



Thiophene-containing β -diketonate complex of copper(II): X-ray crystal structure and electropolymerization

Jocelyn Oyarce, Loreto Hernandez, Guillermo Ahumada, Juan Pablo Soto, María Angélica Del Valle, Vincent Dorcet, David Carrillo, Jean-René Hamon, Carolina Manzur

► To cite this version:

Jocelyn Oyarce, Loreto Hernandez, Guillermo Ahumada, Juan Pablo Soto, María Angélica Del Valle, et al.. Thiophene-containing β -diketonate complex of copper(II): X-ray crystal structure and electropolymerization. Polyhedron, 2017, 123, pp.277–284. 10.1016/j.poly.2016.12.003 . hal-01515133

HAL Id: hal-01515133

<https://univ-rennes.hal.science/hal-01515133>

Submitted on 19 Jun 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ms. Ref. No.: POLY-D-16-01015

Revised version

Thiophene-containing β -diketonate complex of copper(II): X-ray crystal structure and electropolymerization

Jocelyn Oyarce^a, Loreto Hernández^b, Guillermo Ahumada^a,
Juan Pablo Soto^a, María Angélica del Valle^{c*}, Vincent Dorcet^d,
David Carrillo^a, Jean-René Hamon^{d*}, Carolina Manzur^{a*}

^aLaboratorio de Química Inorgánica, Instituto de Química, Pontificia Universidad Católica de Valparaíso, Campus Curauma, Avenida Universidad 330, Valparaíso, Chile

^bLaboratorio de Electroquímica, Instituto de Química y Bioquímica, Facultad de Ciencias, Universidad de Valparaíso, Avda. Gran Bretaña 1111, Playa Ancha, Valparaíso, Chile

^cLaboratorio de Electroquímica de Polímeros (LEP), Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, 7820436 Macul, Santiago, Chile

^dInstitut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Corresponding authors

Phone: +56 32 227 49 32, e-mail address: cecilia.manzur@pucv.cl (C. Manzur)

Phone: +33 22 323 59 58, e-mail address: jean-rene.hamon@univ-rennes1.fr (J.-R. Hamon)

Phone: +56 2 354 44 05, e-mail address: mdvalle@uc.cl (M. A. del Valle)

Abstract

In this work, we report the synthesis of the asymmetrical β -diketone 1-(thiophen-2-yl)-3-(thiophen-3-yl)propane-1,3-dione (HL) and its corresponding *bis*(β -diketonate)copper(II) complex $[\text{Cu}\{1-(\text{thiophen-2-yl})-3-(\text{thiophen-3-yl})-1,3\text{-propanedionate}\}_2]$ (CuL_2), isolated in 60 and 86% yields, respectively. These two new compounds have been characterized by elemental analysis, FT-IR and UV-Vis spectroscopy and, in the case of HL, by ^1H and ^{13}C NMR spectroscopy. Additionally, both compounds were authenticated by X-ray diffraction analysis. The β -diketone HL exists as its keto-enol tautomer both in solution and in the solid-state with the -OH group adjacent to the 3-thienyl unit. The CuL_2 is essentially flat and the Cu(II) center adopts a perfect square planar geometry. The CuL_2 modified electrode was fabricated through the electropolymerization of the monomer in a 0.1 M of tetrabutylammonium tetrafluoroborate (TBATFB) in anhydrous acetonitrile solution, in the potential window -1.0 V to 1.6 V. The thin film $\text{Pt}[(\text{CuL}_2)_n]$ modified electrode response was studied employing a 0.1 M of TBATFB solution in CH_3CN . Likewise, the potentiostatic method was also employed to synthesize the films on Fluorine Doped Tin Oxide electrode (FTO). Images from the electrode surface were obtained using Scanning Electron Microscopy (SEM).

Keywords: copper; 1-(thiophen-2-yl)-3-(thiophen-3-yl)propane-1,3-dione; electropolymerization; X-ray diffraction analysis; electrodeposition

1. Introduction

β -diketones and their transition metal complexes [1] are of current interest because they are easily synthesized, functionalized in three sites of the ligand molecule [2], and they exhibit a variety of pharmacological applications [3] and properties that have made them useful for catalysis in organic reactions [4], and as materials for applications in electroluminescent materials in various emerging optoelectronic and photonic technologies, v. g., LEDs devices [5]. In addition, these compounds exhibit attractive building block features for the preparation of Metal Organic Frameworks (MOFs) [6] and as precursors of polydentate Schiff base ligands [7,8]. So far, there are a lot of β -diketone ligands with features including polymerizable groups such as thienyl and there derivatized rings. Those latter compounds are of particular interest for obtaining covalent coupling of a metal complex to a polymer backbone because they can be electropolymerized [9]. The advantages of this last methodology are well known and include the formation of films whose thickness can be modulated through, for example, modifying electrochemical parameters, changing the nature of the electrolyte support or the nature of the used working electrodes. Thus, it is possible to obtain, in a fast and easy way, modified electrodes to be used in electrocatalytic processes or as potential materials for the manufacture of optoelectronic devices.

In this context, we describe here the electrochemical behavior of a *bis*-(β -diketonate complex) of copper(II) (CuL_2), in which the β -diketonate ligand (L) is asymmetrically substituted with two thienyl groups, and its ability to form deposits *via* electropolymerization. Herein, our work deals (i) with the synthesis, the spectroscopic characterization and the crystal and molecular structures solved by X-ray diffraction analysis of the new β -diketone 1-(thiophen-2-yl)-3-(thiophen-3-yl)propane-1,3-dione (HL) and its corresponding copper(II) complex CuL_2 (see structures in Scheme 1), and (ii) with the preparation and characterization of $(\text{CuL}_2)_n$ deposits obtained by electropolymerization of the monomeric species. To the best of our knowledge, polythienyl bearing β -diketonate complexes have not been described in the literature or deposited on an electrode using an electrochemical oxidation process.

2. Experimental section

2.1. General experimental methods

Reactions were performed under dry dinitrogen atmosphere using standard Schlenk technique. Solvents were dried and distilled under dinitrogen by standard methods prior to use [10]. All chemicals were purchased from commercial sources and used without further purification. FT-IR spectra were recorded from KBr disks on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the 4000-450 cm^{-1} range. Electronic spectra were recorded in CH_2Cl_2 in a Shimadzu UV-1800 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained in $(\text{CD}_3)_2\text{CO}$ on a Bruker 300 FT-NMR spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the residual deuterated solvent peaks [$(\text{CD}_3)_2\text{CO}$: ^1H δ = 2.06 ppm, ^{13}C δ = 28.96, 205.25 ppm]. ^1H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^1H - ^1H COSY and ^1H - ^{13}C HSQC NMR experiments, and are given according to the numbering scheme of Fig. 1. Coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used to describe the signals: s = singlet, dd = double doublet, br = broad. Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1, France. Melting points were measured in evacuated capillaries on a Kofler Bristoline melting point apparatus and were not corrected. For electrochemical experiments, anhydrous acetonitrile (CH_3CN , 99.8%, Aldrich) stored over molecular sieves and tetrabutylammonium tetrafluoroborate (TBATFB, 99.0% Aldrich) previously dried at 120 $^\circ\text{C}$, were used as solvent and supporting electrolyte, respectively. All electrochemical measurements were accomplished on a Voltalab PG2100 potentiostat at r. t. (20 $^\circ\text{C}$) under high purity argon atmosphere, in a three-compartment, three-electrode anchor-type electrochemical cell. A platinum disk (0.07 cm^2 geometric area) was used as working electrode, a platinum wire coil of large geometric area as counter electrode and Ag|AgCl in KCl solution, as reference electrode.

2.2. Synthesis of 1-(thiophen-2-yl)-3-(thiophen-3-yl)propane-1,3-dione (HL)

A Schlenk tube was loaded with a magnetic stirrer, 2.0 g (15.5 mmol) of 3-acetylthiophene 98%, 2.02 g (15.8 mmol) of potassium *tert*-butoxide 95% and 30 mL of dry THF. After 30 minutes of stirring at r. t., ethyl-2-thiophenecarboxylate 95% (2.6 mL, 18.4 mmol) in 20 mL of THF was added dropwise to the orange mixture. Stirring was continued for 5 h, after which time the reaction was quenched by addition of water (10 mL) to dissolve the slurry

suspension and 30 mL of 1.0 M aqueous HCl. The resulting solution was stirred for additional 30 min, and extracted with diethyl ether (3x20 mL). The extracts were combined, dried over MgSO₄ and concentrated under vacuum. The resulting residue was purified by silica gel chromatography (9/1 hexane/ethyl acetate as eluent). The yellow band was collected and slow evaporation of the solvents overnight afforded 2.10 g (60% yield) of HL as light yellow crystalline solid. A suitable single crystal was selected from this crop for X-ray diffraction analysis. M. p. 102 °C. Anal. calcd for C₁₁H₈O₂S₂ (236.31 g mol⁻¹): C, 55.91; H, 3.41; S, 27.14. Found: C, 55.79; H, 3.16; S, 28.75. FT-IR (KBr, cm⁻¹): 3422 (m) ν(O-H), 3099 (m), 3084 (m) ν(C-H arom), 2924 (m) ν(C-H aliph), 1572 (vs) ν(C≡O and C≡C), 785 (vs), 720 (m) δ(C-H out-of-plane thienyl group). ¹H NMR (300MHz, (CD₃)₂CO): δ 16.3 (br s, 1 H, O-H), 8.37 (dd, *J*_{H-H}=3.0, 1.3 Hz, 1 H, H-2 3-Th), 8.08 (dd, *J*_{H-H}=3.8, 1.2 Hz, 1 H, H-5 2-Th), 7.92 (dd, *J*_{H-H}=5.0, 1.1 Hz, 1 H, H-4 2-Th), 7.72 (dd, *J*_{H-H}=5.0, 1.3 Hz, 1 H, H-4 3-Th), 7.63 (dd, *J*_{H-H}=5.1, 3.0 Hz, 1 H, H-5 3-Th), 7.27 (dd, *J*_{H-H}=5.0, 3.9 Hz, 1 H, H-3 2-Th), 6.99 (s, 1 H, CH=C). ¹³C NMR (75.48 MHz, (CD₃)₂CO): δ 183.3 (C=O), 176.2 (CH=C), 142.2 (C-3 3-Th), 137.9 (C-2 2-Th), 133.5 (C-3 2-Th), 131.1 (C-5 2-Th), 129.9 (C-2 3Th), 128.5 (C-4 2-Th), 127.2 (C-5 3-Th), 125.8 (C-4 3-Th), 93.3 (CH=C).

