# CYCLIC VOLTAMMETRIC STUDIES OF FOUR COPPER(II) COMPLEXES WITH A SULFUR -CONTAINING LIGAND

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## ABSTRACT

Solutions of [CuL] $(ClO_4)_2$, [CuLCl] $(ClO_4)$, [CuLBr] $(ClO_4)$, and [CuL$(NCS)_2$], (L=$C_{17}H_{25}N_3S_2$; structure below) in acetonitrile give well-defined cyclic voltammograms with a gold disk as working electrode. One electron metal-centered, reversible or quasi-reversible oxidation-reduction processes were observed. Differences in the cyclovoltammetric behaviour of the four complexes correspond to differences in their structures. The half-wave potentials are not unusually high, and only that of [CuL] $(ClO_4)_2$ falls within the range found for Type1 copper proteins. These observations will be described and discussed.

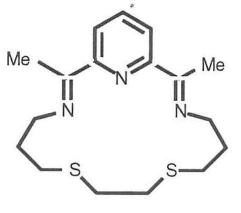
KEYWORDS: Dithia-triaza pyridine-derived macrocyclic ligand; copper(II) complexes; cyclic voltammetry

## INTRODUCTION

The factors which determine the rate of electron-transfer in the so-called "blue copper proteins", such as plastocyanine and azurin,were recently discussed by Wilson *et al* (1). In this contribution, reference is made to two papers published more than twelve years ago by Nelson and co-workers(2,3) in which they described the synthesis of several copper(I) and copper(II) complexes of the macrocyclic ligand **L** {2,15-dimethyl-7,10-dithia-3,14,20-triaza-bicyclo [14.3.1] icosa-1(20),2,14,16,18-pentaene}. Several properties, as well as crystal and molecular structures of these complexes, were also reported and discussed.

To be suitable as low molecular weight, synthetic models for the active sites of those "blue copper proteins", the complexes must possess practically reversible oxidation-reduction processes at relatively high potentials (4,5). In the present paper we report our work on the cyclic voltammetric behaviour of the following complexes:

$[CuL](ClO_4)_2$ **(A)**, $[CuLCl](ClO_4)$ **(B)**, $[CuLBr](ClO_4)$ **(C)**, $[CuL(NCS)_2]$ **(D)**.



**L**

## EXPERIMENTAL SECTION

### Starting materials

The studies were carried out with samples of the complexes which had been supplied years ago by S.M.Nelson; elemental analysis,and infrared and electronic spectra showed they were still in perfect condition.

Acetonitrile (Aldrich, HPLC grade, less than 0.03% $H_2O$) and tetraethylammonium perchlorate TEAP (Fluka, more than 99% pure) were used as received.

### Electrochemical measurements

Cyclic voltammograms were obtained with a PAR Model 174A polarographic analyzer, a PAR Model 175 universal programmer, and a Houston Omnigraph 2000 X-Y recorder. A Metrohm electrolysis cell, Model EA 876/5 was used, with a three -electrode system:a gold disk (Metrohm 6.1204.020, ca.3mm in diameter), as working electrode; a platinum spiral, as counter electrode; a Metrohm EA 44/1 saturated calomel, as reference electrode (SCE).

The SCE was connected to the cell through a salt bridge composed of a 0.1 molar $NaNO_3$ aqueous solution, in contact with the calomel electrode. The salt bridge and cell solutions were separated by a Vycor tip.

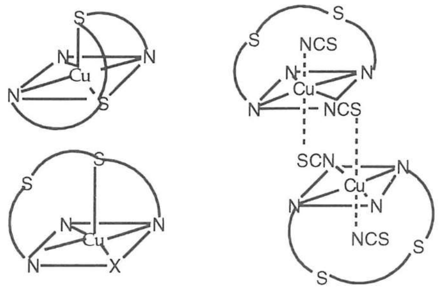
Cyclic voltammograms were obtained, at several scan rates, with freshly prepared solutions, *in situ*, about 1 milimolar in complex. This was achieved by the addition of solid complex to the solvent, with supporting electrolyte (0.1 molar TEAP), already in the cell, while bubbling deoxygenated dinitrogen through. During the experiments, carried out at 25.0±0.1°C, the solutions were kept under a blanket of deoxygenated dinitrogen.

Potentials are quoted versus SCE, and are uncorrected foı liquid junction potentials and *iR* drop; peak currents were corrected for background currents, whenever relevant.

