



# Steric vs electronic effects and solvent coordination in the electrochemistry of phenanthroline-based copper complexes



Mirko Magni<sup>a,\*</sup>, Alessia Colombo<sup>a,\*</sup>, Claudia Dragonetti<sup>a,b</sup>, Patrizia Mussini<sup>a,1</sup>

<sup>a</sup> Dipartimento di Chimica dell'Università degli Studi di Milano, UdR-INSTM di Milano, Via Golgi 19, I-20133 Milano, Italy

<sup>b</sup> Istituto di Scienze e Tecnologie Molecolari del CNR, ISTM-CNR, Via Golgi 19, I-20133 Milano, Italy

## ARTICLE INFO

### Article history:

Received 13 June 2014

Received in revised form 14 July 2014

Accepted 15 July 2014

Available online 1 August 2014

### Keywords:

phenanthroline copper complexes  
steric effects  
electronic effects  
solvent coordination  
ion pairing

## ABSTRACT

The present exhaustive electrochemical study proposes a rationalization of the redox properties of 1,10-phenanthroline-based copper complexes as a function of *i*) ligand molecular structure, evidencing the competition between electronic and steric effects of alkyl/aryl substituents, and *ii*) nature of working medium in terms of both solvent and supporting electrolyte anion. Occupancy of the 2 and 9 positions of the phenanthroline is a powerful tool to modulate the oxidation potentials of this family of complexes in a wide potential range. Solvent molecules play a key role in the metal-centred oxidative electron transfer process (unlike the optical electron transition), acting as ancillary ligands that allow the transition between tetrahedral four-coordinated Cu(I) state to tetragonal five-coordinated Cu(II). Actually clear evidences of the entry of one solvent molecule in the inner coordination sphere of the complexes are proved by the Kolthoff and Lingane method. Proof of ionic couple formation is also found.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Copper complexes have been object of a great variety of studies in many different fields of chemistry [1,2]; one of the very recent applications of this class of metal complexes regards the sustainable energetics concerning the optimization of the third generation of photovoltaic devices, commonly named dye-sensitized solar cells (DSSCs) [3], in which copper complexes have been employed both as sensitizers and as redox mediators acting as “sunlight harvester” and “electron shuttle” between the two cell electrodes respectively [4,5].

Despite, at now, the best promising metal-based candidates to overcome the disadvantage of the most used  $I_3^-/I^-$  electron mediator couple have been cobalt complexes [6,7], copper-based ones have started showing their potentiality especially with phenanthroline ligands as demonstrated by Bai [8] and by our recent paper [9]; the mediator performances appear to be significantly modulated by the phenanthroline structure [5].

Notwithstanding the rich literature concerning electron transfer at copper centers [10], a comprehensive rationalization from the electrochemical point of view of the redox properties of this

class of phenanthroline chelate complexes as a function of their ligand structures was still overdue. The present study tries to fill the gap, investigating electronic and steric effects in a systematic family of alkyl- and aryl-substituted phenanthroline complexes, also considering solvent and supporting electrolyte effects.

