ECLÉTICA
Química
www.scielo.br/eq
www.ecletica.iq.unesp.br
Volume 33, número 3, 2008

# Electrochemical properties of $Cu_4[PhN_3C_6H_4N_3(H)Ph]_4(\mu\text{-}O)_2$, a tetranuclear Copper(II) complex with 1-phenyltriazenido-2-phenyltriazene-benzene as ligand

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**Abstract:** Bis-($\mu_2$-oxo)-tetrakis{[1-feniltriazene-1,3-diil)-2-(phenyltriazenil)benzene copper(II) is a tetranuclear complex which shows four Cu(II) ions coordinated by four 1,2-bis(phenyltriazene)benzene bridged ligands, with one diazoaminic deprotonated chain, and two $O^{2-}$ ligands. The complex reduces at $E_{1/2}$ = -0.95 V vs $Fc^+/Fc$, a two electrons process. Cyclic voltammetric and spectroelectrochemical studies showed a reversible process. When immobilized on carbon paste electrode, the complex electrocatalyses the reduction of $O_2$ dissolved on aqueous solution at –0.3 V *vs* SCE potential. The obtained current shows linearity with $O_2$ concentration.

*Keywords:* copper(II) complex; 1,2-bis(phenyltriazene)benzene ligand; spectroelectrochemical characterization; electrochemical sensor, oxygen reduction.

## Introduction

Compounds containing a chain with three nitrogen atoms, the triazenes, are largely described on the literature [1,2]. Among other uses, they were studied as chemotherapeutic agents. Triazenes and anionic triazenide ligands can show different types of coordination in metal complexes [1-5]. They can be monodentate, (N1,N3)-chelating towards one metal atom or (N1,N3)-bridging over two metal atoms.

Compounds containing two chains of three nitrogen atoms, the bistriazenes, are also known [6-14]. The possibilities of coordination are enhanced when two nitrogen chains are present on the ligand. Complexes of ortho-, meta- and para-bis(phenyltriazene)benzenes ligands were synthesized and characterized. As expected, several different coordination types were observed. Bistriazenes show the coordination properties of triazenes and also the capacity to force close contacts between metal atoms.

Although the structure of complexes with bistriazene ligands have been described, no reports were found in the literature related to electrochemical properties of these compounds. These studies are important for characterization and to a better understanding of their reactivity, stability and possible applications.

The 1,2-bis(phenyltriazene)benzene ligand, $C_6H_5NNN(H)C_6H_4NNN(H)C_6H_5$, was used to synthesize the complex bis-($\mu_2$-oxo)-tetrakis{[1-

phenyltriazene-1,3-diil)-2-(phenyltriazenil)benzene copper(II), $Cu_4[PhN_3C_6H_4N_3(H)Ph]_4(\mu_2\text{-}O)_2$, (which will be represented by $Cu_4L_4$). This molecule is formed by a tetramer of four copper(II) ions and four 1-phenyltriazenido-2-phenyltriazene benzene anions, $[C_6H_5NNNC_6H_4NNN(H)C_6H_5]^-$. Each ligand chelates one metal ion by the deprotonated $N_3$ chain and coordinates monodentate to the neighboring one, using the protonated $N_3$ chain. The p-oxo ligands occupy the twofold axis and bridge two opposite edges of the $Cu_4$ tetrahedron. The crystal structure of this complex was determined by X-Ray crystallography and was described elsewhere [12].

The objective of this work was the characterization of the electrochemical, spectroelectrochemical and electrocatalytic properties of the $Cu_4L_4$ complex. For electrocatalytic studies the complex was incorporated on a carbon paste electrode, and used as electrocatalyst for the $O_2$ reduction reaction in aqueous solution.

## Experimental

*Synthesis*

The ligand 1,2-bis(phenyltriazene)benzene and the complex $Cu_4L_4$ were prepared as described on the literature [12].