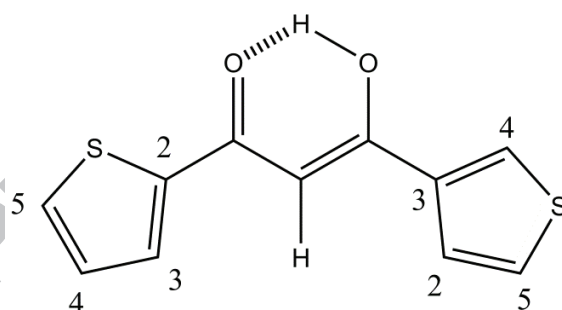


Fig. 1 Labeling scheme used for NMR assignments

2.3. Synthesis of the bis-β-diketonato complex, CuL₂

A Schlenk tube equipped with a reflux condenser was charged with a magnetic stirrer, 200 mg of HL (0.85 mmol), 78.4 mg of copper(II) acetate 98% (0.42mmol) and 20 mL of ethanol. The reaction mixture was refluxed for 2 h. Upon cooling to r. t., a green solid was formed and filtered off, washed with water, ethanol and diethyl ether and dried under vacuum to

afford 193.4 mg (86.3% yield) of CuL_2 . Suitable single crystals for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution, at r. t. M. p. 295 °C. Anal. calcd. for $\text{C}_{22}\text{H}_{14}\text{CuO}_4\text{S}_4$ (534.15 g mol^{-1}): C, 49.47; H, 2.64; S, 24.01; Found: C, 49.49; H, 2.46; S, 26.12. FT-IR (KBr, cm^{-1}): 3103.5 (w) $\nu(\text{C-H arom})$, 1559 (s), 1534 (vs), $\nu(\text{C}=\text{O}$ and $\text{C}=\text{C})$, 767 (m), 707 (w) $\delta(\text{C-H out-of-plane th})$.

2.4. X-ray crystal structures determination

Crystallographic measurements for HL were carried out at $T = 150(2)$ K on a APEXII Bruker-AXS diffractometer equipped with a bidimensional CCD detector, using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). X-ray intensity data for CuL_2 were collected at 150(2) K on a D8 VENTURE Bruker AXS diffractometer equipped with a myltiplayers monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and a CMOS Photon100 detector. For each compound, a crystal of appropriate size was coated in Paratone-N oil, mounted on a Kaptan loop and transferred to the cold gas stream of the cooling device. The structures were solved by direct methods using *SIR97* program [11], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*) [12], with all non-hydrogen atoms being refined anisotropically. The disorder observed for the thiophene fragments in the two compounds was modelled using three sites for the sulphur atoms in each thienyl ring. In HL, the enol H atom was found by difference synthesis and refined isotropically. All the other hydrogen atoms were included in calculated positions and were refined as riding atoms with isotropic displacement parameters. A summary of the details about crystal data, collection parameters and refinement are documented in Table 1, and additional crystallographic details are in the CIF files. ORTEP views are generated using OLEX2 [13].

Table 1 Crystallographic data, details of data collection and structure refinement parameters for compounds HL and CuL_2

	HL	CuL_2
Empirical formula	$\text{C}_{11}\text{H}_8\text{O}_2\text{S}_2$	$\text{C}_{22}\text{H}_{14}\text{CuO}_4\text{S}_4$
Formula mass (g mol^{-1})	236.29	534.11
Collection T (K)	150(2)	150(2)

Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	6.8695(4)	11.9169(6)
b (Å)	15.3683(7)	7.6739(3)
c (Å)	9.9367(5)	11.5858(6)
β (°)	98.234(2)	95.536(2)
V (Å ³)	1038.23(9)	1054.57(9)
Z	4	2
D _{calcd} (g cm ⁻³)	1.512	1.682
Crystal size (mm)	0.60 x 0.55 x 0.50	0.25 x 0.20 x 0.12
F(000)	488	542
Absorption coefficient (mm ⁻¹)	0.486	1.460
θ range (°)	2.996 to 27.475	3.162 to 27.468
Range h,k,l	-8/7, -19/18, -12/12	-15/15, -7/9, -15/15
No. independent refl.	6975	15434
No. unique refl. (>2)	2366	2407
Comp. to θ_{\max} (%)	99.4	99.9
Max/min transmission	0.784/0.705	0.839/0.769
Data/restraints/parameters	2366/12/151	2407/27/141
Final R indices [$I > 2\sigma(I)$]	R ₁ =0.0588, wR ₂ =0.1657	R ₁ =0.0416, wR ₂ =0.0968
R indices (all data)	R ₁ =0.0668, wR ₂ =0.1714	R ₁ =0.0580, wR ₂ =0.1038
Goodness of fit/F ²	1.052	1.049
Largest diff. peak/hole (e Å ⁻³)	0.864/-0.790	0.535/-0.407

2.5. Electrochemical synthesis and characterization

Polymer films were deposited by potentiodynamic method (CV) under the previously optimized experimental conditions, namely potential window -1.0 V to 1.6 V, scan rate 0.05 Vs⁻¹

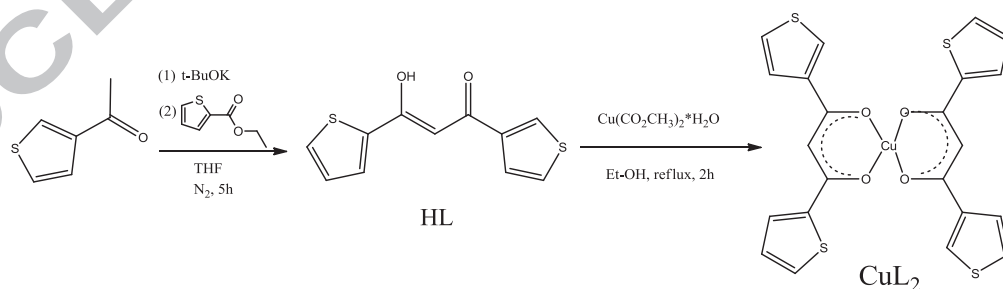
(twenty consecutive cycles). The working solution consisted of 1.0 mM CuL_2 and 0.1 M TBATFB in anhydrous acetonitrile. Subsequently, the $\text{Pt}[(\text{CuL}_2)_n]$ modified electrode response was studied employing a 0.1 M TBATFB solution in CH_3CN . Finally, potentiostatic method was also employed to synthesize the films on Fluorine Doped Tin Oxide (FTO) electrode, and images from the electrode surface were obtained on a fifty LEO VP1400 Scanning Electron Microscope (SEM).

The optimization of the electro-synthesis process of $\text{Pt}[(\text{CuL}_2)_n]$ was carried out by CV varying the potential window on Pt electrode, the supporting electrolyte, the solvent, and concentration. The most appropriate conditions in this case are those indicated in the preceding paragraph. Potentiostatic method was also employed to synthesize the films on FTO electrode, with the aim to perform the morphological analysis of the surface. Working under the same experimental conditions used for CV measurements, it was found that the suitable oxidation potential to polymerize by potentiostatic perturbation (chronoamperometry) is 2.3 V.

3. Results and discussion

3.1. Synthesis and characterization

As shown in Scheme 1, the new asymmetric β -diketone HL was prepared in 60% yield as a yellow solid, following a slightly modified procedure reported in the literature [14]. Its *bis*(β -diketonate) copper(II) complex CuL_2 was isolated in 86% yield, as green microcrystalline powder upon reaction of the protonated ligand HL with copper(II) acetate (2:1 stoichiometric ratio) in refluxing ethanol (Scheme 1).



Scheme 1 Synthesis of β -diketone HL and its corresponding *bis*(β -diketonate)copper(II) complex CuL_2 .

Both compounds are air and thermally stable and exhibit rather good solubility in DMSO, THF, CH₂Cl₂, acetone, acetonitrile but are insoluble in alcohols and hydrocarbons. Their compositions and identities were deduced from satisfactory elemental analysis, ¹H and ¹³C NMR spectroscopy (HL) and absorption spectroscopy. In addition, the crystal and molecular structures of HL and CuL₂ were determined by single-crystal X-ray diffraction analysis (see below).

The more salient features of the solid-state FT-IR spectrum of the β-diketone HL are: (i) the presence of a band at 3422 cm⁻¹ assigned to the ν(O-H) stretching vibration, and (ii) a broad and strong band at 1572 cm⁻¹ attributed to the C=O and C=C stretching modes, clearly showing the existence of the keto-enol tautomeric form [15,16]. In the spectrum of complex CuL₂, the ν(O-H) vibration vanished while the broad one splitted into two intense sharp bands at 1560 and 1534 cm⁻¹. Moreover, they are shifted to lower wave numbers, consistent with the coordination of the Cu(II) center to the oxygen atoms of the β-diketonate ligands and with an increased quasi-aromaticity of the six membered chelate rings [17]. In addition, the two absorption bands observed for HL in the 785-708 cm⁻¹ region, due to the substituted thienyl rings [18], are virtually unchanged in the spectrum of the CuL₂ complex, thus indicating that the thiophene sulfur atoms are not coordinated to the Cu(II) center.

Meanwhile, the ¹H NMR spectrum of HL recorded in deuterated acetone solution at 298 K, showed a broad signal at 16.3 ppm and a sharp singlet at 6.99 ppm, each resonance having an integral value of 1 H, due to the intramolecularly hydrogen bonded enolic proton and the methine proton, respectively, demonstrating that the enol form, stabilized by intramolecular hydrogen bonding, predominates in solution with a population of *ca.* 95%. Those chemical shift data do not, however, indicate the dominant structure of the enol tautomer in solution, which can be either (2-Th)-C(OH)=CHC(O)-(3-Th) or (2-Th)-C(O)CH=C(OH)-(3-Th). The behavior of HL slightly contrasts with the 18/82 diketone/keto-enol ratio reported by Conradie *et al.* [19] for the symmetric 1,3-*bis*(thiophen-2-yl)-propane-1,3-dione in CDCl₃. However, the solvents are different, and we have previously observed complete enolization of a diketone/keto-enol mixture on passing from chloroform to acetone, a more polar solvent [16b]. In addition, each of the six magnetically non equivalent protons of the two different thienyl rings showed up as a double doublet between 8.37 and 7.27 ppm (see Section 2.2 for complete assignments).

The ¹³C NMR spectrum confirms both the asymmetry of the molecule and the existence of the keto-enol isomer in solution with two carbonyl carbon signals at 183.3 ppm (C=O) and

176.2 ppm (=C-OH), and that of the methine carbon at 93.3 ppm. In agreement with the proposed structure, the magnetically non equivalent thienyl carbons give rise to eight lines in the range 142.2 to 125.8 ppm (see Section 2.2 for complete assignments).

