

SYNTHETIC AZAMACROCYCLES IN THE REDUCTION OF CARBON DIOXIDE: REVIEW AND PERSPECTIVES

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Abstract

One of the most important objectives of several research groups around the world are related to the synthesis, spectroscopic and electrochemical characterization of coordination compounds of several transition elements with macrocyclic ligands containing four, six or eight nitrogen atoms to be used as catalysts in the electro reduction of carbon dioxide. A revision and a critical discussion on the information related to these coordination compounds as redox-catalysts are presented in this review. In particular, the perspectives for the reduction of carbon dioxide using hemiporphyrizine ligands are presented and discussed.

Key words: Azamacrocycles; Transition metal complexes; Carbon dioxide reduction; Electrochemical methods.

Resumen

Azamacrociclos sintéticos en la reducción de dióxido de carbono: Revisión y perspectivas. Uno de los objetivos más importantes de varios grupos de investigación del mundo se relaciona a la síntesis y caracterización espectroscópica y electroquímica de compuestos de coordinación de diversos metales de transición con ligandos macrocíclicos conteniendo cuatro, seis u ocho átomos de nitrógeno para ser utilizados como catalizadores en la electroreducción de dióxido de carbono. En este artículo se presenta una revisión y discusión crítica relacionada a estos compuestos de coordinación como catalizadores redox. En particular, se presentan y discuten las perspectivas para la reducción de dióxido de carbono utilizando ligandos hemiporfirazínicos.

Palabras clave: Azamacrociclos; Complejos de metales de transición; Reducción de dióxido de carbono; Métodos electroquímicos.

1. Introduction

The conversion of carbon dioxide into organic compounds in order to use them as fuels and in industrial applications has been studied since the last century. Electrochemical methods which are less energy consuming to reduce carbon dioxide to carbon monoxide, formaldehyde, formate, methanol, oxalate, etc, have been developed since the last decade. However, efficient reduction methods in big scale have not been fully designed yet. For these projects to be possible, the necessary technologies for the elimination and transformation of carbon dioxide must be more sophisticated in the future.

On the other hand, due to the fact that carbon dioxide is one of the gases that significantly contribute to the so called "greenhouse effect" and it is mainly produced by more developed societies, several areas of science and technology are involved in the study of solutions [1].

Several studies involving carbon dioxide have been informed during the last years. For example, its reduction on metallic electrodes or in the presence of coordination compounds with macrocyclic ligands, the identification and characterization of products and the mechanisms involved, the use of modified electrodes, among others [2,3].

A revision and a critical discussion on the information related to poly-aza-macrocycles with transition metals as redox-catalysts is presented in this review [4]. Acyclic ligands will not be considered [5].

In particular, hemiporphirazine ligands and complexes will be shown with more detail. This kind of ligand shows some differences compared to phthalocyanines and porphyrines, these differences being related to asymmetric resonances, lower aromatic character, asymmetric coordination site, electronic absorption spectra without Q and Soret bands, among others.

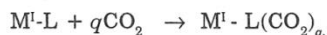
2. Review and perspectives

The transformation of carbon dioxide has been investigated through electrolysis using metallic electrodes and organic and inorganic compounds as mediators [6]. The conversion of carbon dioxide by metallic electrodes in acidic media is known for a long time; it was rather successful because it has been possible to obtain formic acid as the principal product [7,8]. However, the energetic cost is not low, due to the high cathodic potential necessary to apply. An additional problem is to find cathode electrodes which can discriminate the reduction of carbon dioxide to that of water.

Azamacrocycles showing low electronic delocalization. The information related to the electro-catalytic reduction of carbon dioxide by complexes with aliphatic Curtis type azamacrocycles as shown in Figure 1 is extensive [9].

One of the first relevant contributions was presented by Sauvage *et al* [10] some years ago; they found that aqueous solution of the complex $[\text{Ni}(\text{cyclam})]^{2+}$ (see Fig. 1) and using a working electrode of mercury, efficiently assist the transformation of carbon dioxide into carbon monoxide; this process being selective related to the reduction of water [11].