Ferrocene, as an external standard, was used for two purposes: as a criterion for electrochemical reversibility and the number of electrons involved and to test the reliability of the reference system (SCE and salt bridge), by occasional checks of the reproducibility of the E values of the $Fc^+/Fc$ couple, which were $E_{1/2}$ =+340 mV ($\Delta E$=70 mV) under these experimental conditions.

## RESULTS AND DISCUSSION

To ilustrate the three different coordination modes of the ligand (3), schematic formulas of the complexes are given in Figure 1.



X= Cl; Br

Fig 1 - schematic structural formulas of the complexes

Figure 2 depicts typical voltammograms, run in the cathodic direction, at three scan rates: $50 mVs^{-1}$, $100\ mV\ s^{-1}$, $200\ mV\ s^{-1}$. The experimental results are summarized in Table 1.

Given the differences in the coordination environments and geometries of the complexes it is not surprising to find differences in their cyclovoltammetric behaviour.

As reported by Nelson *et al.* (3), in the solid state $[CuL(NCS)]_2$ is dimeric, with $NCS^-$ bridges. Conductance and spectral data in acetonitrile solution indicate the breaking of $NCS^-$ bridges and dissociation of one $NCS^-$anion.By comparison with $[CuL(NCS)](ClO_4)$, it may be assumed that the species in solution is $[CuL(NCS)]^+$with one sulfur atom of the macrocycle also coordinated. The other three complexes are ionic and monomeric.

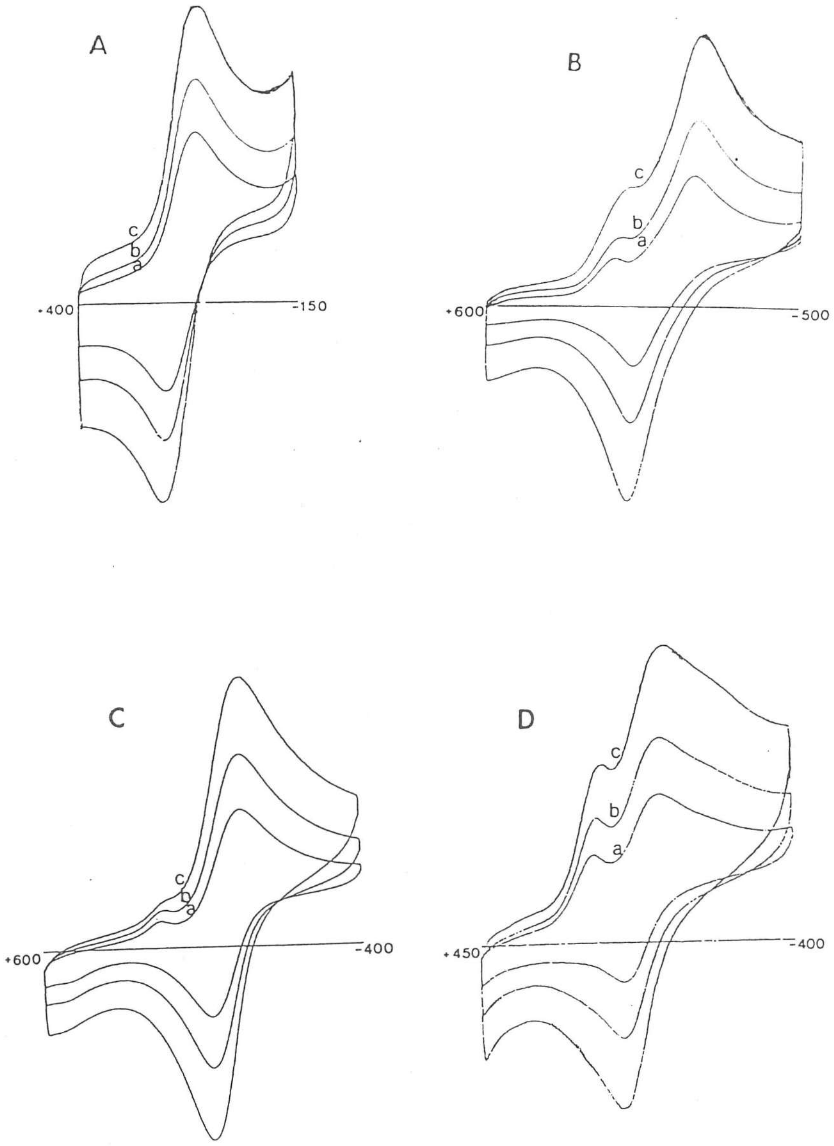


Fig.2 - Cyclic voltammograms of [CuL] $(ClO_4)_2$ (**A**), [CuLCl] $(ClO_4)$ (**B**), [CuLBr] $(ClO_4)$(**C**) and $[CuL(NCS)_2]$ (**D**) .Scan rates: a,50; b,100; c,200 $mVs^{-1}$.