The electronic absorption spectra in the UV-visible region for HL and CuL₂ were recorded in CH₂Cl₂ solution (Fig. 2). Upon deconvolution of the spectra with Gaussian curves, the two experimental absorption bands in HL give rise to a set of three transitions, while the four experimental absorption bands in CuL₂ give rise to a set of five transitions (Table 2). The lower-energy absorption bands in HL are assumed to originate from intraligand π - π^* transitions, which are slightly shifted towards lower energies in CuL₂ because of increased π delocalization in the chelate ring. In addition, the band at 306 nm observed for the CuL₂ complex is assumed to originate from ligand-to-metal charge transfer (LMCT), while the broad band observed at 635 nm is due to d-d transitions and is indicative of the square-planar Cu(II)-complexes with D_{4h} symmetry [20].

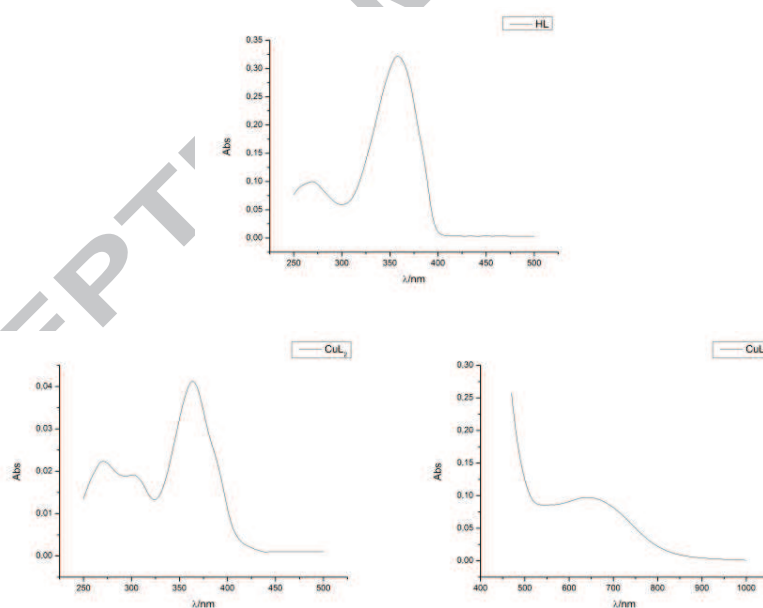


Fig. 2 Experimental UV-vis spectra of HL (top) and CuL₂ (bottom: UV (left), vis. (right)) recorded in CH₂Cl₂ solution at 20 °C

Table 2 Electronic Spectral Data for HL and CuL₂

Compd.	λ_{\max} / nm (log ϵ) (CH ₂ Cl ₂)
HL	267 (4.98)
	347 (5.38)
	370 (5.21)
CuL ₂	269(4.33)
	306(4.15)
	363(4.61)
	393(3.68)
	635(1.99)

3.2. X-ray Crystallographic Study

Diffraction-quality single crystals for X-ray structure investigation were obtained for the dicarbonyl derivative HL and for its copper(II) complex CuL₂ by slow evaporation of solutions of the compounds in *n*-hexane/ethyl acetate mixture and dichloromethane, respectively. Molecular structures of HL and CuL₂ with partial atom labelling scheme are displayed in Figs. 3 and 4, respectively. Crystal data for the structures of HL and CuL₂ are summarized in Table 1, and selected bond distances and angles are listed in Table 3. Both compounds crystallize in the monoclinic centrosymmetric P2₁/c space group with in each case, a single molecule in the asymmetric unit. All close intermolecular contacts correspond to van der Waals interactions. In both compounds, orientational disorder of the thienyl rings is observed with the sulphur atoms in each thienyl ring occupying three sites.

In β -diketone HL, the planes of the 2-thienyl ring and of the 3-thienyl ring make similar angles of 6.45 and 6.65°, respectively, with the plane of the enol ring. Thus, the three units can be considered to be approximately coplanar taking into account the large thermal motion in the molecule. The molecular parameters indicate the formation of a single enol form rather than a tautomeric equilibrium between the two enol forms in the solid state. The two C-O and two C-C bond lengths in the enol ring are significantly different (Table 3). Indeed, the C(5)-O(1) (1.277(3) Å) and C(6)-C(7) (1.381(4) Å) bonds display double bond character, while the C(7)-O(2) (1.311(3) Å) and C(5)-C(6) (1.418(4) Å) bonds exhibit single bond character (Fig. 3) [21]. Those

bond lengths as well as the bond angles (see Table 3) in the backbone of the enol ring are in agreement with those measured for the other reported thienyl-containing β -diketone compounds [19,22].

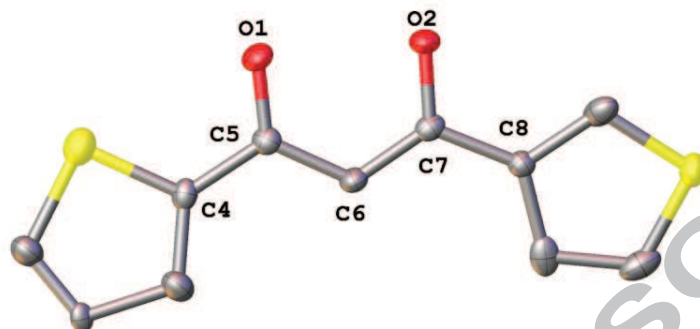


Fig. 3 Molecular structure of the β -diketone HL with partial atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50 % probability.

The H atom in the intramolecular hydrogen bond is asymmetrically positioned and is closest to the oxygen atom adjacent to the 3-thienyl group ($O(2)-H(2C) = 0.895(19)$ Å). The short $O(1)\cdots O(2)$ separation of $2.488(3)$ Å is typical of an enolized β -diketone [19,22]. A similar localization of the hydroxyl proton was also observed for 2-thienyl-containing β -diketones (2-Th) $C(O)CH=C(OH)R$ ($R = CF_3$ [22a], Ph [19]) and was explained by the electron-withdrawing power of the CF_3 group and a larger angle observed between the phenyl and enol planes, respectively. In the present case, the dihedral angles between the aromatic rings and the enol plane are identical within the experimental error, giving rise to similar conjugation between the two different thienyl moieties and the pseudo-aromatic enol core. Thus, the resonance driving force arguments [23] do not apply here. A possible explanation could come from a stronger interaction between the sulfur atom of the 2-thienyl ring with the carbonyl oxygen ($S\cdots O(1) = 2.959(3)$ Å) than between the 3-thienyl sulfur and enol oxygen atoms ($S\cdots O(2) = 3.94(2)$ Å), albeit the role of packing forces could not be excluded.

Table 3 Selected bond distances (Å) and angles ($^\circ$) for compound HL and CuL_2

	HL	CuL_2
--	----	---------

Bond distances		
Cu(1)-O(1)	-	1.915(2)
Cu(1)-O(2)	-	1.912(2)
C(4)-C(5)	1.462(4)	1.473(4)
C(5)-C(6)	1.418(4)	1.396(4)
C(6)-C(7)	1.381(4)	1.395(4)
C(7)-C(8)	1.466(4)	1.473(4)
O(1)-C(5)	1.277(3)	1.286(3)
O(2)-C(7)	1.311(3)	1.283(3)
O(2)-H(2C)	0.895(19)	-
Bond angles		
O(1)-Cu(1)-O(1) ^{#1}	-	180.0
O(2)-Cu(1)-O(2) ^{#1}	-	180.0
O(1)-Cu(1)-O(2)	-	93.59(8)
O(1)-Cu(1)-O(2) ^{#1}	-	86.41(8)
Cu(1)-O(1)-C(5)	-	125.33(19)
Cu(1)-O(2)-C(7)	-	125.88(19)
O(1)-C(5)-C(4)	117.7(2)	115.1(2)
O(1)-C(5)-C(6)	121.3(2)	125.2(3)
O(2)-C(7)-C(8)	115.6(2)	115.0(2)
O(2)-C(7)-C(6)	121.8(2)	125.1(3)
C(5)-C(6)-C(7)	119.8(2)	124.1(3)
C(7)-O(2)-H(2C)	100(3)	-

Symmetry code : #1 -x, -y, -z

Complex CuL₂ crystallizes with the Cu(II) metal ion occupying a crystallographic inversion center and coordinated by an ideal square planar geometry of four oxygen atoms (Fig. 4). The O-Cu-O diagonal angles are equal to 180°. The structure shows that the β-diketonate

ligands are coordinated to copper(II) in a bidentate fashion. They form two six-membered chelate rings with O(1)-Cu(1)-O(2) bite angles of $93.59(8)^\circ$. The similarity within the pairs of Cu-O, C-C bond lengths, and Cu-O-C, O-C-C bond angles in the chelate ring (Table 3) indicates the latter is behaving as a delocalized metallacycle. The C(5)-C(6) and C(6)-C(7) bond lengths were found to be 1.396(4) and 1.395(4) Å, respectively. These values are typical of C-C partial double bonds [21]. The mean Cu-O distance is 1.913(2) Å which lies in the range previously reported for *bis*(β -diketonate)Cu(II) complexes [24]. As a whole, the molecule is essentially flat. *By symmetry the CuO₄ core is a perfect plane.* Deviations of the C(5), C(6) and C(7) carbon atoms of the β -diketonate backbone from the CuO₄ least-square mean plane are 0.180, 0.236 and 0.117 Å, respectively. The maximum deviation (0.616 Å) is measured for the C(1C) carbon of the 2-thienyl group. The 2-thienyl and the 3-thienyl rings make dihedral angles of 8.31° and 6.47° , respectively, with the plane of the metallacycle.

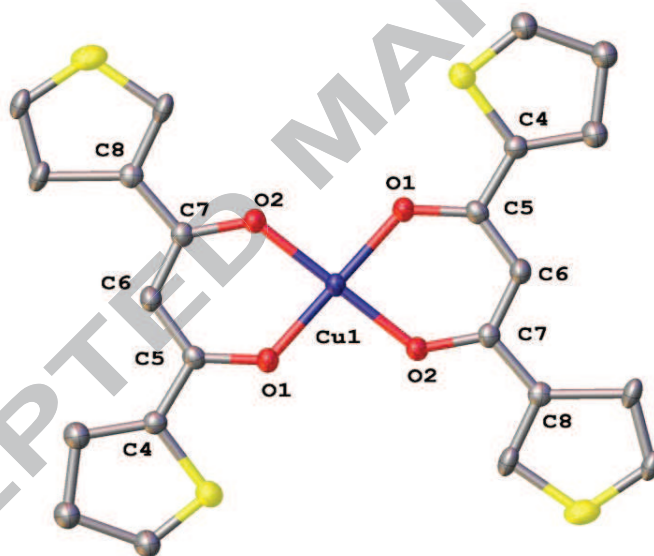


Fig. 4 Molecular structure of the CuL₂ complex with partial atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50 % probability.