*Electrochemical measurements*

Cyclic voltammetry was carried out with a Microquímica instrument, consisting of a MQPG-01 potentiostat. A platinum disc and saturated calomel (SCE) were used as working and reference electrodes. A platinum sheet was used as the auxiliary electrode. For controlled potential electrolyses, cylindrical Pt grids were used as working and auxiliary electrodes and the potential was fixed at -0.4 V *vs* SCE. For spectroelectrochemical measurements the Microquímica potentiostat was used in parallel with a Pharmacya Biotech, Ultrospec 2000 spectrophotometer. A three-electrode system was designed for a rectangular quartz cell of 0.03 cm internal path-length. A gold minigrid was used as a transparent working electrode, in the presence of a small saturated calomel reference and a platinum auxiliary electrode. Tetrahydrofuran P.A. (Vetec) was used as solvent and 0.1 mol $L^{-1}$ tetrabutylammonium hexafluorophosphate (Sigma), as supporting electrolyte, in nitrogen atmosphere. The concentration of the $Cu_4L_4$ complex was 1 mmol $L^{-1}$. Ferrocene (Merck) 1 mmol $L^{-1}$ was added to the $Cu_4L_4$ solution in the final of the experiment of cyclic voltammetry in tetrahydrofuran medium to use its potential of oxidation as an internal potential standard.

For oxygen reduction reaction studies, a carbon paste electrode was constructed by mixing 20 mg of graphite powder (Merck), 5 mg of $Cu_4L_4$ complex and one drop of mineral oil (Nujol). For electrochemical measurements, aqueous solution, at pH 4.5, containing potassium chloride (Reagen) 1 mol $L^{-1}$ as supporting electrolyte, was used. Dissolved oxygen concentration was controlled by bubbling $N_2$ or atmospheric air. Oxygen concentrations were determined by Winkler method [15].

## Results and discussion

*Electrochemical characterization*

The cyclic voltammogram of $Cu_4L_4$ complex is represented in Fig. 1a. It was observed a reversible reduction process at $E_{1/2} = –0.95$ V *vs* $Fc^+/Fc$. In the cyclic voltammogram of the free ligand 1,2-bis(phenyltriazene)benzene no redox process occurs at this potential, indicating that this is due to copper(II) ions (Figure 1b).

Two electrons transfer was determined by controlled potential electrolyses. As there are four copper(II) ions, it may occur the process $Cu(II)_4 \rightleftharpoons Cu(II)_2Cu(I)_2$, with localization of the two electrons in two copper ions, or delocalization of them around the copper tetramer.

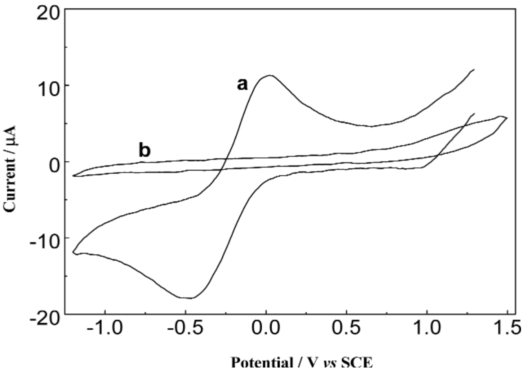

**Figure 1.** Cyclic voltammogram of the 1 mmol $L^{-1}$ $Cu_4L_4$ complex (a) and 1 mmol $L^{-1}$ 1,2- bis(phenyltriazene)benzene ligand (b), in tetrahydrofuran, containing tetrabutylammonium hexafluorphosphate 0.1 mol $L^{-1}$ at a scan rate of 100 mV $s^{-1}$.

*Spectroelectrochemistry*

The reversibility of the $Cu_4L_4$ redox process was also observed by spectroelectrochemistry. The electronic spectrum of the ligand 1,2-bis(phenyltriazene)benzene shows an intense band at 378 nm (ε=32120 $mol^{-1}$ L $cm^{-1}$) (Fig. 2c) due to transitions in the triazene group [2,13,14]. In the complex this band appears at 388 nm (ε=33860 $mol^{-1}$ L $cm^{-1}$) (Fig. 2a). The spectrum of the complex also shows a broad and low intense band in the 600-800 nm region, due to d-d transitions in the copper(II) ion [16]. The intensity of this band decreases and the band at 388 nm is shifted to 395 nm when the complex is reduced at –1.0 V *vs* SCE (Fig. 2b). When the complex is oxidized again at 0.5 V *vs* SCE the initial spectrum is observed (Fig. 2a), indicating that there was no decomposition of the reduced form.

