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UNUSUAL ELECTROCHEMICAL BEHAVIOUR OF AN UNUSUAL COPPER(II) MACROCYCLIC COMPLEX

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Green solutions of  $[CuL(H_2O)][CuO_4]_2.H_2O$  (L=C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>; structure below) in acetonitrile slowly become red. The process can be followed by cyclic voltammetry and differential pulse polarography. An initial reversible one-electron redox process vanishes with time; concurrently another appears, at more negative potentials. This behaviour will be described and discussed.

KEYWORDS: colour change in solution; cyclic voltammetry; differential pulse polarography

#### INTRODUCTION

Years ago the synthesis of a macrocyclic ligand by a "2 + 2" condensation of 2,6-diacetylpyridine with <u>o</u>-phenylenediamine was described<sup>1</sup>, both in the absence and in the presence of Cu(II). Two copper(II) complexes were also reported, a di-copper(II) nitrate<sup>1,2</sup> and a mono-copper(II) perchlorate complex<sup>2</sup>.

It was later shown<sup>3</sup> that the product of direct condensation had quite a different structure from that previously proposed 1,2

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and that the formation of the mononuclear copper(II) perchlorate complex involved an oxidative dehydrogenation of the original (7+12+7) inner ring system into a macrocycle with a (15+6+3) inner ring system, with loss of two hydrogen atoms<sup>4</sup>. Their structures, as determined by x-ray analysis, are shown in the figure below.



This oxidative dehydrogenation would probably involve a  $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{II}$  redox cycle, a hypothesis which could find some support from the redox properties of the complex. We now report our findings on the very unusual electrochemical behaviour of the no less unusual complex,  $[CuL(H_2O)][CtO_4]_2$ . $H_2O$ , previously described<sup>4</sup>.

# EXPERIMENTAL

The complex was prepared according to the published method<sup>2,4</sup>. All chemicals were reagent grade and used without further purification. Dry acetronitrile was kept over molecular sieves and filtered immediately before use.

Electrochemical experiments were carried out at 25.0<sup>±</sup>0.1<sup>°</sup>C under a blanket of dry, oxygen-free N<sub>2</sub>, in a Metrohm (model EA 876/5) polarographic cell. A P.A.R. model 174A polarographic analyzer and a P.A.R. model 175 universal programmer were used; current-voltage curves were recorded on a Houston Omnigraphic 2000 X-Y recorder.

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A three-electrode system was used: platinum bead, hanging mercury drop, or dropping mercury as working electrodes; a platinum spiral, as counter-electrode; a Metrohm EA 441/1 saturated calomel electrode (S.C.E.), as reference electrode. This reference electrode was separated from the bulk solution via a Vycor-tipped bridge containing 0.1 M aqueous sodium nitrate.

Solutions were either 0.1  $\underline{M}$  or 0.05  $\underline{M}$  in tetraethylammonium perchlorate and  $10^{-3}$  -  $10^{-4}$   $\underline{M}$  in complex.

Dry, oxygen-free  $N_2$  was used for degassing the solutions. To avoid loss of solvent by evaporation, the inert gas was presaturated with the appropriate solution of supporting electrolyte in acetonitrile.

All potentials are reported vs. S.C.E., and are uncorrected for liquid junction potentials. The potential range was checked by running a supporting electrolyte blank prior to every scan.

Currents are expressed in arbitrary units (centimeters of peak heights), directly proportional to electrical units.

#### RESULTS AND DISCUSSION

Cyclic voltammograms (hanging mercury drop and platinum bead electrodes) and differential pulse polarograms (dropping mercury electrode) were obtained for [CuL(H<sub>2</sub>O)][ClO<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O in acetonitrile. It was observed that the colour of the solution slowly changed with time, both in daylight and in the dark, with or without applied potential, although the change was faster in the first case. Initially the solution was green, becoming red after a few hours.

This change in colour of the solution had its counterpart in the electrochemical behaviour, as clearly shown by successive cyclic voltammograms and differential pulse polarograms.