The constant of the complex-carbon dioxide interaction for the equilibrium:



where $\text{M}=\text{Ni}$, Co , $\text{L}=\text{ligands derived from cyclam}$, $\text{Me}_6[14]\text{ane}$, Figure 1, in the presence and absence of water has been evaluated [12-14]. It has been found that the redox response of these complexes follow an electrochemical-chemical, EC, mechanism; which allowed the evaluation of the above mentioned constant. In addition it has been found that the charge transfer from the cobalt atom to the carbon dioxide molecule is a very

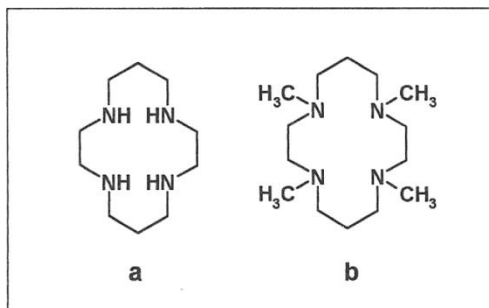


Fig. 1. Azamacrocyclic ligands with low electronic delocalization: a) «cyclam», b) «Me₆[14]ane».

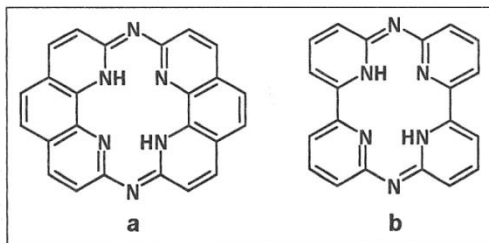


Fig. 2. Hexa-azamacrocyclic ligand with moderate electronic delocalization: a) bis-phenanthroline, b) bis-bipyridine.

important energetic factor that highly contributes to the stabilization of the $\text{M}^{\text{I}}\text{-L}(\text{CO}_2)_q$ adducts [14].

The results obtained in these cases point out the importance not only of the structure of the ligands, the metallic ion, solvent, sweep speed, electrolyte but the material of the working electrodes [10,15].

Azamacrocycles showing moderate electronic delocalization. Bis-phenanthroline and bis-bipyridine hexaazamacrocycles, Figure 2, and complexes with several metals have highly efficient shown catalytic current in the presence of carbon dioxide. The solubility of these complexes in common organic solvents is a limiting factor that has been partially solved by appropriate substitution on the ligands [9, 16-21].

Phthalocyanines and Porphyrines.

The electrocatalysis of carbon dioxide using complexes of several metals with azamacrocyclic ligands which show extensive π electronic delocalization such as phthalocyanines and porphyrines, Figure 3, has been extensively studied during the last decades [22-25].

This kind of complexes are sparingly soluble in most common solvents showing poor

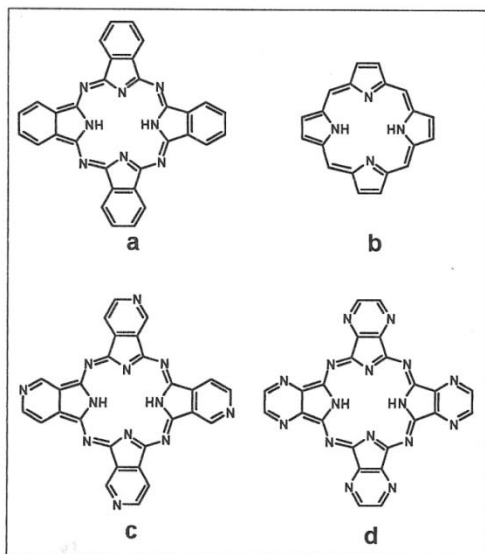


Fig. 3. Azamacrocyclic ligands with an extensive electronic π delocalization: a) phthalocyanine, b) porphyrine, c) pyridino-porphyrine (one isomer), d) pyrazino-porphyrine.

catalytic efficiency in homogeneous solutions. Due to this fact it has been necessary to use alternative methodologies to study them as catalysts, namely:

- (a) deposit of the complex on the electrode surface and elimination of the solvent;
- (b) contact of the electrode with the solution which contains the complex to allow its adsorption;
- (c) electro-polymerization of the complex, *ie.*, chemical modification of the surface.

