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# Synthesis, spectroscopic and cyclic voltammetry studies of copper(II) complexes with open chain, cyclic and a new macrocyclic thiosemicarbazones

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#### Abstract

New copper complexes have been prepared from benzilbisthiosemicarbazone  $(L^{1}H_{6})$  and from the cyclic 6-methoxi-1,6-diphenyl-4-thio-3,4,5,6-tetrahydro-2,3,5-triazine  $(L^{2}H_{2})$ . The complexes were characterized by mass spectrometry, IR, electronic and electron paramagnetic resonance spectra. Complexes from  $L^{1}H_{6}$  (1–5) present 1:1 stoichiometry and show different characteristics with a variable grade of deprotonation in the ligand, depending on the salt used (chloride, nitrate or sulfate) and the presence of acid in the medium. A macrocyclic Schiff base, 3,4,9,10-tetraphenyl-1,2,5,6,8,11-hexaazacyclododeca-7,12-dithione-3,4,9,10-tetraene ( $L^{3}H_{2}$ ), containing thiosemicarbazone moieties is readily prepared and characterized for the first time, with fairly good yield, from the mesocycle ( $L^{2}H_{2}$ ) in methanol with copper chloride as template. Near quantitative synthesis of the precursor,  $L^{2}H_{2}$ , which is a potential chemotherapeutic agent against cancer, has been achieved by reacting benzil and thiosemicarbazide in the absence of metal salt and using a high dilution technique. Macrocyclic complexes **6** and **7** containing thiosemicarbazone moieties were obtained from  $L^{2}H_{2}$  and copper nitrate and sulfate. Direct reaction between the copper salt and the macrocyclic thiosemicarbazone ( $L^{3}H_{2}$ ) gave similar complexes but with a lower grade of purity. Macrocyclic complexes **6** and **7** present metal–ligand ratios of 1:2 and 1:1 and the ligand is in a deprotonated form. The redox behaviour was explored by cyclic voltammetry.  $L^{1}H_{6}$  complexes show Cu(II)/Cu(I) couples and quasireversible waves associated with the Cu(III)/Cu(II) process. The reduction/oxidation potential depends on the structure and conformation of the central atom in the coordination compounds. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Thiosemicarbazones; Macrocyclic ligands; Electrochemistry; Copper complexes; Dithio-Schiff base complexes

# 1. Introduction

Schiff base macrocyclic ligands based on thiosemicarbazones and their complexes have received considerable attention since, because of their pharmacological properties, they have numerous applications, for example as antibacterial and anticancer agents [1–3]. They can yield mono- or polynuclear complexes, some of which are biologically relevant [4– 7]; for example, some copper complexes can serve as models for enzymes such as galactose oxidase and may be used as effective oxidant and redox catalysts [8,9]. Furthermore, they allow selective complexation and extraction of metallic cations and anions of biochemical and environmental importance [10–13]. The number and relative position of donor atoms and the cavity size in the macrocyclic compounds give these molecules special reactivity. For a particular dicarbonyl and diamine as precursors, control of the reaction conditions allows the condensation product formed to be determined: [1+1], [1+2] and [2+2] condensation products, with open chain and cyclic structures. Alternatively, the high dilution technique is a good method to obtain macrocyclic Schiff bases [14]. The most important factors are the solvent, pH, temperature and the presence of metal ions. Metal salts have been used as templating agents to yield macrocyclic Schiff bases from diamine and dicarbonyl as precursors [15,16], but transition metals such as copper and nickel, which have been used in the preparation of aza crowns, are surprisingly absent [17]. If the metal is present, the size, charge and favourable geometries of the metal have to be considered.

Biological activities may be related to the redox properties of complexes. For some copper(II) compounds a lower reduction potential seems to be related to an increased anti-

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fungal activity [1,3]. Some copper complexes exhibit the abilities of superoxide dismutase (SOD) and chemical nucleases [18,19]. Moreover, copper is also toxic in elevated concentration so many investigations have attempted to develop sensors to determine its presence with high selectivity. Potentiometric measurements with copper ion-selective electrodes (ISE) allow the free ion concentration to be determined directly in water samples. The possible biomimetic activity and the potential application as sensors for copper complexes can be evaluated from the electrochemical behaviour and visible and EPR spectra.