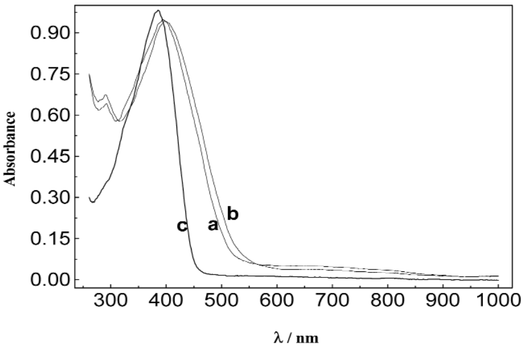

**Figure 2.** Electronic spectra of 1 mmol $L^{-1}$ $Cu_4L_4$ at 0.5 V (a) and –1.0 V vs SCE (b) applied potentials, and of the ligand 1,2-bis(phenyltriazene)benzene (c) in tetrahydrofuran, containing tetrabutylammonium hexafluorphosphate 0.1 mol $L^{-1}$.

*Oxygen reduction reaction*

The $Cu_4L_4$ complex incorporated on carbon paste electrode shows the reduction process at $E_{1/2}$ = -0.17 V *vs* SCE (Fig. 3a). When oxygen was dissolved in the aqueous solution, it was observed an increase in the cathodic and decrease in the anodic peak current (Fig. 3b), indicating electron transfer from reduced immobilized $Cu_4L_4$ to dissolved $O_2$.

In the Fig. 4 it is shown the intensity of the current observed for $O_2$ reduction by $Cu_4L_4$ as a function of the applied potential, obtained by chronoamperometry. It is observed that the electrocatalytic process begins at -0.1 V, and the current increases until -0.3 V *vs* SCE. In the carbon paste electrode with no $Cu_4L_4$ complex incorporated the oxygen reduction begins only at -0.4 V.

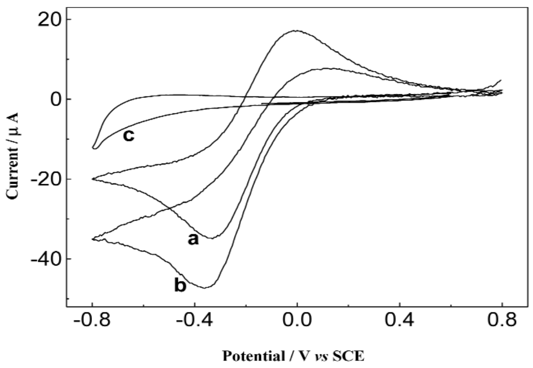

**Figure 3.** Cyclic voltammogram of the $Cu_4L_4$ complex incorporated on a carbon paste electrode in aqueous solution at $N_2$ atmosphere (a) and saturated with $O_2$ (b), and of the carbon paste electrode without $Cu_4L_4$ incorporated in $O_2$ saturated solution (c), containing KCl 1 mol $L^{-1}$ at a scan rate of 25 mV $s^{-1}$.

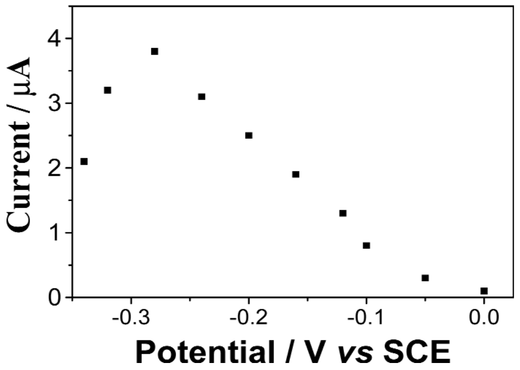

**Figure 4.** Current for $O_2$ reduction by $Cu_4L_4$ complex incorporated in a carbon paste electrode as a function of the applied potential, obtained by chronoamperometry, in $O_2$ saturated aqueous solution, containing KCl 1 mol $L^{-1}$.