The (c) alternative presents some advantages related to the control of some variables, such as absorptions, potential control, chemical stability of the catalyst, among others. Additionally, it eliminates the diffusion of the catalyst, so making possible to reach a better control of the homogeneity and the magnitude of surface to be covered, among other factors [26-35].

The study of chemical modifications for compounds which contains amino and aminopyridine has generated a new methodology based in the use of electrodes chemically modified by this kind of substituted macrocycles. Figure 4 shows tetraphenylporphyrines covalently bonded to the electrode by pyridines [36,37]. It has been found that these modified electrodes show a high

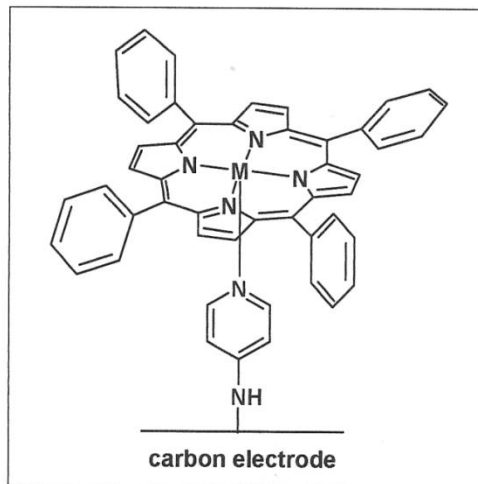


Fig. 4. Tetraphenylporphyrine complex covalently bonded to glassy carbon electrode through substituted pyridine.

efficiency in the reduction of carbon dioxide [38,39].

It has been recently informed that the reduction of carbon dioxide assisted by electropolymerized cobalt(II) tetraaminophthalocyanine mainly lead to the obtention of formic acid; nickel(II) tetraaminophthalocyanine favors the formation of formic acid and formaldehyde, while formaldehyde and hydrogen are obtained when iron(II) derivative of tetraaminophthalocyanine is used [40].

Electro-polymerized cobalt(II) tetraaminotetraphenylporphyrine catalyzes the reduction of carbon dioxide in aqueous media to carbon monoxide and formic acid; hydrogen is also produced [41]. The yield of each product being dependent on the morphology of the polymeric deposits [40,41].

Pyridino and Pyrazino Porphyrines. Pyridino-porphyrines are ligands with highly delocalized π electronic density, Figure 3. Some of their water soluble derivatives are well known [42]; structural isomers have been studied and characterized by common spectroscopies and cyclic voltammetry [43-46]. Complexes with soluble derivatives of these ligands has been recently employed for obtaining conducting electro-polymers [46-49].

Pyrazino porphyrine complexes has been synthesized by Linstead [50], Figure 3. They are species soluble in common organic solvents.

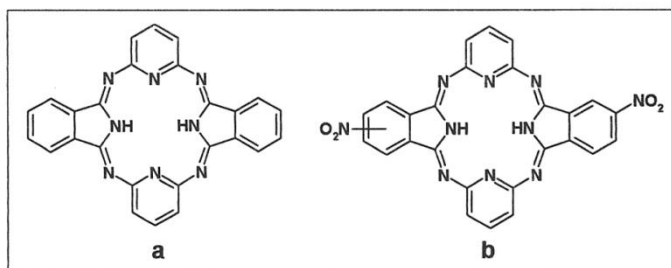


Fig. 5. a) Hemiporphyrizine, HpH₂, b) di-nitrohemiporphyrizine, (NO₂)₂HpH₂.