Cyclic voltammograms of green, freshly prepared acetonitrile solutions, either with a hanging mercury drop or a platinum bead electrode, are characterized by the presence of three redox processes in the range +0.350V to -1.200V: one at ca. +0.15V, a second at ca.-0.40V, and a third at ca. -0.95V. This third process has no anodic peak directly associated with it, and probably corresponds to an irreversible reduction to copper(0), because a deposit of copper on to the platinum bead was observed after a few cycles. In Figure 1 a typical cyclic voltammogram is shown.



Fig. 1. Cyclic voltammogram of a freshly prepared green solution of [CuL(H<sub>2</sub>O)][CLO<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O, 1.60x10<sup>-4</sup>M in complex and 0.05 M in tetraethylammonium perchlorate. Hanging mercury drop; E vs. SCE; 100 mV.s<sup>-1</sup>. With a hanging mercury drop electrode the first wave behaves as in a reversible, one-electron redox process. Within experimental error, peak potentials, peak separations, half-wave potentials and the ratios of peak currents were independent of scan rates from 50 to 500 mV.s<sup>-1</sup>; peak separations were of the order of 70-80 mV, and the ratios of peak currents very close to 1.

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TABLE I. Characteristics of the First Wave

(hanging mercury drop electrode)

v(mV.s <sup>-1</sup> )	50	100	200	500
<sup>E</sup> p,a (mV)	÷190	+190	+190	+195
Ep,c (mV)	+120	+120	+120	+115
$\Delta E_{p}$ (mV)	70	70	70	80
E <sup>1</sup> /2 (mV)	+155	+155	+155	+155
<sup>i</sup> p,a (cm)	2.6	3.2	4.5	6.5
<sup>i</sup> p,c (cm)	2.4	3.3	4.6	6.3
<sup>i</sup> p,a <sub>/i</sub> p,c	1.08	0.97	0.98	1.03

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Moreover, the peaks currents were proportinal to  $v^{\frac{1}{2}}$ , as shown in Figure 2.



Fig. 2. Plot of  $i_{p,a}$  and  $i_{p,c}$  vs.  $v^{\frac{1}{2}}$  (hanging mercury drop electrode)

With a platinum bead electrode, under the same experimental conditions, the first wave behaves as in a quasi-reversible, one-electron redox process. As can be seen from Table II, with increasing scan rate the cathodic peak potential became slightly less positive, and the anodic slightly more positive, thus giving peak separations, increasing from 85 mV, at 100 mV.s<sup>-1</sup>, to 125 mV, at 500 mV.s<sup>-1</sup>. However the half-wave potential appeared to be practically independent of the scan rate, and not very different from the value obtained with

# TABLE II. Characteristics of the First Wave

(platinum bead electrode)

v (mV.s <sup>-1</sup> )	100	. 200	500
<sup>E</sup> p,a (mV)	+190	+195	+200
<sup>E</sup> p,c (mV)	+ 85	+ 80	+ 75
∆E <sub>p</sub> (mV)	105	115	125
E <sup>1/2</sup> (mV)	+138	+138	+138
<sup>i</sup> p,a (cm)	6.4	8.3	10.5
<sup>i</sup> p,c (cm)	7.0	8.7	10.9
<sup>i</sup> p,a/ <sub>i</sub> p,c	0.91	0.95	0.96

a hanging mercury drop electrode. Also the ratio of peak-currents with the platinum bead electrode were not as close to one as those with the hanging mercury drop electrode.

As shown in Figure 3, the cathodic peak currents were proportional to  $v^{1/2}$ , but the anodic were not, thus suggesting that the origin of the irreversibility lies mainly on the anodic half of the cycle.



Several new features appeared in cyclic voltammograms of visibly red solutions, as exemplified in Figure 4 (cf. Figure 1). From left to right: the first wave reproduced the wave of freshly prepared green solutions; the second wave became much better defined; several ill-defined reduction peaks appeared in the region of the third redox process.

This second wave corresponds to a quasi-reversible, one-electron redox process. The peak separation is 105 mV, at 100 mV.s<sup>-1</sup>, and the ratio of anodic to cathodic peak currents is 1, within experimental error. From this wave, the half-wave potential can be estimated at -0.390 V.