3.3. Electrochemical polymerization

3.3.1. Preparation of modified electrode Pt|(CuL₂)_n by cyclic voltammetry (CV) and chronoamperometry

Voltammetric profiles recorded by CV, corresponding to the electro-synthesis of $(\text{CuL}_2)_n$ on Pt, is shown in Fig. 5a. After several optimization attempts, varying monomer concentration, supporting electrolyte, potential window, solvent, etc. it was established that the appropriate window for the electropolymerization of CuL_2 , in the electrolytic medium employed, was in the range -1.0 and 1.6 V on Pt electrode. Fig. 5 shows in this case a current density increases from cycle 1 to 20, which means the formation of polymeric deposit occurs without electrode surface passivation, *i. e.* it is possible that the polymer displayed conductivity.

Fig. 5b shows the voltammetric response of CuL_2 polymer ($\text{Pt}[(\text{CuL}_2)_n$ modified electrode) by scanning between 1.2 and -1.0 V at 100 mVs^{-1} , in a solution without monomer, which revealed that the deposit has not been over-oxidized, therefore, its chemical characteristics should be very similar to that of polythiophene [25,26]. In fact, the color of $(\text{CuL}_2)_n$ is light brown like a polythiophene deposit (Fig. 5b). Also it is possible to observe the p-doping (E_{cp}) and p-undoping (E_{ap}) peak potentials, representing respectively the amount of energy required for $(\text{CuL}_2)_n$ becoming positively charged, adsorbing anions from the solution, and its reverse discharge process expelling the anions. The p-doping charge is 1.38 mC cm^{-2} and that of p-undoping is 1.39 mC cm^{-2} (both charges referenced to the geometric area of the support electrode, *i. e.* 0.07 cm^2), so the process of p-doping/undoping or charge/discharge of this polymer can be considered fully reversible, since the charge quotient is very close to one. This property is very interesting for future applications, like extraction process from contaminated solutions [27-29].

This response also shows two small peaks in anodic (pox) and cathodic ($pred$) direction, respectively. The difference between E_{pox} (0.053 V) and E_{pred} (-0.600 V), 0.54 V , suggests a quasi-reversible electrochemical process, given by Cu ion inside the polymer, however, it looks very little because of overlapping with the polymer response.

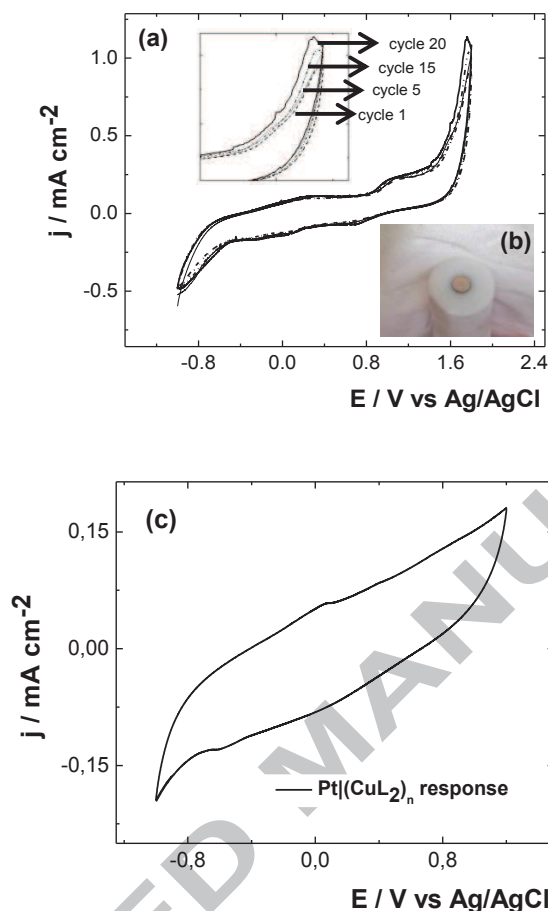


Fig. 5 (a) Voltammetric profiles during CuL_2 electro-polymerization; interface: $\text{Pt}|0.01 \text{ mol L}^{-1} \text{ CuL}_2 + 0.1 \text{ mol L}^{-1} \text{ TBATFB}$ in CH_3CN ; $v = 50 \text{ mVs}^{-1}$. (b) Polymer of CuL_2 on Pt disc: $\text{Pt}[(\text{CuL}_2)_n]$. (c) $\text{Pt}[(\text{CuL}_2)_n]$ response in $0.1 \text{ mol L}^{-1} \text{ TBATFB}$ in CH_3CN ; $v = 100 \text{ mVs}^{-1}$.

Subsequently, $(\text{CuL}_2)_n$ was electro-synthesized by chronoamperometry on FTO electrode, in order to determine the Nucleation and Growth Mechanism (NGM), and to observe the surface by SEM. To this purpose, a constant potential of 2.3 V was applied for 500 s. The analysis of the transient recorded during this electrosynthesis process (Fig. 6) enables to appreciate a significant difference in the nucleation and growth induction time (τ), being much higher for CuL_2 than other monomers like thiophene, reported elsewhere [30-33]. This can be explained considering the steric demand of CuL_2 (Fig. 4) which renders difficult the formation of oligomers and thus the delay in High Density Oligomeric Region (HDOR) [30-33].

After time τ , when nucleation occurs, the figure in the insert of Fig. 6 shows time-current deconvolution of the transient recorded during 60 s of polymerization, in order to determine the NGM by which the deposit is formed, as described in similar studies [30-33]. The equation that enabled deconvoluting this transient responds to the following equation [34]:

$$j = P_1[1 - \exp(-P_2 t^2)] \quad (1)$$

which corresponds to an instantaneous nucleation with charge-controlled three-dimensional growth (IN3Dct) mechanism. P_1 and P_2 corresponds, respectively, to

$$P_1 = nFk$$

$$P_2 = \pi N_0 k^2 M^2 / \rho^2$$

where n is the number of electrons involved, F is the Faraday constant, k is the growth rate constant, N_0 is the nuclei number formed at $t = 0$, M is the monomer molar mass, and ρ is the film density. Values of P_1 and P_2 that allowed accurate simulation of the experimental transients are $2.036 \cdot 10^{-5}$ and $1.47 \cdot 10^{-3}$, respectively. A clear correlation between experimental and simulated transients is observed and, consequently, this NGM would be reliable.

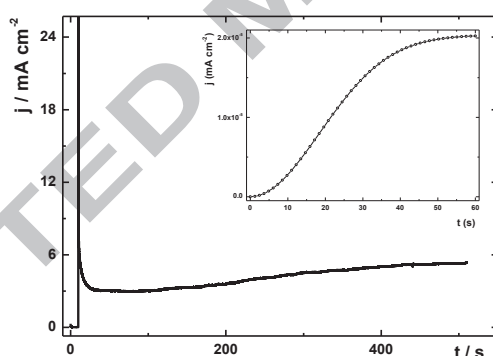


Fig. 6 j/t transient registered during CuL_2 electro-polymerization on FTO. Interface: $\text{Pt}|0.01 \text{ molL}^{-1} \text{ CuL}_2 + 0.1 \text{ molL}^{-1} \text{ TBATFB}$ in CH_3CN .

3.3.2. SEM Characterization

To determine deposit morphology and particularly to validate the simulations leading to NGM determination, SEM was utilized to characterize the coating (Fig. 7): a fully coated electrode (Fig. 7a) by a deposit formed of regular particles with uniform size is clearly visible in the microphotographs (Fig. 7b) [30-34].

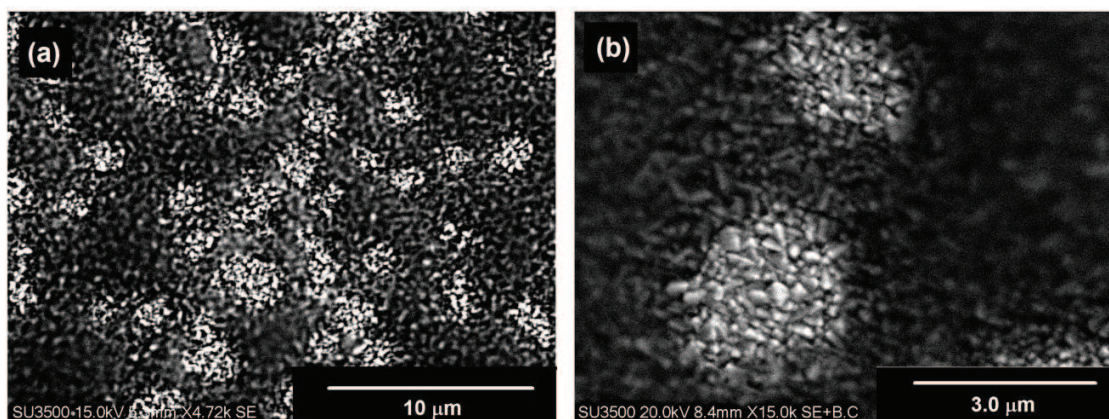


Fig. 7 FTO|(CuL₂)_n SEM images with magnifications (a) 10 and (b) 3 μm.

4. Conclusions

The new asymmetrical β-diketone 1-(thiophen-2-yl)-3-(thiophen-3-yl)propane-1,3-dione (HL) and its corresponding *bis*(β-diketonate)copper(II) complex [Cu{1-(thiophen-2-yl)-3-(thiophen-3-yl)-1,3-propanedionate}₂] (CuL₂) were synthesized and characterized by analytical and spectroscopic methods as well as by X-ray diffraction study. The keto-enol form of HL was found to be predominant in solution. In the solid-state, the enol group is adjacent to the 3-thienyl fragment. In CuL₂, the Cu(II) metal ion occupies a crystallographic inversion center and sits in a perfect square planar coordination environment made of four oxygen atoms. Electrochemical experiments have established that the formation of (CuL₂)_n polymeric deposit occurs, with a degree of electronic communication between the organic skeleton and copper complex, thus establishing that it is possible to obtain modified electrodes from the electropolymerization of the thienyl groups attached to a β-diketonate complex. This is the first example disclosing the generation of a polythienyl-containing β-diketonate complex and its deposition on an electrode using an electrochemical oxidation process.

Appendix A. Supplementary data

CCDC 1509142 for HL and 1509143 for CuL₂ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data

Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Financial support from the Fondo Nacional de Desarrollo Científico y Tecnológico [FONDECYT (Chile), grant no. 1140903 (C.M. and D.C.)], FONDEQUIP [EQM130154], the Vicerrectoría de Investigación y Estudios Avanzados, Pontificia Universidad Católica de Valparaíso, Chile (C.M. and D.C.), the CNRS and the Université de Rennes 1 is gratefully acknowledged. FEDER funds are also acknowledged for their participation in the purchase of the D8 VENTURE Bruker AXS diffractometer. G.A. thanks the CONICYT (Chile) for support of a graduate fellowship N°21120098. This research has been performed as part of the Chilean-French International Associated Laboratory for “Inorganic Functional Materials” (LIAMIF-CNRS N°836).