The redox properties include oxidation and reduction of the central metal ion, various oxidation and reduction reactions of the ligand, and processes which involve both the central atom and the ligand [20]. The redox potentials of the Cu(III)/Cu(II) and Cu(II)/Cu(I) couples have been shown to be markedly affected by the nature of the solvent, background electrolyte and by the structure of the chelating ligand and of the complex as a whole. Redox potentials of Cu(II)–Cu(I) systems depend on the relative thermodynamic stabilities of the two oxidation states in a given ligand environment. The factors influencing the metal-located redox properties of the copper systems have been extensively studied. The influence of various structural features has been gauged, including ring size, degree and arrangement of unsaturation and alkyl substitution [21–23].

In previous work, we obtained different condensation products from the reaction of benzil and thiosemicarbazide depending on the reaction conditions: open chain molecule, benzilbisthiosemicarbazone  $L^{1}H_{6}$ , and a cyclic [1+1] molecule  $L^{2}H_{2}$ . Both compounds were obtained in the absence of metal salts (nickel, copper or iron), because in the presence of these salts the product isolated was always a thiosemicarbazide complex, even when working with high dilution conditions [24]. However, the reaction between the open chain molecule and iron chloride in methanol and in the presence of lithium hydroxide gave an iron complex of a macrocyclic species, but it is not possible to obtain the free macrocycle from this complex [25]. We have prepared metal complexes from  $L^{1}H_{6}$  with several metal salts [24,26]. Redox properties of cobalt(II) and nickel(II) complexes have been explored [26]. Some copper derivatives have shown that the changes in the coordination sphere are connected with the halfwave potential values for the Cu(II)/Cu(I) redox couple, and these results and the spectral data on solution agree with the superoxide dismutase (SOD) mimetic activity [27]. Moreover, carbon paste ion selective electrodes based on thiohydrazone and thiosemicarbazone complexes exhibit rapid response, adequate sensitivity and selectivity for copper ions [28].

As a part of our work involving the preparation of free iminomacrocyclic compounds and their metal complexes, we are interested in obtaining the free [2+2] condensation product from benzil and thiosemicarbazide. The aim of our work is to compare the reactivity of different macroligands containing the same functional group, but with variable number

and different structure, with a particular metal ion. In addition, we are trying to determine the best conditions to control the nature of copper complexes, since the different structures can improve their potential applications. Therefore, we report the reactions of an open chain ligand, benzilbisthiosemicarbazone  $L^{1}H_{6}$ , a cyclic molecule 6-methoxi-1,6-diphenyl-4thio-3,4,5,6-tetrahydro-2,3,5-triazine  $L^2H_2$  (Fig. 1) with copper(II) chloride, nitrate and sulfate in variable work conditions. Since a new free macrocycle 3,4,9,10-tetraphenyl-1,2,5,6,8,11-hexaazacyclododeca-7,12-dithione-3,4,9,10tetraene  $L^{3}H_{2}$  (Fig. 1) has been obtained from the reaction of  $L^2H_2$  with copper chloride, we have studied its interactions with copper nitrate and sulfate. We have studied the electrochemical behaviour of complexes by cyclic voltammetry, because their applications as SOD mimetic complexes and as copper sensors are related to the redox properties.

# 2. Experimental

# 2.1. Reagents

Copper salts were commercial products of highest chemical grade (Fluka). Solvents were purified according to standard procedures.

# 2.2. Synthesis of the organic molecules

Benzilbisthiosemicarbazone,  $L^{1}H_{6}$ , was prepared following the procedure previously reported [24].

 $L^2H_2$  was prepared by modifying the published procedure [25]. A solution of thiosemicarbazide (1.14 g, 12.5 mmol) in methanol (150 cm<sup>3</sup>), a solution of hydrochloric acid (25 cm<sup>3</sup>, 2 M), 1 cm<sup>3</sup> of HCl (12 M) and a solution of benzil (2.63 g, 12.5 mmol) in methanol (100 cm<sup>3</sup>) were added alternately dropwise and slowly with strong stirring to 75 cm<sup>3</sup> of methanol. After completion of the addition of all reactants, the mixture was heated for 8 h. Overnight a crystalline solid was formed, which was filtered off, washed and dried in vacuo (yield 95%).



Fig. 1. Structures proposed for the organic molecules.

