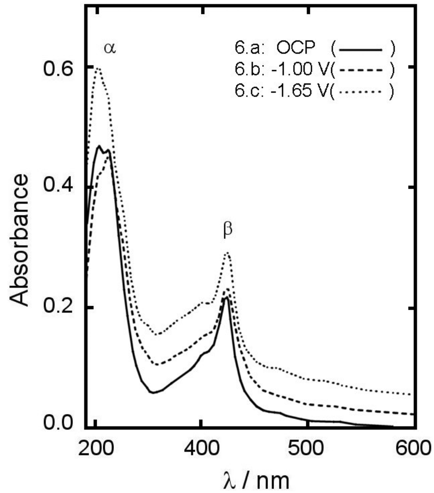

FIGURE 6 Electronic spectra of the complex in DMF under CO_2. [HAM-Co(II)] $\approx 5 \times 10^{-5}$ M, [PTBA] = 0.01 M. Applied potentials: OCP (6.a); −1.00 V. (6.b); −1.65 V (6.c).

takes place [12]. The change in intensity between spectrum 5.b and 5.c, if both spectra correspond to the singly reduced complex, indicates that the electrolyzed species are not stable and lose charge rapidly. The species electrolyzed at −1.65 V maintains a potential where the quantity of Co(I) is higher than when the species is electrolyzed at −1.0 V. Although electrolyzed species are not stable under the conditions of the experiment it is possible to see the charge transfer band that appears when sufficiently negative potentials are applied. When the solution is bubbled with CO_2 the spectra of the complex change in comparison to the behavior under N_2. Figure 6 depicts the spectra of HAM-Co (II) at the same potentials as Fig. 5 but now in the presence of CO_2. When negative potentials are applied, the intensity of the whole spectrum increases, the charge transfer band does not appear and there are no isosbestic points. All these features can be explained in terms of a fast interaction between the reduced metal center and the CO_2 molecule that does not permit an electron transfer from the Co(I) to the ligand. It is very noticeable that the intensity of the bands at open circuit potentials and when the metal is reduced are comparable. But when the complex is reduced (−1.65 V) the intensity of the whole spectrum increases, perhaps because products of the reduction change the optical density of the solution. A similar effect has been obtained when hydrazine is oxidized to N_2 by Co polymeric phthalocyanines [30]. From the results of electrolysis at constant potential, which shows products of the reduction only when the applied potential corresponds to the reduction of the ligand, it is clear that the doubly reduced species is the active species for catalysis. When the applied potential only reduces (−1.0 V) Co, a partial-intermolecular charge transfer between the metal center and the CO_2 probably occurs, which avoids the metal–ligand charge transfer band but does not promote any reaction product. CO and formic acid appear only when the potential is more negative than the potential corresponding to the ligand process. On the other hand, the reduced ligand does not catalyze reduction of CO_2. Thus, reduction of the charge-transfer intermediate between the metal center and the CO_2 regenerates the catalysts and gives CO.

CONCLUSIONS

The role of the metal center and ligand in electrocatalysis of the reduction of CO_2 mediated by a hexa-aza-macrocyclic cobalt complex has been proved in this work. We have found significant differences in the electrochemical characteristics and the electronic spectra of the Co complex and the free ligand. There is a clear correlation between the potential of the Co(II)/Co(I) redox couple and the potential where a new band appears at *ca.* 380 nm. Also, the current discharge corresponding to the CO_2 reduction takes place at potentials even more negative than the redox couple of the ligand. All these facts indicate that the species responsible in the electrochemical reduction of CO_2 is Co(I), forming an intermediate that is destroyed and converted to products when the ligand is reduced.

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