References

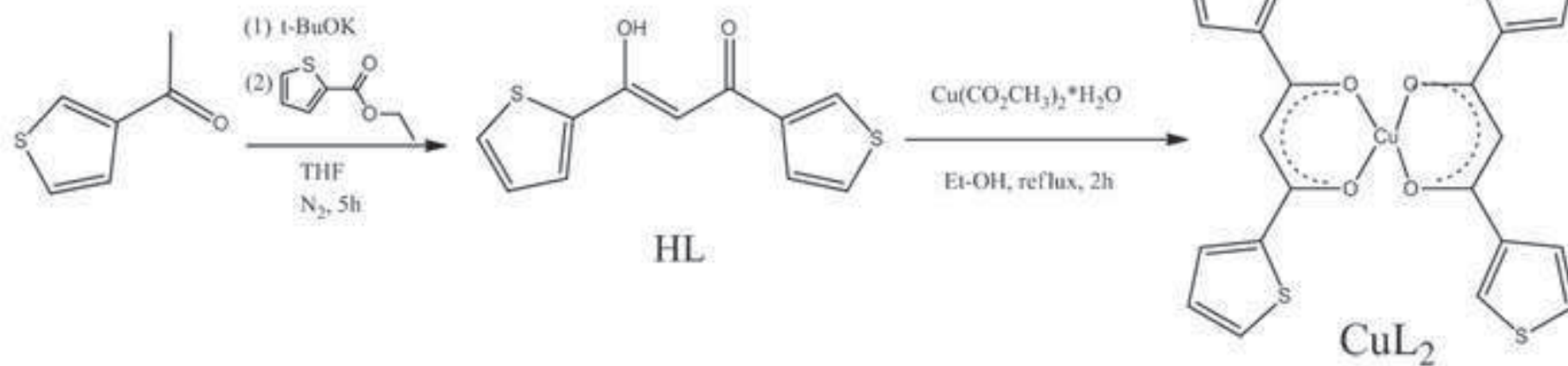
- [1] (a) R.C. Mehrotra, Metal β -diketonates and Allied Derivatives, Academic Press Inc., New York, 1978; (b) D.J. Bray, J.K. Clegg, L.F. Lindoy, D. Schilter, Adv. Inorg. Chem. 59 (2006) 1; (c) G. Aromí, P. Gamez, J. Reedijk, Coord. Chem. Rev. 252 (2008) 964.
- [2] (a) T.V. Deepthi, P. Venugopalan, Inorg. Chim. Acta 450 (2016) 243; (b) N. Novoa, T. Roisnel, V. Dorcet, J.-R. Hamon, D. Carrillo, C. Manzur, F. Robin-Le Guen, N. Cabon, J. Organomet. Chem. 762 (2014) 19, and references cited therein.
- [3] (a) R.M. Lord, J.J. Mannion, A.J. Hebden, A.E. Nako, B.D. Crossley, M.W. McMullon, F.D. Janeway, R.M. Phillips, P.C. McGowan, ChemMedChem 9 (2014) 1136; (b) A. Sudo, S. Hirayama, T. Endo, J. Polym. Sci.: Parte A: Polym. Chem. 48 (2010) 479; (c) V.D. John, K. Krishnankutty, Appl. Organometal. Chem. 20 (2006) 477; (d) A.V. Kel'in, Curr. Org. Chem. 7 (2003) 1691; (e) A.V. Kel'in, A. Maioli, Curr. Org. Chem. 7 (2003) 1855; (f) V.D. John, G. Kuttan, K. Krishnankutty, J. Exp. Clin. Cancer Res. 21 (2002) 219; (g) R. Karvembu, C. Jayabalakrishna, K. Natarajan, Trans. Met. Chem. 27 (2002) 574; (h) M. Nagabushan, S.V. Bhide, J. Am. Coll. Nutr. 11 (1992) 192; (i) K. Elizabeth, M.N.A. Rao, Ins. J. Pharm. 58 (1990) 237; (j) G.D. Diana, P.M. Carabateas, R.E. Johnson, G.L. Williams, F. Pancic, J.C. Collins, J. Med. Chem. 21 (1978) 889.
- [4] (a) K.S. Williamson, T.P. Yoon, J. Am. Chem. Soc. 132 (2010) 4570; (b) A. Sudo, S. Hirayama, T. Endo, J. Polymer Sci.: Part A: Polymer Chem. 48 (2010) 479; (c) M. Bialek,

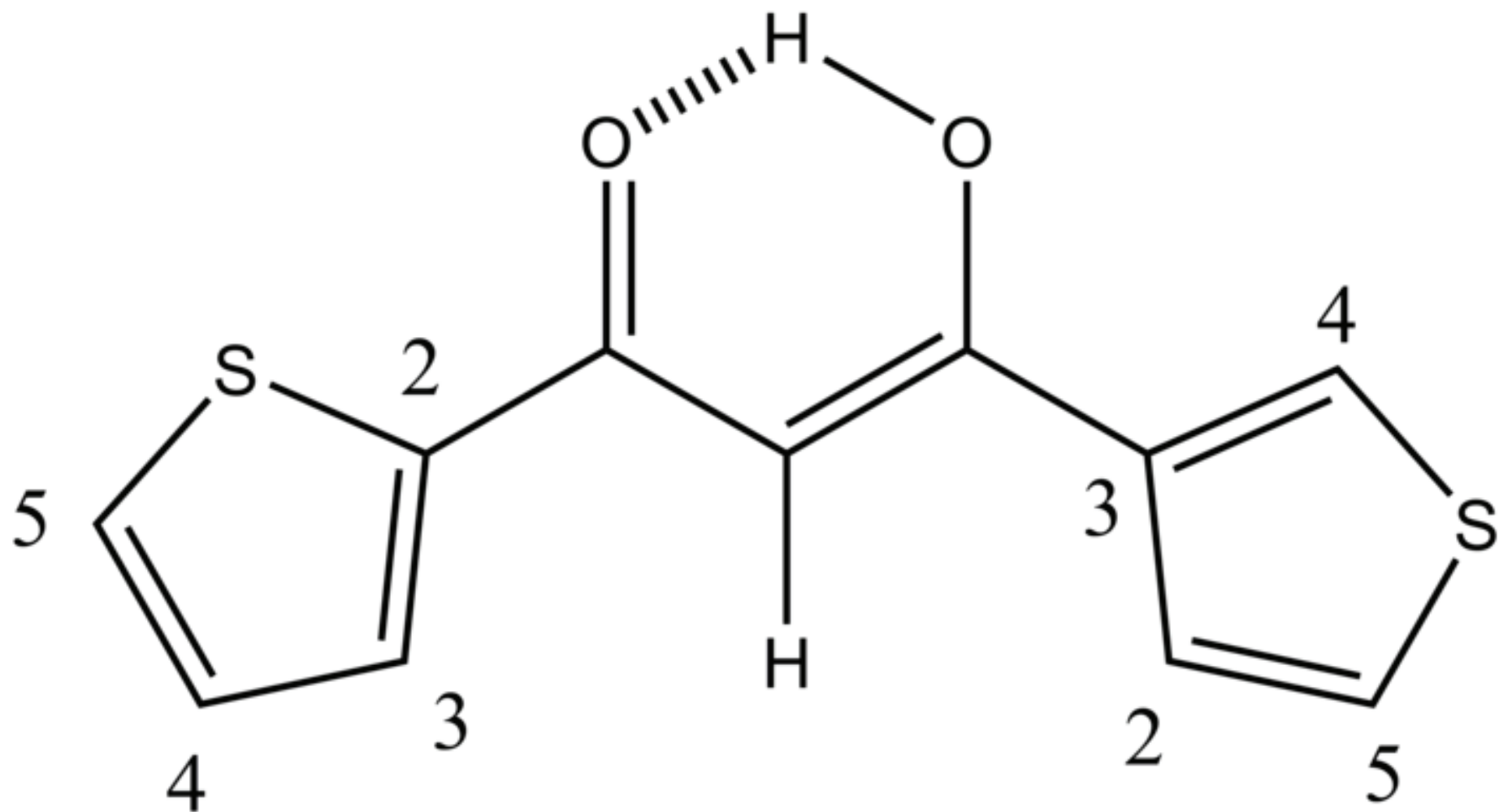
- H. Cramail, A. Deffieux, S.M. Guillaume, *Eur. Polymer J.* 41 (2005) 2678; (d) L.C. Ferreira, M.A.S. Costa, P.I.C. Guimaraes, L.C. de Santa Maria, *Polymer* 43 (2002) 3857; (e) S.D. Evans, R.P. Houghton, *J. Mol. Catal. A: Chem.* 164 (2000) 157; (f) R.A. Ligabue, A.L. Monteiro, R.F. de Souza, M.O. de Souza, *J. Mol. Catal. A: Chem.* 157 (2000) 73.
- [5] (a) A.P. Ramos, D.C. dos Reis, R.R. Pereira, L.G. Días, R.R. Gonçalves, *Dalton Trans.* 44 (2015) 3829; (b) G. Shao, H. Yu, N. Zhang, Y. He, K. Feng, X. Yang, R. Cao, M. Gong, *Phys. Chem. Chem. Phys.* 16 (2014) 695; (c) S. Xu, R.E. Evans, T. Liu, G. Zhang, J.N. Demas, C.O. Trindle, C.L. Fraser, *Inorg. Chem.* 52 (2013) 3597; (d) M.L.P. Reddy, V. Divya, R. Pavithran, *Dalton Trans.* 42 (2013) 15249; (e) C. Freund, W. Porzio, U. Giovanella, F. Vignali, M.C. Pasini, S. Destri, *Inorg. Chem.* 50 (2011) 5417.
- [6] A.D. Burrows, C.G. Frost, M.F. Mahon, P.R. Raithby, C.L. Renouf, C. Richardson, A.J. Stevenson, *Chem. Commun.* 46 (2010) 5067.
- [7] (a) P. Guerriero, S. Tamburini, P.A. Vigato, *Coord. Chem. Rev.* 139 (1995) 17; (b) P.A. Vigato, S. Tamburini, *Coord. Chem. Rev.* 248 (2004) 1717; (c) P.A. Vigato, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* 256 (2012) 953.
- [8] (a) N. Novoa, T. Roisnel, P. Hamon, S. Kahlal, C. Manzur, H.M. Ngo, I. Ledoux-Rak, J.-Y. Saillard, D. Carrillo, J.-R. Hamon, *Dalton Trans.* 44 (2015) 18019; (b) A. Trujillo, M. Fuentealba, D. Carrillo, C. Manzur, I. Ledoux-Rak, J.-R. Hamon, J.-Y. Saillard, *Inorg. Chem.* 49 (2010) 2750.
- [9] (a) C. Friebe, H. Görls, M. Jäger, U.S. Schubert, *Eur. J. Inorg. Chem.* (2013) 4191; (b) C. Friebe, M.D. Hager, A. Winter, U.S. Schubert, *Adv. Mater.* 24 (2012) 332; (c) A. Pietrangelo, B.C. Sih, B.N. Boden, Z. Wang, Q. Li, K.C. Chou, M.J. MacLachlan, M.O. Wolf, *Adv. Mater.* 20 (2008) 2280; (d) M.O. Wolf, *J. Inorg. Organomet. Polym. Mater.* 16 (2006) 189; (e) B.J. Holliday, T.M. Swager, *Chem. Commun.* (2005) 23; (f) J. Roncali, *J. Mater. Chem.* 9 (1999) 1875; (g) J. Roncali, *Chem. Rev.* 92 (1992) 711.
- [10] W.L.F. Armarego, C.L.L. Chai, *Purification of Laboratory 776 Chemicals*, Fifth ed., Butterworth-Heinemann, Elsevier Inc., Amsterdam, The Netherlands, 2003.
- [11] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [12] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112.
- [13] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 42 (2009) 339.
- [14] M. Fuentealba, J.-R. Hamon, D. Carrillo, C. Manzur, *New J. Chem.* 31 (2007) 1815.
- [15] J. Emsley, *Struct. Bonding* 57 (1984) 147.