A solution of copper chloride dihydrate (0.23 g, 1.40 mmol) in methanol (50 cm<sup>3</sup>) was added to a solution of  $L^2H_2$  (0.41 g, 1.40 mmol) in methanol (50 cm<sup>3</sup>). The mixture was stirred for 2 h at room temperature. The cream solid  $L^3H_2$  formed was filtered off, washed several times with methanol and dried in vacuo (yield 79%), m.p. 205°C. *Anal*. Calc. for C<sub>30</sub>H<sub>22</sub>N<sub>6</sub>S<sub>2</sub>: C, 67.92; H, 4.15; N, 15.85; S, 12.07. Found: C, 67.82; H, 4.28; N, 15.75; S, 12.13%. Selected spectroscopic data: m/z (FAB) 529.1 (C<sub>30</sub>H<sub>21</sub>N<sub>6</sub>S<sub>2</sub>, 100%). <sup>13</sup>C NMR (DMSO, 300 MHz): 166.90 (CS), 156.57, 155.97 (CN), 134.89, 134.54, 131.31, 129.79, 129.47, 128.67, 128.57 (Ph).

# 2.3. Synthesis of the complexes from $L^{1}H_{6}$ and copper(II) chloride dihydrate

To  $L^{1}H_{6}$  (0.20 g, 0.56 mmol) in methanol (25 cm<sup>3</sup>) was added a solution of copper(II) chloride dihydrate (0.10 g, 0.56 mmol) in methanol (40 cm<sup>3</sup>). The mixture was stirred for 5 h at room temperature, heated under reflux for 5 h or heated under reflux for 5 h in the presence of LiOH. In all cases a brown solid **1** was formed, which was filtered off, washed with methanol and dried in vacuo (yield 40%).

To  $L^{1}H_{6}$  (0.20 g, 0.56 mmol) in methanol (25 cm<sup>3</sup>) was added a solution of copper(II) chloride dihydrate (0.05 g, 0.28 mmol) in methanol (20 cm<sup>3</sup>). The mixture was stirred for 12 h at room temperature. The reddish solid **2** formed was filtered off, washed with methanol and dried in vacuo (yield 20%).

A solution of copper(II) chloride dihydrate (0.24 g, 1.40 mmol) and hydrochloric acid (50 cm<sup>3</sup>, 12 M) in methanol (50 cm<sup>3</sup>), was added to  $L^{1}H_{6}$  (0.50 g, 1.40 mmol) in methanol (100 cm<sup>3</sup>). The mixture was refluxed for 3 h with stirring. The green solid **3** formed was filtered off, washed with methanol and dried in vacuo (yield 85%).

The same solid was obtained if the acid (2 M) was added dropwise.

A suspension of  $L^{1}H_{6}$  (0.75 g, 2.10 mmol) in dichloromethane (25 cm<sup>3</sup>) was mixed with a suspension of copper(II) chloride dihydrate (0.36 g, 2.10 mmol) in the same solvent (20 cm<sup>3</sup>). The mixture was refluxed for 2 h with stirring. The green solid formed was filtered under nitrogen and dried in vacuo. The solid decomposes very quickly in the presence of air.

The reaction was carried out using toluene and cyclohexane as solvent with the same results described above.

A solution of copper(II) chloride dihydrate (0.10 g, 0.58 mmol) in methanol (50 cm<sup>3</sup>) was added to a suspension of  $L^{1}H_{6}$  (0.20 g, 0.58 mmol) and benzil (0.12 g, 0.58 mmol) in methanol (60 cm<sup>3</sup>). The mixture was refluxed for 4 h with stirring. The brown solid formed was filtered off, washed with methanol and dried in vacuo (yield 45%).

# 2.4. Synthesis of complexes from $L^{1}H_{6}$ and copper(II) nitrate trihydrate

A solution of copper(II) nitrate trihydrate (0.36 g, 1.50 mmol) in methanol (20 cm<sup>3</sup>) was added to  $L^{1}H_{6}$  (0.53 g,

1.50 mmol) in methanol (20 cm<sup>3</sup>). The mixture was stirred for 3 h at room temperature. The brown solid **4** formed was filtered off, washed with methanol and dried in vacuo (yield 65%).