The current, obtained by chronoamperometry, for oxygen reduction at a fixed potential (-0.30 V *vs* SCE), is shown in Fig. 5. It was obtained a linear relationship with the concentration of dissolved oxygen in aqueous solution, represented by the equation $I = 1.056[O_2] + 1.365$, with a linear correlation coefficient of 0.9967, for oxygen concentrations between 1.1 and 5.2 ppm. In accord with this result, it is possible the use of this electrode as a sensor for $O_2$ in aqueous solution. Due to the insolubility of $Cu_4L_4$ in aqueous medium the electrode achieved high stability. It was used continuously and maintained the response for at least 180 hours.

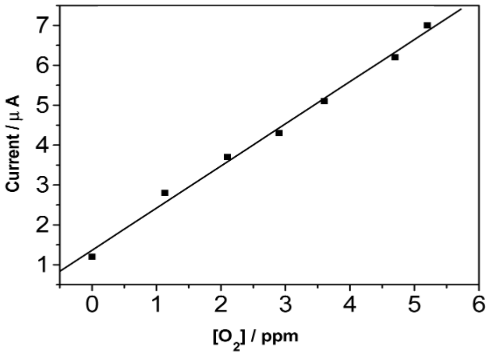

**Figure 5.** Current, obtained by chronoamperometry, at -0.3 V vs SCE, by the carbon paste electrode with $Cu_4L_4$ complex incorporated as a function of oxygen concentration dissolved in aqueous solution, containing KCl 1 mol $L^{-1}$.

## Conclusions

This is the first study about electrochemical properties of a bistriazene complex. It was demonstrated the high capacity of the ligand to coordinate and to bridge metallic ions. The stability of the tetramer formed by four copper(II) ions in the bis-($\mu_2$-oxo)-tetrakis{[1-phenyltriazene-1,3-diil)-2-(phenyltriazenil)benzene copper(II) complex was not affected even after the reduction process, and this permitted the use of the complex as an electrocatalyst.

## Acknowledgements

C.R.M.P. is indebted to FAPERGS. A. H. and L. S. S. are indebted to CNPq and to FAPERGS, respectively, for a fellowship. We apologize to Prof. Dr Ademir Neves and Msc. Ademir dos Anjos of the UFSC for use of his laboratory and help in the coulometric measurements.

Received June 02 2008
Accepted August 14 2008

A. Hermann, L. S. Silva, C. R. M. Peixoto, A. B. de Oliveira, J. Bordinhão e M. Hörner. Propriedades eletroquímicas do $Cu_4[PhN_3C_6H_4N_3(H)Ph]_4(\mu\text{-}O)_2$, um complexo tetranuclear de Cobre (II) com o ligante 1-feniltriazenido-2-feniltriazeno-benzeno.

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**Resumo:** Bis-($\mu_2$-oxo)-tetrakis{[1-feniltriazeno-1,3-diil)-2-(feniltriazenil)benzeno cobre(II) é um complexo tetranuclear que apresenta quatro íons Cu(II) coordenados por quatro ligantes 1,2-bis(feniltriazeno)benzeno em ponte, com uma cadeia diazoamínica desprotonada, e dois ligantes $O^{2-}$. O complexo apresenta um processo de redução por dois elétrons a $E_{1/2}$ = -0,95 V vs $Fc^+/Fc$. Voltametria cíclica e espectroeletroquímica demonstraram um processo reversível. Quando imobilizado em eletrodo de pasta de carbono, o complexo eletrocatalisa a redução de $O_2$ dissolvido em solução aquosa a –0,3 V *vs* SCE. A corrente obtida apresenta linearidade com a concentração de $O_2$.

*Palavras-chave:* complexo de cobre (II); ligante 1,2-bis(feniltriazeno)benzeno; espectroeletroquímica; redução de oxigênio.

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