## 2. Experimental

### 2.1. Synthesis of copper complexes

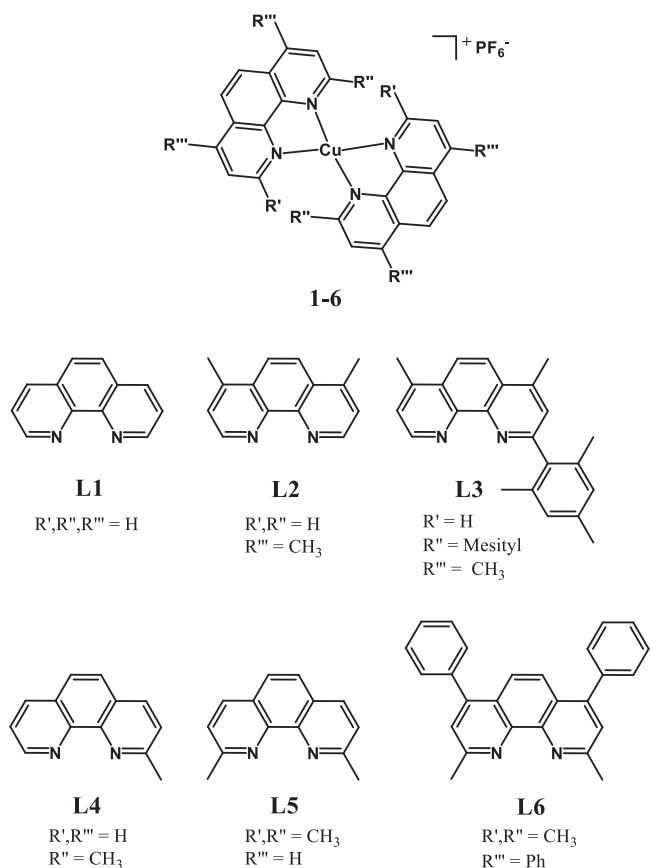
The ligands **L1–L6** and the related hexafluorophosphate copper (I) complexes **1–6** object of this work are summarized in the Fig. 1.

The symmetric phenanthrolines **L1**, **L2**, **L5** and **L6** were purchased from Sigma Aldrich. The asymmetric ligands were synthesized as follow (Scheme 1): 2-mesityl-4,7-dimethyl-1,10-phenanthroline, **L3**, [9] was prepared through a two-step procedure: *i*) nucleophilic aromatic substitution of 4,7-dimethyl-1,10-phenanthroline (Aldrich) with mesityllithium, obtained reacting bromomesitylene (Aldrich) with *tert*-butyllithium (Aldrich) and *ii*) rearomatization of the intermediate species; 2-methyl-1,10-phenanthroline, **L4**, was synthesized through a condensation reaction, starting from commercially available 8-amino-quinoline (Aldrich) according to the Bernhard and coworkers' procedure [11]. Copper complexes **1–6** were synthesized starting from tetrakis(acetonitrile) copper(I) hexafluorophosphate according to the literature [9,12]. (Scheme 1)

\* Corresponding authors. Tel.: +39 02 50314400.

E-mail addresses: [mirko.magni@unimi.it](mailto:mirko.magni@unimi.it) (M. Magni), [alessia.colombo@unimi.it](mailto:alessia.colombo@unimi.it) (A. Colombo).

<sup>1</sup> ISE member.



**Fig. 1.** Molecular structures of the hexafluorophosphate Cu(I) complexes **1-6** and the related ligands **L1-L6**.

## 2.2. Electrochemical and spectrophotometric measurements

The experimental apparatus and protocol for electrochemical study were the same reported in a previous work [13], employing