A solution of copper(II) nitrate trihydrate (0.36 g, 1.50 mmol) in methanol (20 cm<sup>3</sup>) and 50 cm<sup>3</sup> of nitric acid (15 M) was added to  $L^{1}H_{6}$  (0.53 g, 1.50 mmol) in methanol (20 cm<sup>3</sup>). The mixture was stirred for 2 h at room temperature. The green oil formed was concentrated in a rotary evaporator to half the initial volume and then the solvent was evaporated slowly at room temperature. Finally needle shaped yellow crystals were separated.

Identical results were obtained adding the acid (2 M) dropwise.

# 2.5. Synthesis of complexes from $L^{1}H_{6}$ and copper(II) sulfate pentahydrate

To a suspension of  $L^{1}H_{6}$  (0.10 g, 0.30 mmol) in methanol (40 cm<sup>3</sup>) was added a solution of copper(II) sulfate pentahydrate (0.06 g, 0.28 mmol) in methanol (40 cm<sup>3</sup>). The mixture was stirred for 6 h at room temperature. The reddish solid formed was filtered off, washed with methanol and dried in vacuo (yield 20%).

To a suspension of  $L^{1}H_{6}$  (0.10 g, 0.30 mmol) in methanol (40 cm<sup>3</sup>) were added three drops of sulfuric acid (18 M) and then a solution of copper(II) sulfate pentahydrate (0.07 g, 0.28 mmol) in methanol (40 cm<sup>3</sup>). The mixture was stirred for 12 h at room temperature. On slow diffusion of ether through the dark blue oil formed, a crystalline dark blue solid **5** was obtained. The solid was filtered off, washed with ether and dried in vacuo (yield 51%).

## 2.6. Synthesis of complexes derived from $L^2H_2$

A solution of copper(II) nitrate trihydrate (0.15 g, 0.63 mmol) in methanol (20 cm<sup>3</sup>) was added to a suspension of  $L^2H_2$  (0.37 g, 1.26 mmol) in methanol (20 cm<sup>3</sup>). The mixture was stirred for 12 h at room temperature. The brown solid **6** formed was filtered off, washed with methanol and dried in vacuo (yield 27%).

A solution of copper(II) sulfate pentahydrate (0.10 g, 0.40 mmol) in methanol  $(20 \text{ cm}^3)$  was added to a suspension of  $L^2H_2$  (0.24 g, 0.80 mmol) in methanol (20 cm<sup>3</sup>). The mixture was stirred for 12 h at room temperature. The orangebrown solid **7** formed was filtered off, washed with methanol and dried in vacuo (yield 37%).

#### 2.7. Synthesis of complexes from $L^{3}H_{2}$

A solution of copper(II) chloride dihydrate (0.02 g, 0.23 mmol) in dried methanol (10 cm<sup>3</sup>) was added to a suspension of  $L^{3}H_{2}$  (0.11 g, 0.23 mmol) in dried methanol (10 cm<sup>3</sup>). The mixture was heated under reflux with stirring for 2 h. The red solid **8** formed was filtered off, washed with methanol and dried in vacuo (yield 27%).

A solution of copper(II) nitrate trihydrate (0.02 g, 0.90 mmol) in methanol (20 cm<sup>3</sup>) was added to a suspension of  $L^{3}H_{2}$  (0.05 g, 0.90 mmol) in methanol (20 cm<sup>3</sup>). The mixture was heated under reflux with stirring for 2 h. The clear brown solid **9** formed was filtered off, washed with methanol and dried in vacuo (yield 47%).

#### 2.8. Physical measurements

Microanalyses were carried out using a Perkin-Elmer 2400 II CHNS/O elemental analyser. Copper was analysed on a Hitachi Z-8200 atomic absorption spectrophotometer.

IR spectra in the 4000–400 cm<sup>-1</sup> range were recorded as KBr pellets on a Bomen-100 spectrophotometer and in the range 550–200 cm<sup>-1</sup> on a Bruker IFS 66V spectrophotometer. UV–Vis spectra in solution were registered on an Ati-Unicam UV2 spectrophotometer and the solid reflectance spectra on a Pye-Unicam SP-8-100 spectrophotometer. Conductivity data were measured using freshly prepared DMF solutions (ca.  $10^{-3}$  M) at 25°C with a Metrohm Herisau model E-518 instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-300 spectrophotometer using dimethylsulfoxide-d<sub>6</sub> as solvent and TMS as internal reference. EPR spectra in the solid state were run on a Bruker ER 200D X-band spectrophotometer.

Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix.

Electrochemical measurements were performed with a BAS CV 27 voltammograph and a BAS A-4 XY register using a glassy carbon ( $\phi$  5 mm) working electrode, a platinum wire as auxiliary, and a double junction, with porous ceramic wick, Ag/AgCl reference electrode, standardized for the redox couple ferricinium/ferrocene ( $E_{1/2} = +0.400$  V,  $\Delta E_{\rm p} = 60$  mV). Cyclic voltammetry studies of ligands and complexes were carried out on 0.01 M solutions in dimethylsulfoxide ( $L^{1}H_{6}$  complexes) and dichloromethane ( $L^{2}H_{2}$ derivatives) containing 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte. The range of potential studied was between +1and -1.5 V. All solutions were purged with nitrogen steam for 5 min before measurement and the working electrode was polished before each experiment with diamond paste. The procedure was performed at room temperature and a nitrogen atmosphere was maintained over the solution during the measurements.

#### 3. Results and discussion

The reaction of  $L^2H_2$  with copper chloride in methanol at room temperature yields a cream solid. The analytical data show the modification of the reactant. The mass spectrum shows a peak at 529 amu corresponding to the macrocyclic species  $[C_{30}H_{21}N_6S_2]^+$ . The <sup>1</sup>H NMR spectrum in DMSO confirms the absence of methanol inserted or as a crystallization molecule. The <sup>13</sup>C NMR spectrum shows signals corresponding to one thio group, seven phenyl carbons and two imine carbons, confirming the proposed structure. The absorption bands observed in the IR spectrum are consistent with the functional groups present in the molecule.

The reaction of compound  $L^2H_2$  with copper chloride, under the described conditions, is the first direct procedure to isolate a free macrocycle  $L^3H_2$  containing thiosemicarbazone moieties. The copper chloride acts as a selective template in the reaction from the mesocycle. This effect is original because the template usually acts from diamine and dicarbonyl as precursors, but with benzil and thiosemicarbazide the condensation reaction does not work [24].

The direct reaction, using the high dilution technique, improves the yield of the cyclic ligand  $L^2H_2$ , which could be useful in the future since this molecule is a potential anticancer agent and it is being currently tested against the full panel of 60 human tumours (NSC no. 711635-Y) by the National Cancer Institute (USA).

The complexes characterized are stable to air and moisture. The analytical data of complexes are consistent with the stoichiometries proposed which are summarized in Table 1.

# 3.1. $L^{1}H_{6}$ complexes

Complexes from  $L^1H_6$  present different formulae and variable grades of deprotonation depending on the halide and/ or the working conditions, in particular the presence of protons.

From the copper chloride reactions, three type of complexes with the same stoichiometry are obtained. In methanol as solvent, complexes 1, 2 and 3 are isolated; the last compound appears only in the presence of hydrochloric acid. Working in a molar ratio 1:2, the complex 2 is obtained. This product had been obtained previously in ethanol under reflux [24]. The reaction in the presence of benzil yields complex 1.

The reactions with nitrate give only the complex **4** because by working in the presence of nitric acid only a ligand breakdown product is obtained. However, with sulfate two different complexes are obtained, **5** and **2**, depending on whether or not protons are present in the medium.

The analytical data of complexes are in agreement with the ligand acting as a monoanion in complexes 1 and 4, a dianion in complex 2 and a neutral molecule in complexes 3 and 5. The mass spectra of complexes show a peak at 418 amu corresponding to  $[C_{16}H_{15}N_6S_2Cu]^+ + 1$  and in addition for complex 4 the spectrum exhibits the peak corresponding to the molecular mass.

The conductivity data in DMF indicate that the complexes are non-electrolyte compounds, but complex **5** is a 1:1 electrolyte [29]. Therefore chloride and nitrate are bonded to the copper ion, while the sulfate ion is outside the metal coordination sphere.

#### 3.1.1. IR spectra

The most significant IR bands, useful for determining the ligand mode of coordination, are listed in Table 2. The most important bands of the ligand were assigned according to published data [24].