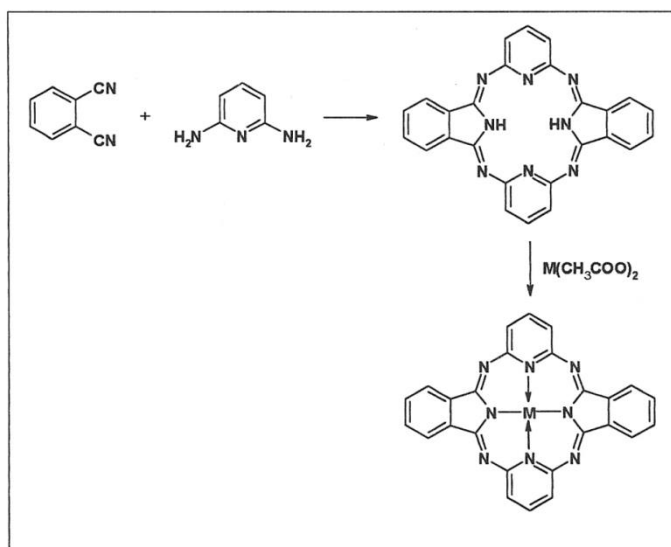


Fig. 6. Scheme of synthesis for hemiporphyrizine, HpH₂ and [M(Hp)], complexes (M = Co, Ni, Cu).

Alkyl, alkoxy carbonyl and thioalkyl substituted derivatives are known [51]. Some of them were characterized by cyclic voltammetry [51,52].

Hemiporphyrazines. Complexes derived from hemiporphyrazines show structures with high π electronic delocalization. However this delocalization is not aromatic as it is in the case of phthalocyanines, porphyrines, pyridinoporphyrazines and pyrazino-porphyrazines. In addition, it presents special coordination properties related to its weak ligand field and ellipsoidal type symmetry of the ligand around the coordination site. These ligands, Figure 5, and complexes with several metals were obtained some

years ago [53,54]. The name *hemi* (in hemiporphyrizine) means that a couple of trans-isoindol groups characteristic of the phthalocyanines are bridged by pyridine in this case.

These macrocyclic systems has not been extensively studied [55,56]. The reduction of the aromatic character of these ligands has been demonstrated in several structural studies with different metals, namely [Si(Hp)Cl₂] [57], [Ge(Hp){OSi(CH₃)₃}] [58], [Sn(Hp)Cl₂] [59], [Ni(Hp)(C₅H₅N)₂] [60] (Hp = hemiporphyrizine).

The stoichiometry of the complexes depend on the conditions of synthesis: [M(Hp)] or [M(Hp)]{(HX)_n} (n=1,2; HX= H₂O, HCl, HBr; M= Ni, Cu, Co, Zn) [61]. The coordination of HX

is stabilized via interaction with the external nitrogen atoms of the ligand in these cases.

It has been also found by measuring magnetic moments that low spin [Co(Hp)] suffers a transition to high spin (4,5 Bohr Magnetons) when a water molecule is axially coordinated. On the other hand, [Ni(Hp)] is diamagnetic while [Ni(Hp)(H₂O)₂] shows a magnetic moment value of 3,0 Bohr Magnetons. Electronic structures of these complexes were interpreted and its main

transitions were assigned by theoretical calculations. The spectra do not show Soret type bands, but other transitions localized in the macrocyclic ligand were found, its position being independent of the metals [62].

In addition, these ligands present a flexible coordination site, which can suffer possible out of plane rhombohedral distortions. It is believed that this fact and the eventual presence of suitable substituents can act as an additional contribution to the stabilization of low oxidations states of the coordinated metals.

Synthesis de Hemiporphyrazines.

Figure 6 shows the reaction Scheme for the general procedure to synthesize HpH₂ ligand and [M(Hp)] (M=Co,Ni,Cu) complexes. An analogous procedure was employed to obtain di-nitro-susbtituted hemiporphyrazine ligand and complexes. Di-amino-substituted complexes were obtained by reduction of nitro-derivatives [63,64].

Perspectives for the Reduction of Carbon Dioxide Using Hemiporphyrazines.

One of the most important objectives of our research group have been related to the synthesis, spectroscopic and electrochemical characterization of coordination compounds of nickel(II), cobalt(II) and copper(II) with azamacrocyclic ligands derived from hypiridines and phenanthrolines as catalyst in the electro reduction of carbon dioxide. Nickel(II) complexes have shown the better response [16-21].