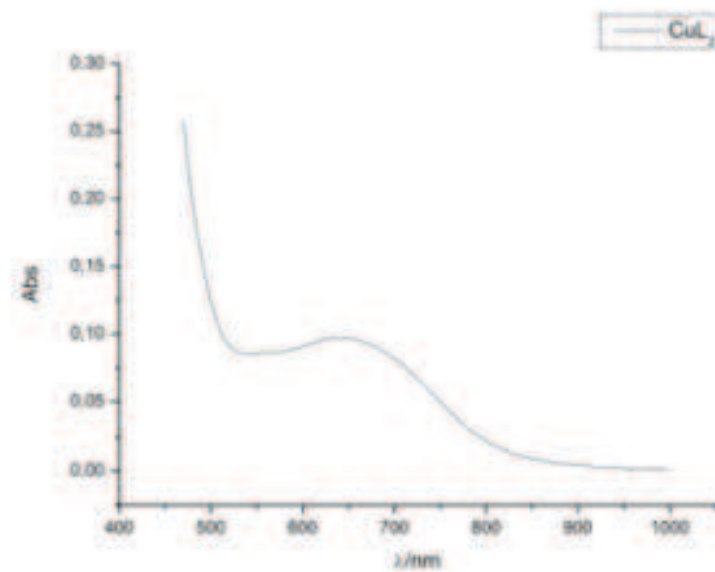
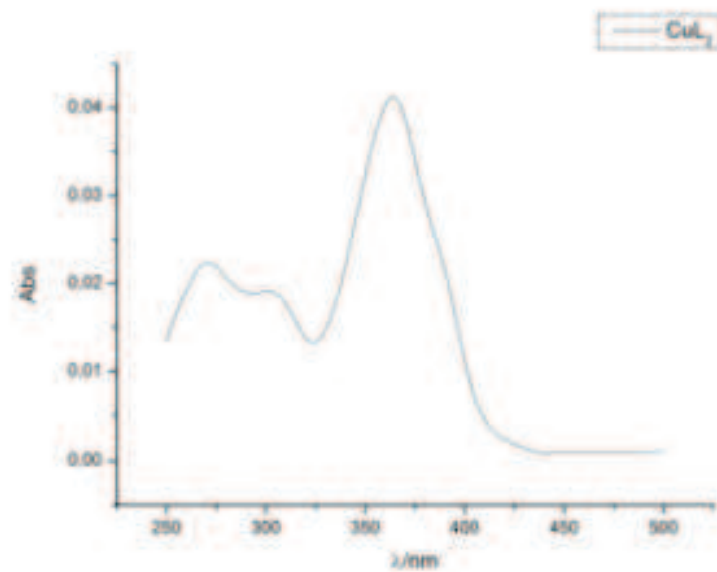
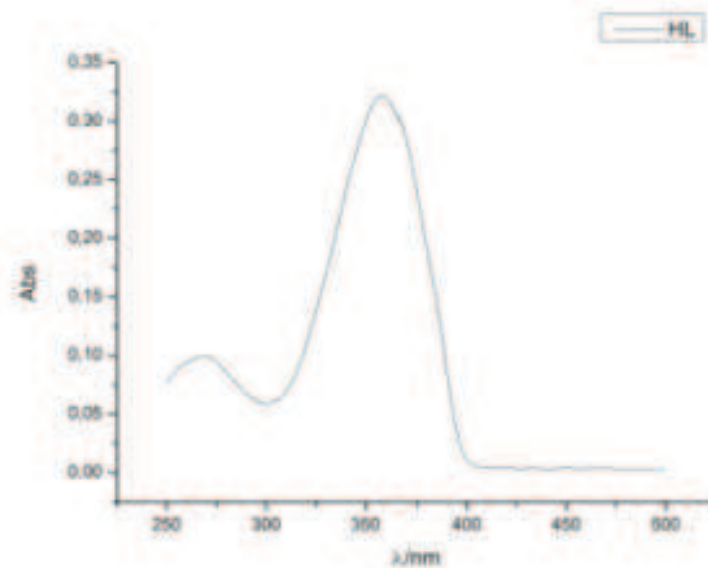
- [16] (a) G. Ahumada, T. Roisnel, S. Sinbandhit, C. Manzur, D. Carrillo, J.-R. Hamon, J. Organomet. Chem. 737 (2013) 1; (b) S. Celedon, M. Fuentealba, T. Roisnel, J.-R. Hamon, D. Carrillo, C. Manzur, Inorg. Chim. Acta 390 (2012) 184.
- [17] (a) G. Schmidt, U. Brhrens, J. Organomet. Chem. 503 (1995) 101; (b) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley and Sons, New York, 1970.
- [18] (a) P. Molina, A. Arques, I. Cartagena, Comprehensive Heterocyclic Chemistry III, Elsevier, New York, 2008, Vol. 3, Chapter 09, pp. 625-739. (b) J.J. Peron, P. Saumagne, J.M. Lebas, Spectrochim. Acta 1970, 26A, 1651.
- [19] M.M. Conradie, A.J. Muller, J. Conradie, S. Afr. J. Chem. 61 (2008) 13.
- [20] A.P.B. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1980.
- [21] (a) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1; (b) F.H. Allen, Acta Crystallogr. Sect. B, 58 (2002) 380.
- [22] (a) R.D.G. Jones, Acta Crystallogr. Sect. B, 32 (1976) 1224; (b) L.A.M. Baxter, A.J. Blake, G.A. Heath, T.A. Stephenson, Acta Crystallogr. Sect. C, 46 (1990) 508.
- [23] W.C. Du Plessis, T.G. Vosloo, J.C. Swarts, J. Chem. Soc. Dalton Trans. (1998) 2507.
- [24] (a) L.A.M. Baxter, A.J. Blake, R.O. Gould, G.A. Heath, T.A. Stephenson, Acta Crystallogr. Sect. C, 49 (1993) 1311; (b) S. Layek, S. Kumari Anuradha, B. Agrahari, R. Ganguly, D. D. Pathak, Inorg. Chim. Acta 453 (2016) 735.
- [25] M.A. del Valle, M. Gacitúa, F.R. Díaz, F. Armijo, J.P. Soto, Electrochim. Acta 71 (2012) 277.
- [26] M.A. del Valle, M. Gacitúa, F.R. Díaz, F. Armijo, R. del Río, Electrochem. Commun. 11 (2009) 2117.
- [27] G.C. Arteaga, M. Antilén, M. Faúndez, F.R. Díaz, F. Armijo, L.A. Hernández, A. Ramos, M.A. del Valle, Int. J. Electrochem. Sci. 8 (2013) 2898.
- [28] M.A. del Valle, D. Colomer, F.R. Díaz, L.A. Hernández, M. Antilen, M.A. Gacitúa, A. Ramos, G.C. Arteaga, J. Appl. Electrochem. 42 (2012) 867.
- [29] G.C. Arteaga, M.A. del Valle, M. Antilén, M. Faúndez, M.A. Gacitúa, F.R. Díaz, J.C. Bernède, L. Cattin, Int. J. Electrochem. Sci. 6 (2011) 5209.
- [30] M.A. del Valle, L.I. Canales, A. Ramos, F.R. Díaz, L.A. Hernández, F. Armijo, J.C. Bernède, L. Cattin, G. Louarn, Int. J. Electrochem. Sci. 8 (2013) 1422.
- [31] G.C. Arteaga, M.A. del Valle, M. Antilén, F.R. Díaz, M.A. Gacitúa, P.P. Zamora, J.C. Bernède, L. Cattin, G. Louarn, Int. J. Electrochem. Sci. 7 (2012) 7840.
- [32] J.P. Soto, F.R. Díaz, M.A. del Valle, J.H. Vélez, G.A. East, Appl. Surf. Sci. 254 (2008) 3489.