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Analytical data	and some physical prop	erties of complexes					
	$CuC_{16}H_{15}N_6S_2Cl~(1)$	$CuC_{16}H_{14}N_{6}S_{2}\left( 2\right)$	$CuC_{16}H_{16}N_{6}S_{2}Cl_{2}\left( 3\right)$	$CuC_{16}H_{15}N_6S_2NO_3$ (4)	$CuC_{16}H_{16}N_6S_2SO_4 \cdot H_2SO_4 \cdot 2CH_3OH\left(\textbf{5}\right)$	$Cu(C_{30}H_{21}N_6S_2)_2CH_3OH$ (6)	$CuC_{30}H_{20}N_6S_2$ (7)
C (%) found	41.64	45.70	38.82	39.63	33.76	62.20	57.90
Calc.	41.29	45.98	39.14	39.95	31.97	63.45	60.86
N (%) found	18.32	19.15	16.74	20.77	12.79	14.48	13.42
Calc.	18.50	20.12	17.12	20.39	12.39	14.56	14.20
H (%) found	3.31	3.38	3.59	2.98	3.48	3.32	3.13
Calc.	3.30	3.55	3.33	3.12	3.83	3.98	3.38
S (%) found	13.80	15.16	12.92	13.02	19.56	10.88	11.05
Calc.	13.97	15.32	13.05	13.31	18.89	11.09	10.81
Cu (%) found	14.13	15.12	11.53	13.22	7.35	5.77	10.80
Calc.	13.98	15.19	12.94	13.22	9.37	5.50	10.73
pf (°C)	228	210	230	208	> 260	184	> 260
Colour	brown	red	green	brown	blue	brown	orange-brown

The absence of any bands in the 2600–2800 cm<sup>-1</sup> region of the IR spectra of  $L^1H_6$  and its complexes suggests the absence of any thiol tautomer in the solid state [30].

The spectrum of complex 2 shows three bands in the 3500– 3000 cm<sup>-1</sup> region, which indicate the total deprotonation of the ligand. Spectra of complexes 3 and 5 exhibit a larger number of bands in the amine stretching region, which confirms that the neutral form of the ligand is bonded in these complexes. Spectra of complexes 1 and 4 show an intermediate situation, more bands than complex 2 and less than complex 3, which agrees with a partial loss of the acidic hydrogens present in  $L^1H_6$ . These conclusions are according to the analytical data of complexes and the mass spectrum of complex 4.

The IR spectra of the complexes, except complex **5**, show the band assigned to the azomethine nitrogen shifted to lower wavenumber [31]. Coordination of these nitrogens is confirmed with the presence of new bands assignable to  $\nu$ (Cu– NC) in the spectra of complexes (Table 2) [32].

In the spectra of complexes **3** and **5**, in which the ligand acts in its neutral form, the band assigned to  $\delta(NH_2)$  remains in the same position as in the free ligand, so the primary amines are not bonded to the copper ion. In addition, coordination via the sulfur atoms is indicated by a decrease in the frequency of the thioamide band. The presence of a new band assignable to  $\nu(CuS)$  confirms that the sulfur atoms are involved in the coordination.

The spectrum of complex **4** shows bands corresponding to the nitrate anion coordinated to the copper. Except for these bands, this spectrum is very similar to the spectra of **1** and **2** in the 1700–700 cm<sup>-1</sup> region so the ligand coordination modes must be the same. The three spectra show a band at 1634 cm<sup>-1</sup>, which could be related to the  $\delta$ (NH<sub>2</sub>) shifted because of bonding to copper or the new CN group since the ligand is deprotonated. The new bands appearing below 500 cm<sup>-1</sup> confirm that the primary amines are bonded to the metal ion. Therefore L<sup>1</sup>H<sub>6</sub> acts as a tetradentate ligand through four nitrogen atoms.

From the IR spectra data, one can deduce that the coordinative behaviour of  $L^1H_6$  depends on whether it is deprotonated or acts in its neutral form. In complexes **1**, **2**, and **4**, which contain the ligand in deprotonated form, it is bonded to the copper through four nitrogen atoms (provided by the imine and the primary amine groups). However, in complexes **3** and **5**, in which  $L^1H_6$  acts as a neutral molecule, the sulfur atoms participate in the coordination. The copper coordination sphere is completed by the anions present in complexes **1**, **3** and **4**.