**Table1**

Electrochemical data for the copper(II) complexes in MeCN solution, 0.1M in TEAP[a]

| Compound | Scan Rate ($mV.s^{-1}$) | $E_{p,c}$ (mV) | $E_{p,a}$ (mV) | $\Delta E_p$ (mV) | $E_{1/2}$ (mV) | $i_{p,a}/i_{p,c}$ |
|---|---|---|---|---|---|---|
| [CuL] $(ClO_4)_2$ (**A**) | 50 | +120 | +180 | 60 | +150 | 1,00 |
| | 100 | +115 | +180 | 65 | +147.5 | 0.98 |
| | 200 | +115 | +180 | 65 | +147.5 | 0.97 |
| [CuLCl] $(ClO_4)$ (**B**) | 50 | $+160^{b}$<br>-130 | +70 | 200 | -30 | 0.92 |
| | 100 | $+150^{b}$<br>-140 | +80 | 220 | -30 | 0.92 |
| | 200 | $+135^{b}$<br>-150 | +90 | 240 | -30 | 0.88 |
| [CuLBr] $(ClO_4)$ (**C**) | 50 | $+250^{b}$<br>-20 | +80 | 100 | +30 | 0.99 |
| | 100 | $+240^{b}$<br>-20 | +80 | 100 | +30 | 0.98 |
| | 200 | $+230^{b}$<br>-20 | +80 | 100 | +30 | 0.98 |
| $[CuL(NCS)_2]$ (**D**) | 50 | $+140^{b}$<br>-35 | +60 | 95 | +13 | 0.84 |
| | 100 | $+130^{b}$<br>-45 | +65 | 110 | +10 | 0.77 |
| | 200 | $+120^{b}$<br>-60 | +70 | 130 | +5 | 0.73 |

a: Potencials vs. SCE, uncertainty ± 5mV.
b: No anodic counterpart

With this exception, no further evidence of solvolysis was detected. For instance, there was no significant change in voltammograms recorded several hours apart with the same solutions in acetonitrile.

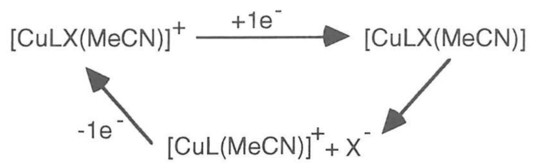
All four oxidation-reduction processes seem to be metal-centered, and to involve only one electron.

The tabulated values show that the couple $[CuL]^{2+}/[CuL]^{+}$ is clearly reversible, with $E_{1/2}$ (approx. +390mV vs. NHE) well within the range found in Type1 copper proteins(4). In the two complexes of this couple, copper is pentacoordinated in the crystalline solids, the geometry of the copper(II) complex being closer to *spy* (3) and that of copper(I) closer to *tbp* (2). Thus unless the solvent is coordinated, giving the same geometry for the species in solution, oxidation-reduction will involve a structural rearrangement (6), much faster than the scan rates used.

The couple $[CuLBr]^{+}/[CuLBr]$ can be considered practically reversible, but **B** and **D** can, at most, be considered quasi-reversible. In the case of the chlorocomplex **B**, $E_{1/2}$ is independent of scan rate, in spite of the increase in $\Delta E_p$, and the slight decrease in the peak currents ratio, with an increasing scan rate. The redox behaviour of **D** is an even less reversible process, probably as a consequence of the above mentioned solvolysis. In the cases of **B**, **C**, and **D** an irreversible reduction wave was observed at positive potentials. This wave might have its origin in the reduction of some of the azomethine groups of coordinated ligands.