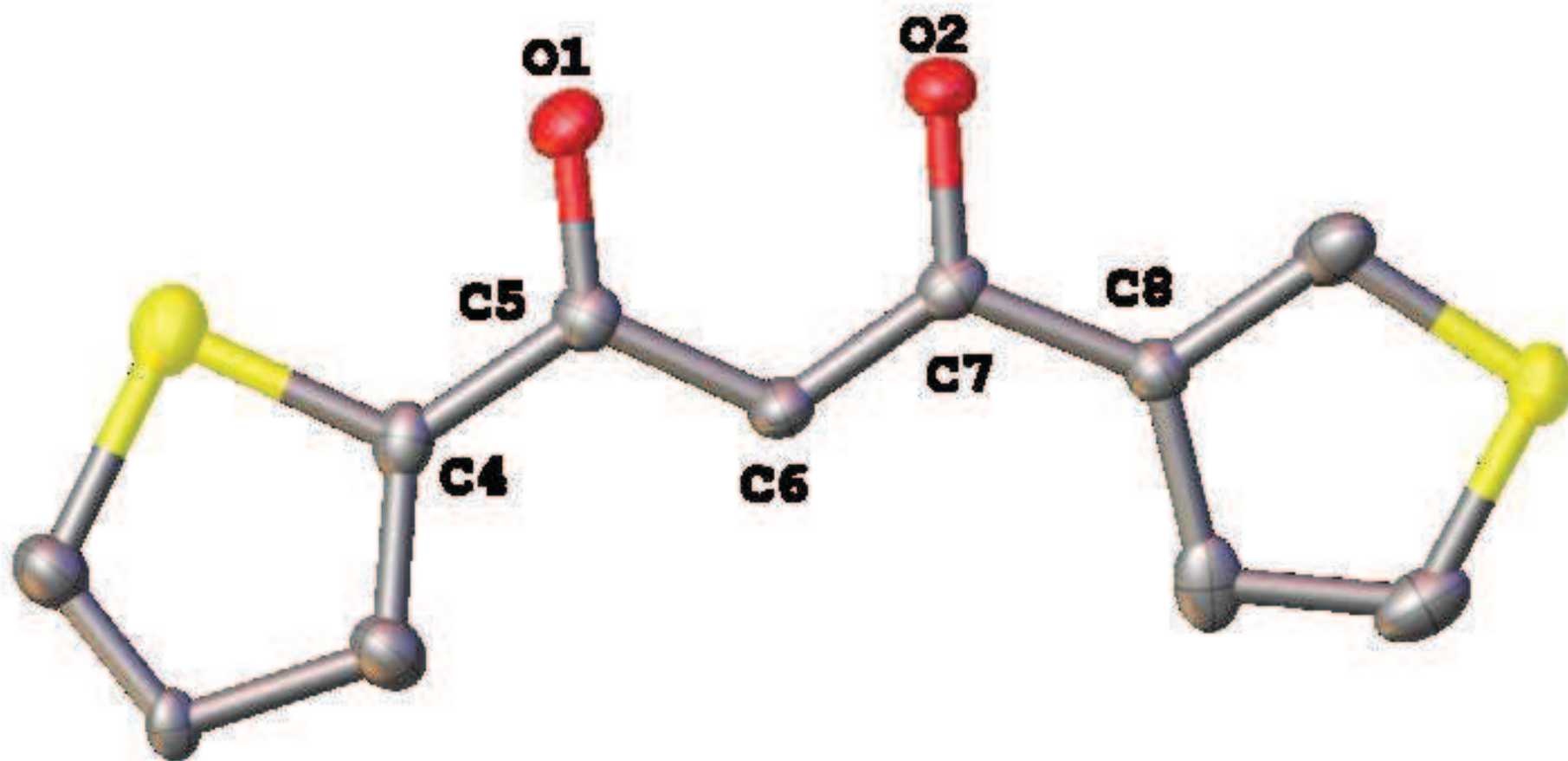
[33] M.A. del Valle, M.A. Gacitúa, L.I. Canales, F.R. Díaz, J. Chil. Chem. Soc. 54 (2009) 260.

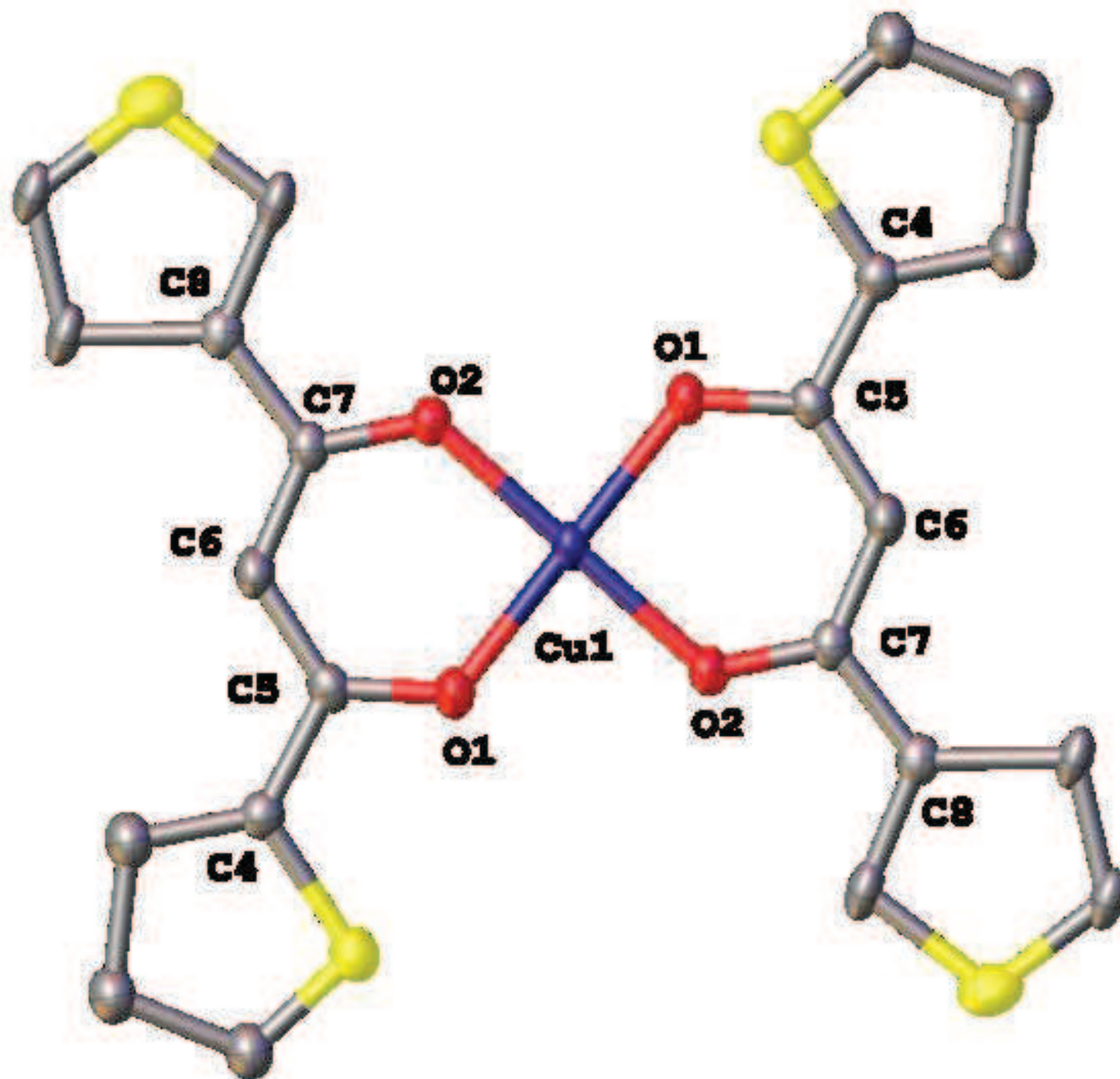
[34] D. Pletcher, R. Greff, R. Peat, L.M. Peter, J. Robinson in Instrumental Methods in Electrochemistry, Southampton Electrochemistry Group, Woodhead Publishing, 1985.

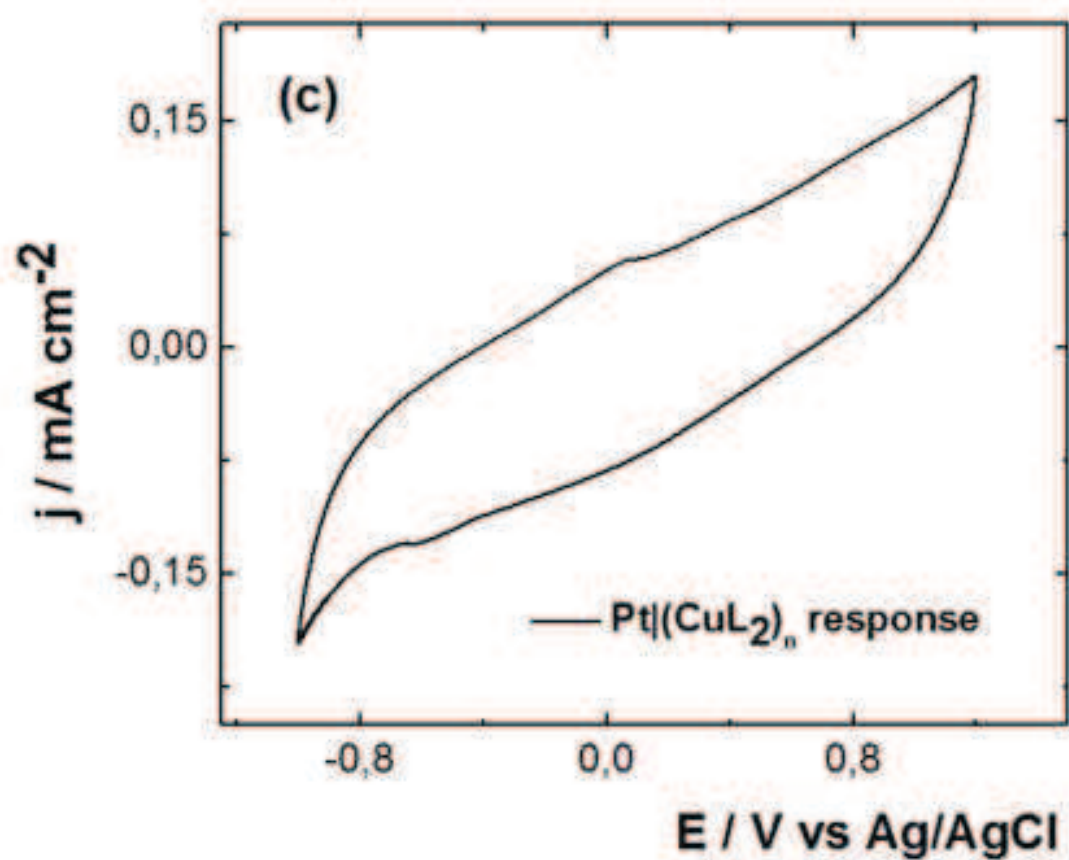
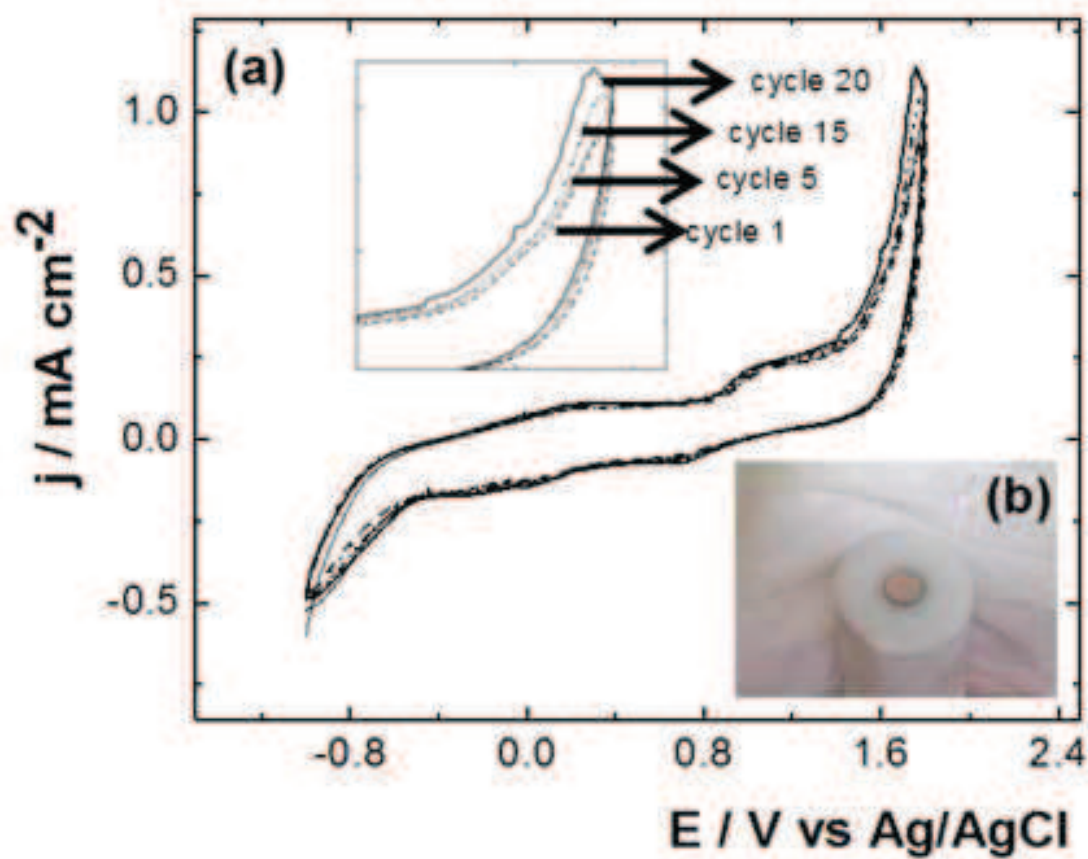