#### 3.1.2. Electronic and EPR spectra

The significant electronic absorption bands in the spectra of complexes recorded in solution and in solid state are presented in Table 3.

The reflectance spectra of complexes **3**, **4** and **5** present bands in the same region, so the copper will have the same environment, with a distorted octahedral geometry around

Table 1

Table 2
Relevant IR spectral data and assignament of $L^1H_6$ complexes (cm <sup>-1</sup> )

	$\nu(\mathrm{NH}) + \nu(\mathrm{NH}_2)$	$\nu(C=N) + \delta(NH_2)$	Thioamide I	Thioamide IV	<i>v</i> (Cu–N)/ <i>v</i> (Cu–S)	ν(Cu–X)
L <sup>1</sup> H <sub>6</sub>	3420 °, 3330 °, 3250, 3090	1610, 1585	1465 <sup>a</sup>	837		
$CuC_{16}H_{15}N_6S_2Cl(1)$	3443, 3240 <sup>a</sup> , 3084 <sup>a</sup>	1626, 1611, 1575	1445, 1527	848	447, 427	329
$CuC_{16}H_{14}N_{6}S_{2}$ (2)	3343, 3271, 3102	1626, 1600, 1569	1467, 1427	836	449, 428	
$CuC_{16}H_{16}N_{6}S_{2}Cl_{2}$ (3)	3333, 3240 <sup>a</sup> , 3084	1609, 1575	1535, 1446 <sup>a</sup>	768	427, 297	284
$CuC_{16}H_{15}N_{6}S_{2}NO_{3}(4)$	3438 <sup>a</sup> , 3406 <sup>a</sup> , 3269, 3082	1634, 1608, 1575	1551, 1532, 1447	848	447, 428	335, 350
$CuC_{16}H_{16}N_6S_2SO_4 \cdot 2CH_3OH(5)$	3308 °, 3140, 3100 °	1653, 1632	1560	784	292	

<sup>a</sup> Several bands.

Table 3

Complex	Diffuse reflectance	Solution				EPR		
	Solid	DMF	DMSO	MeOH	DMF+HX	$g_{\parallel}$	$g_{\perp}$	$g_0$
1	372, 466, 666(sh) <sup>a</sup>	500, 550(sh)	500, 550(sh)	483		2.17	2.07	2.10
2	420, 490, 540(sh)	500, 550(sh)	500, 550(sh)	484		2.14	2.05	2.08
3	424, 590-690	500, 550(sh)	500, 550(sh)	484	694, 767	2.18	2.07	2.11
4	600-520	500, 550(sh)	500, 504	500, 544(sh)		2.15	2.06	2.09
5	580	500, 550(sh)	500, 550(sh)	483	694, 767			2.07

<sup>a</sup> sh shoulder.

the metal ion [33]. Therefore, the nitrate ion acts as a bidentate ligand in complex **4**. The spectrum of complex **2** agrees with a quasiplanar disposition for the copper ion. The spectrum of complex **1** is different from the others, the number and positions of the absorption bands suggest a pentacoordinated geometry.

Structures for each coordination number are illustrated in Fig. 2, where we have plotted the output of the calculation carried out using the Hyperchem program (semiempirical method, ZINDO/1).

The solution spectra of all complexes in DMSO, DMF and methanol present the same absorption bands (solutions are red), so the solvent molecules partially replace the anion in the coordination sphere of copper, giving a quasiplanar environment in all complexes. The spectrum of complex **2** does not change in solution because the disposition in the solid state was already quasiplanar.

For complexes **3** and **5** the spectra in DMF were registered after the addition of hydrochloric acid (2 M). An important change was observed: the solution colour changes to green and the position of the band indicates a significant modification in the copper coordination sphere giving a pseudo-octahedral geometry for the copper ion as in the complexes in the solid state (Fig. 3) [33].

We studied the variation of UV–Vis spectra of  $10^{-3}$  M copper(II) chloride dihydrate solution in DMSO after successive additions of  $10^{-3}$  M L<sup>1</sup>H<sub>6</sub> solution in the same solvent with the total volume constant and in the presence of [NBu<sub>4</sub>] [PF<sub>6</sub>] to maintain the ionic force. The visible spectra were recorded and the absorbance variations represented versus the molar fraction of ligand added/Cu (Fig. 4).