Comparison of the tabulated values for **B** and **C** reveals two interesting facts:

1. **B** is the only complex with a negative value for $E_{1/2}$, 85 mV lower than that for **C**, although these complexes only differ in the anionic ligand.This is not entirely unusual,a similar event has been reported (7),and is probably connected with the greater affinity of $Cu^{+}$to $Br^{-}$.
2. Within experimental errors , the values of $E_{p,a}$ for **B** and **C** are practicaly the same suggesting that, by reduction, they produce the same species in solution. This is consistent with the well-known fact that acetonitrile stabilizes Cu(I),and that $[CuL]^{+}$has no apparent reactivity towards halide ions(2). It seems, therefore, reasonable to assume that a kind of ECE mechanism is involved.Since solvation (not solvolysis) is a general phenomenon, the following scheme is proposed:



## CONCLUSIONS

In the search for "good" synthetic models of the Type 1 copper centers of the "blue copper proteins" a very large number of complexes, with a variety of potentially tetradentate ligands, with a system of $N_2S_2$donor atoms, have been, and are being, extensively studied(4).

As an extension of this type of work, copper complexes with many other ligands, cyclic and acyclic, have been described.

If, as recently stated, complexes with $N_2S_3$-type, potentially pentadentate ligands are relatively rare(8), those with a $N_3S_2$-type ligand are even rarer. To the best of our knowledge, the macrocycle **L** is the only such ligand whose copper complexes have been synthesized, properly characterized, and carefully studied(2,3)

High values of oxidation-reduction potentials for the Cu(II)/Cu(I) couple in these complexes is generally associated with the coordination of two(9) or three (8,10) sulfur atoms from the ligand. The values reported in Table 1 confirm this opinion, as only complex **A,** with two coordinated sulfur atoms, has a potential sufficiently high to be comparable with that of Type1 copper proteins.

## ACKNOWLEDGMENT

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## REFERENCES

1. S.Flanangan, J.A. Gonzàlez, J.E.Bradshaw, L.J. Wilson, D.M. Stanbury, K.J.Haller, W.R. Scheidt, in *Bioinorganic Chemistry of Copper*, K.D. Karlin and Z.Tyeklár, Eds.(Chapman & Hall, New York,**1993),** pp.91-97.
2. M.G B.Drew, C.Cairns, S.G.McFall, S.M.Nelson, *J.Chem. Soc., Dalton Trans.*, **1980,** 2020.

3. M.G.B.Drew, C.Cairns, S.M.Nelson, J.Nelson, *J.Chem.Soc., Dalton Trans.*, **1981**, 942.
4. J.O.Cabral, in *Molecular Electrochemistryof Inorganic, Bioiorganic and Organometallic Compounds,* A.J.L.Pombeiro, e J.A.McCleverty, Eds., (Kluver Academic Publishers, the Netherlands, **1933)**, pp.151-170, and references therein.
5. Y.Lu,L.B.LaCroix,M.D..Lowery, E.I.Solomon, C.J.Bender, J.Peisach, J.A.Roe, E.B.Gralla, J.S.Valentine, *J.Am.Chem.Soc.* **1993** , *115* , 5907.
6. E.W.Ainscough, A.M.Brodie, S.L.Ingham, J.M.Waters, *J.Am .Chem.Soc., Dalton Trans.*, **1994**, 215.
7. Y.Nishida, M.Takeuchi, N.Oishi, S.Kida, *Inorg. Chim Acta.*, **1985**, *96*, 81.
8. B.Adhikary, C.R.Lucas, *Inorg. Chem.*, **1994,** *33*, 1376.
9. W.G.Hanstra , M.F.Cabral, J.de O.Cabral, W.L.Driessen, J. Reedijk,*Inorg.Chem.* **1992**, *31*, 3150.
10. V.V. Pavlishchuk, A.W. Addison, *Inorg.Chim.Acta,* **1993**, *203,* 29.

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# An Electrochemical Study of Silver Electrodeposition Coupled with Hydrogen Peroxide on Carbon Microelectrodes

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## Abstract

Distributions of the induction times of silver potentiostatic electrodeposition coupled with hydrogen peroxide oxidation/reduction onto carbon microelectrodes have been obtained. The nucleation process has been shown to be affected by kinetic complexities due to the disproportionation of hydrogen peroxide and therefore neither the pure birth model nor the birth and death electronucleation model have shown to be applicable to this system. The double potential step and linear sweep voltammetry measurements point to the formation of silver peroxy species during the electrodeposition process.

## Introduction

The early stages of the electrochemical deposition of silver centres *i. e.*, the nucleation process on metallic surfaces has been repeatedly investigated either using carbon macroelectrodes and microelectrodes [1-6]. It has been observed that the centres are

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