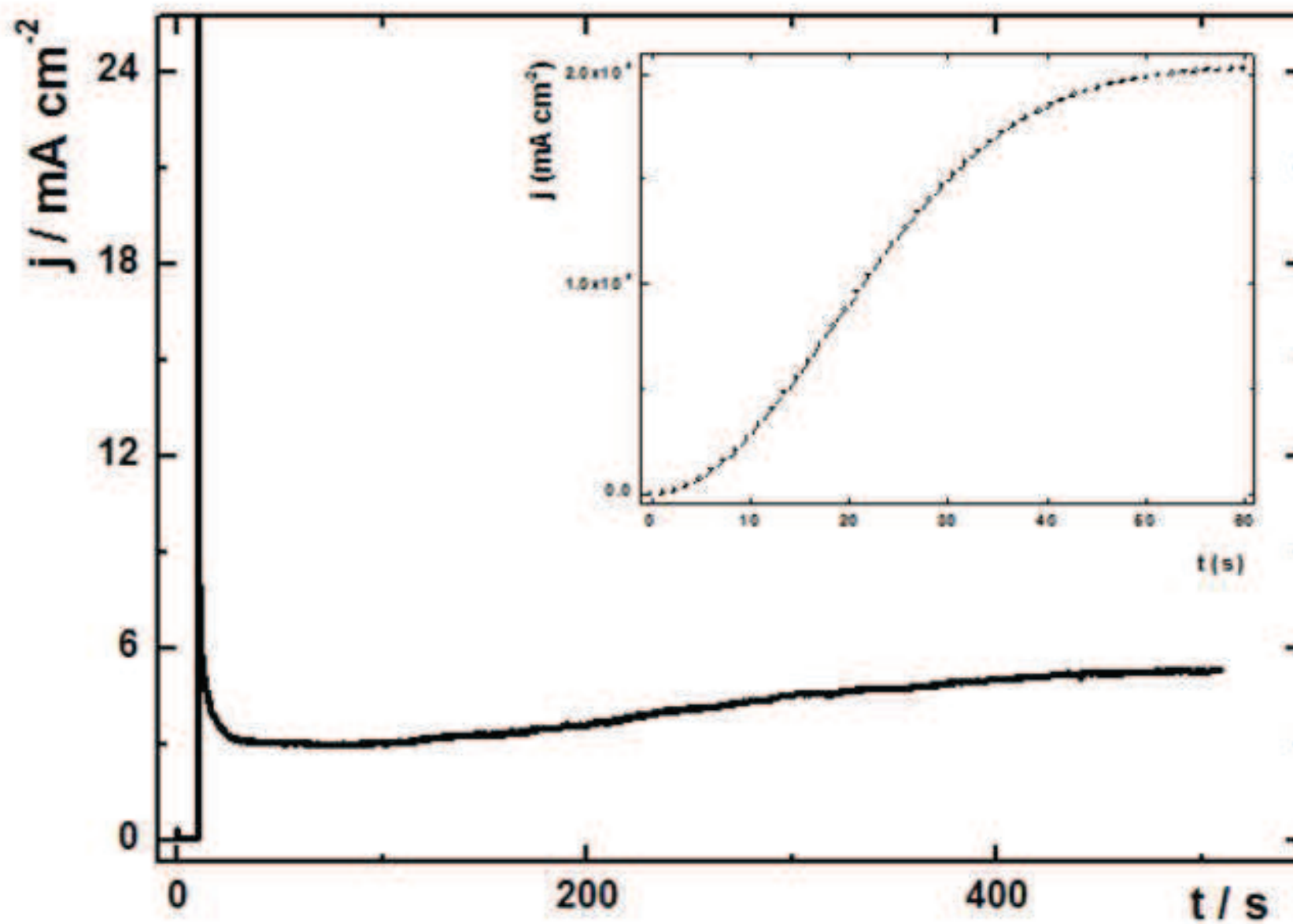


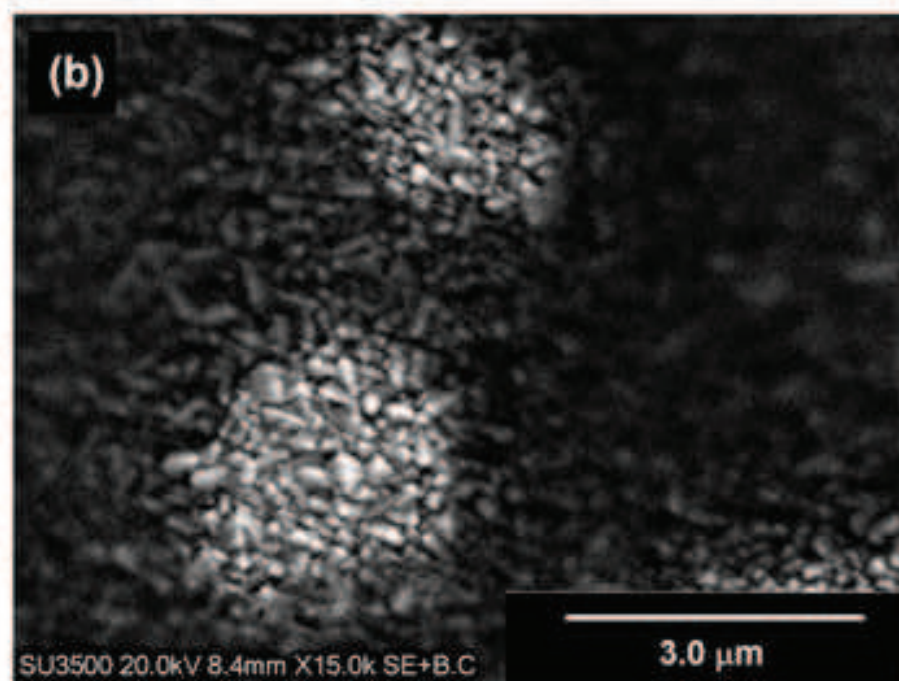
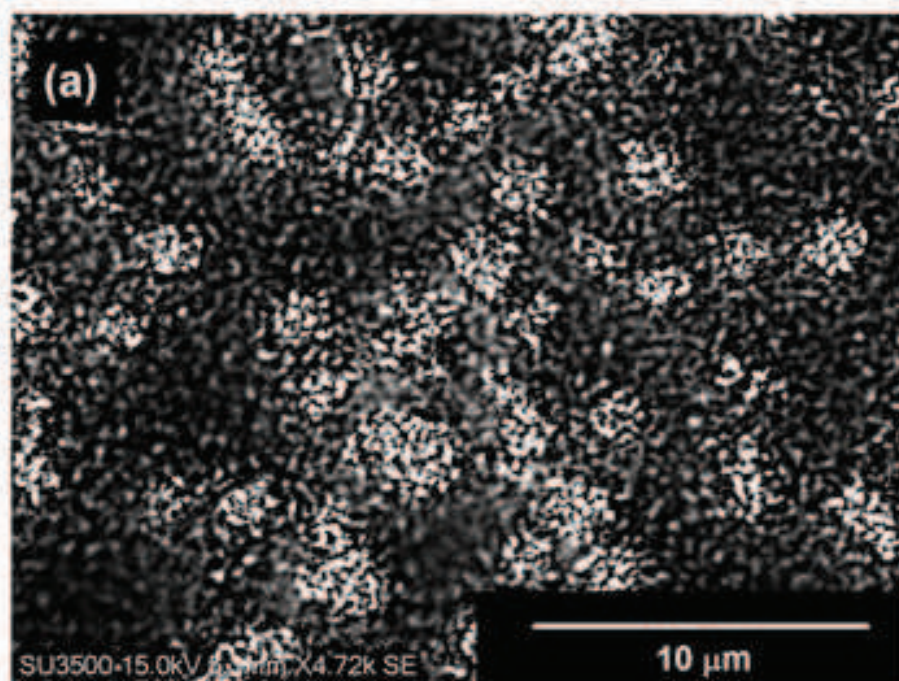




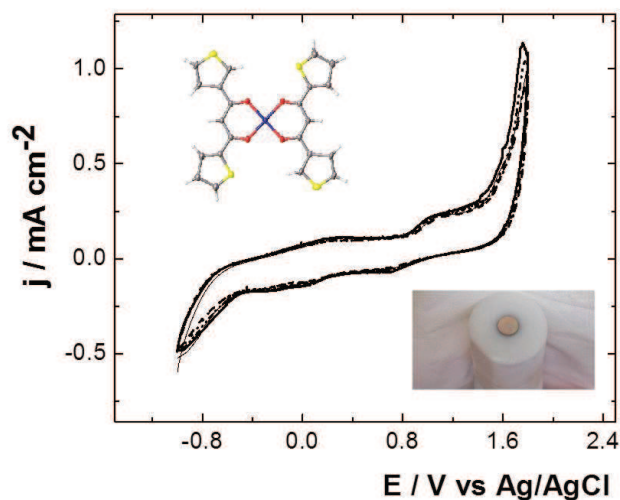








Graphical Abstract Synopsis



Electropolymerization of the β -(diketonate)copper(II) complex (illustrated) allows the fabrication of modified electrodes; a film was also synthesized on Fluorine Doped Tin Oxide electrode using potentiostatic methods, and the morphology of the deposit was studied by *Scanning Electron Microscopy*.