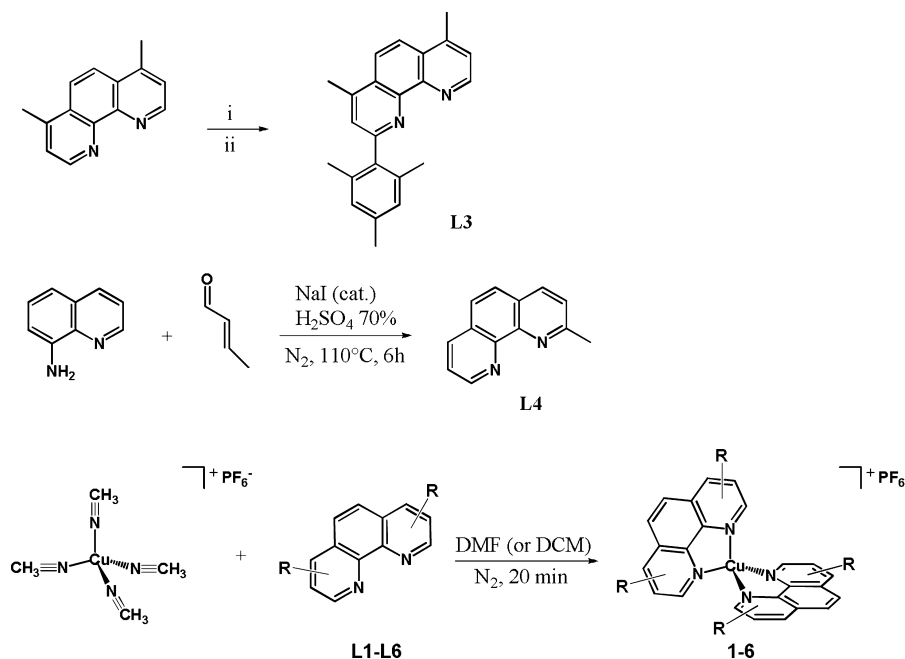
a three-electrode cell with a glassy carbon (Metrohm, surface area 0.071 cm<sup>2</sup>) as working electrode, a saturated calomel electrode as operative reference one and a platinum foil as counter-electrode in a solution well-deaerated by nitrogen bubbling. To avoid contamination of the working solution (*i.e.* water and chloride ions), the reference electrode was inserted in a glass jacket (ending in a glass frit, allowing the electrical continuity) filled with the same solution of the working medium. An instrumental compensation (*i.e.* positive feedback) of the ohmic drop between the working and reference electrode was carefully performed. The recorded potentials were all referred to the intersolvental reference redox couple ferricenium/ferrocene, Fc<sup>+</sup>/Fc [14]; in our conditions the half-wave potential of the Fc<sup>+</sup>/Fc couple,  $E_{1/2}$  Fc<sup>+</sup>/Fc, was *ca.* 0.48 V, 0.39 V, 0.44 V vs SCE in N,N'-dimethylformamide, acetonitrile and dichloromethane respectively.

All solvents (N,N'-dimethylformamide, DMF; acetonitrile, ACN; dichloromethane, DCM) and tetrabutylammonium-based supporting electrolytes (TBABPh<sub>4</sub>; TBAPF<sub>6</sub>; TBAClO<sub>4</sub>) were purchased from Sigma Aldrich as electrochemical grade chemicals.

UV-visible absorption spectra were recorded using a Jasco V-530 spectrophotometer.

### 2.2.1. Kolthoff and Lingane method

To evaluate the possible solvent involvement as ancillary ligand in copper complexes, an adapted version was applied of the classical Kolthoff and Lingane approach [15]. Oxidative cyclic voltammetry patterns were recorded for the complexes in the low polar solvent DCM as such and with increasing additions of small volumes of polar DMF (in the 1:1 to 110:1 molar ratio range, with respect to the copper complex). The negative shifts of the half-wave potential for the Cu<sup>+</sup>/Cu<sup>2+</sup> process, normalized by  $k/n$  ( $k$  = Nernst constant,  $n$  = exchanged electrons per mole of complex), were plotted against  $\log_{10} C_{\text{DMF}}$  yielding straight lines with slopes and intercepts accounting for complexation numbers of DMF and formation constants of DMF: complex adducts, respectively. In order to rule out possible potential drift effects of the SCE reference electrode during the progressive DMF additions to the working medium (DCM + TBAPF<sub>6</sub> 0.1 M), we validated the results adding, during a second repeated measurement series, an equimolar amount of



**Scheme 1.** Top: reaction scheme for the synthesis of **L3** ligand [9]; i) mesityllithium, toluene, 0 °C, r.t., 20 h; ii) MnO<sub>2</sub> activated, toluene/DCM 5:3, r.t., 20 h. Middle: reaction pathway for the preparation of the **L4** phenanthroline [11]. Bottom: general procedure for the synthesis of copper complexes **1-6** [9,12].

Download English Version:

<https://daneshyari.com/en/article/185306>

Download Persian Version:

<https://daneshyari.com/article/185306>

[Daneshyari.com](https://daneshyari.com)