Figure 7 shows cyclic voltammetry results for [Ni{(NO)₂Hp}], where the reduction process for the imino nitrogen atoms are observed at ca. -0.74 V (vs SCE). Metal and azomethine

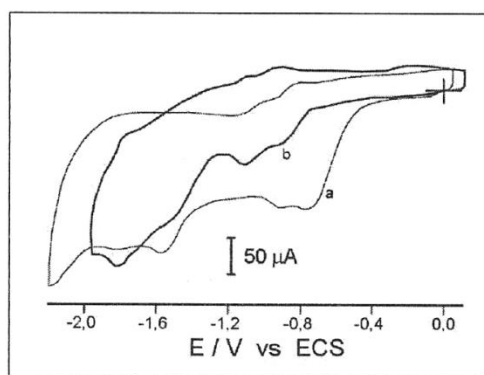


Fig. 7. Cyclic Voltammograms in nitrogen atmosphere for, (a) the ligand (NO₂)₂HpH₂ and, (b) the complex [Ni(NO₂)₂Hp]. Concentrations, 1x10⁻⁴ M. in N,N'-dimethylformamide; electrolyte, 1x10⁻² M tetraethylammonium perchlorate; electrode glassy carbon; sweep speed, 200 mVs⁻¹.

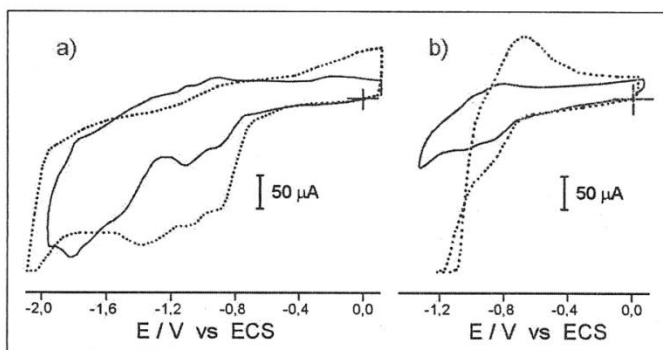


Fig. 8. Cyclic Voltammograms for [Ni(NO₂)₂Hp] in N₂ (—) and CO₂ (.....). a) glassy carbon electrode; b) platinum electrode. Concentrations: 1x10⁻⁴ M. in N,N'-dimethylformamide; electrolyte, 1x10⁻² M tetraethylammonium perchlorate; electrode glassy carbon; sweep speed, 200 mVs⁻¹.

nitrogen atoms reduction processes also appear in a region around -0.92 V. Analogous results were obtained for nickel(II), copper(II) and cobalt(II) complexes with unsubstituted (and methyl substituted) hemiporphyrines [65,66].

These electrochemical results and other characteristics already mentioned, such as the high π electronic delocalization, although not aromatic, some special coordination properties with small molecules, due to its coordination site, the easy control of stoichiometry of some complexes, which facilitates low oxidations states on the metal, lead to the conclusion that these complexes can be potentially useful in assisting the electrocatalytic reduction of carbon dioxide [65,66] in organic and aqueous solvents, in homogeneous phase or in heterogeneous phases such as modified electrodes. Some complexes with aminosubstituted hemiporphyrine ligands could be suitable materials to obtain autoassembled monolayers in highly oriented pyrolytic graphite (HOPG) surfaces, covalently bonded: HOPG-NH-Complex-NH₂ [40].

Figure 8 shows some results on the electrocatalytic reduction of carbon dioxide in platinum and carbon electrodes using [Ni(NO₂)₂Hp] as catalyst in N-N'-dimethylformamide. The catalytic effect is greater in platinum than in carbon. Studies are in progress [63,64].

Acknowledgements

JC thanks Fondecyt, CONICYT, Project # 1060030 and Dicyt, USACH, Project # 2070727 for financial assistance. JCC thanks Mecosup-CONICYT fellowship.

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Manuscrito recibido el 26 de diciembre de 2007.

Aceptado el 6 de febrero de 2008.