+ 400mV to -1200 mV, (2) from +350 mV to -50mV, (3) from -200 mV to -600 mV.

The change in colour of the solution was also studied using differential pulse polarography over a period of time. In the range +300 mV to -500 mV, a freshly made green solution only showed one peak at +0.095 V; in the course of time, a second peak appeared at -0.425V. The intensity of the first peak decreased with time, becoming almost unmeasurable after 24 hours. Simultaneously the second peak increased in intensity. The experimental results are shown in Table III.

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## TABLE III. Change of Peak Currents with Time

TIME (hours)	FIRST PEAK ( +0.095V)	SECOND PEAK ( -0.425 V)	
0	10.4	· _	
2	10.1	0.9	
4	7.6	2.5	
24	0.5 (?)	9.2	

Figure 5 illustrates these observations for three periods of time.



Fig. 5. Differential pulse polarograms of a solution 1.44x10<sup>-3</sup>M in complex and 0.1 M in tetraethylammonium perchlorate. DME: 1 drop per second. Pulse width: 50 mV. Scan rate: 2 mV.s<sup>-1</sup>. Polarograms: fresh solution (time 0) \_\_\_\_; after 4 hours, ----; after 24 hours, -.-. Both peak widths at half height are of the order of 100 mV, not far from the theoretical value of 90.4 mV for a one-electron reversible reaction<sup>5</sup>. Taking into the account the pulse width, halfwave potentials of +0.120 V and -0.400 V vs. S.C.E. can be estimated, in quite good agreement with those obtained from cyclic voltammetry, +0.155 V and -0.390 V, respectively.

These experiments clearly show the unusual behaviour of  $[CuL(H_2O)][CRO_4]_2.H_2O$  when dissolved in acetonitrile. A redox potential of 0.120 - 0.155 V vs. S.C.E. supports the idea of the involvement of a  $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{II}$  cycle in the synthesis of the complex.

The nature of the red product, or products, remains unknown. If it were a "spontaneous" reduction to  $Cu^{I}$ , as previously suggested<sup>6</sup>, an irreversible wave would be expected in the region of -0.40 V vs. S.C. E., but such a wave was only observed at *ca*. -0.95 V. Unfortunately, all attempts at isolating the red species were unsuccessful, but everything points to copper(II) species derived from the original complex.

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DIRECT POLAROGRAPHIC DETERMINATION OF EDTA IN OPHTHALMIC PRODUCTS BASED ON THE ANODIC OXIDATION OF THE DROPPING MERCURY ELECTRODE

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## SUMMARY

A direct polarographic method for EDTA determination based on the measurement of the anodic wave (DCP) or peak height (DPP) observed at +0.100 V,vs SCE, in the oxidation of the dropping mercury electrode in the presence of EDTA at pH=6.0 is described. The conditions for a simple and reproducible method using the standard additions technique for the analysis of this chelating agent in ophthalmic products are studied. Finally, the differential pulse polarographic method is applied to the analysis of EDTA in eye drops and contact lens wetting and cleaning solutions.

# INTRODUCTION

The pronounced ability of aminopolycarboxylic acids, mainly ethylenediaminetetraacetic acid (EDTA), as chelating agent of cations is used in many practical applications. The masking of metal ion impurities by EDTA improves the stability of foods, pharmaceutical and personal care products, etc.(1).EDTA is often added to ophthalmic products in order to avoid precipitates and to maintain clarity; it is also added because it prevents the development of resistence to many common antibacterial agents by removing calcium and magnesium ions from the outer cell wall of the bacteria, particularly <u>Pseudomonas</u> (2).

The oxidation of the dropping mercury electrode in the presence of EDTA has been studied by several authors. GOFFARD et al.(3) ascribe the observed anodic wave to a polarographic process controlled by the diffusion of EDTA towards the mercury electrode with the formation of HgY<sup>2-</sup>. NIKI et al.(4) using alternating current polarography describe the adsorption onto the electrode surface of the HgY<sup>2-</sup> complex. JACKSON and OSTERYOUNG (5)

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