Fig. 2. Possible structures for  $L^{1}H_{6}$  complexes: (a) complex 1, (b) complex 2, (c) complex 3.

From the first addition, a new band appears at 448 nm in the visible spectrum whose absorbance increases lineally until a 2 molar fraction; after that the value is constant.



Fig. 3. UV–Vis spectra of complex 3 [CuL<sup>1</sup> $H_6Cl_2$ ]: (a) DMF solution; (b) DMF + HCl (2 M).

The spectra were registered after 2 days, and the position of the band is shifted to 500 nm (identical position to that in the isolated complexes in DMSO solutions). The absorbance increases until a 1.5 molar fraction and then is constant (Fig. 4). Therefore, in DMSO a 1:1 molar ratio complex is formed but in this solvent an excess of the ligand is necessary.

The EPR parameters observed for complexes in the solid state (300 K) are presented in Table 3. In Fig. 5 the spectrum of complex **1** is shown.

The EPR spectra, which do not show hyperfine coupling, confirm the copper oxidation state and the mononuclear nature for the complexes. Complexes **1**, **2**, **3** and **4** give typical axial spectra, but complex **5** has a slightly axial isotropic spectrum. Values of  $g_{\parallel}$  and  $g_{\perp}$  are in the range for this kind of complexes. In all of the complexes,  $g_{\parallel} > g_{\perp} > 2$  values are consistent with a  $d_{x^2-y^2}$  state. Complex **2** presents a lower  $g_{\parallel}$ 



Fig. 5. Solid state EPR spectrum of complex 1.

value, which agrees with the  $L^1H_6$  being tetradentate dianion and pseudo-planar, while the higher value is presented for complex **3** in which the ligand is neutral and the copper is hexacoordinated [8,30,34].

#### 3.2. Complexes derived from $L^2H_2$

Reactions of the mesocyclic ligand  $L^2H_2$  with copper(II) nitrate and sulfate hydrate give stable solids in air and moisture. The colour, melting point and analytical data are included in Table 1. The formulae of complexes depend on the metal salt used.

Reaction with nitrate gives complex **6**, whose analytical data and mass spectra indicate that the complex contains the deprotonated macrocyclic ligand  $L^{3}H$ . The mass spectrum shows a peak at 529 amu corresponding to the macrocycle molecular mass  $[C_{30}H_{21}N_{6}S_{2}]^{+}$  and a peak corresponding to the fragment  $[CuC_{30}H_{21}N_{6}S_{2}CH_{3}OH]^{+}$ . From the reaction with sulfate the complex **7** was obtained. Its analytical



Fig. 4. Absorbance evolution of the L<sup>1</sup>H<sub>6</sub> copper complex, in DMSO solution, versus ligand/Cu molar fraction; ( $\diamondsuit$ ) direct measurements; (+) after 24 h.

Table 4					
Relevant IR	spectral data	and assignmer	nt of $L^2H_2$ con	mplexes (cm <sup>-</sup>	1)

	ν(N–H)	ν(C=N)	Thioamide I	Thioamide IV	ν(Cu–N)/ν(Cu–S)
$L^{2}H_{2}$ $L^{3}H_{2}C_{30}H_{22}N_{6}S_{2}$ $Cu(C_{30}H_{21}N_{6}S_{2})_{2}CH_{3}OH(6)$	3184, 3131 3057 3053	1608 1599, 1581 1601, 1583, 1575, 1550	1550 1480 1485	846 866 865	439
$CuC_{30}H_{20}N_6S_2$ (7)	3053	1600, 1582, 1575, 1550	1488	878, 866	436

data suggest a 1:1 deprotonated ligand:copper ratio. The mass spectrum confirms the macrocyclation of the ligand. In addition, in both reactions  $L^{3}H_{2}$  is isolated from the reaction liquor. Therefore, the macrocyclic ligand is formed in all reactions where the copper ion acts as template. The characteristics of the final product depend on the salt used. A free macrocycle is obtained in the reaction with copper chloride, while complexes were isolated from the reaction with nitrate and sulfate.

### 3.2.1. IR spectra

The IR spectrum of complex **6** shows only a band assignable to  $\nu$ (NH), the thioamide I slightly shifted to higher frequencies and four bands in the region of stretching vibration of the imine group (Table 4). These modifications suggest that the L<sup>3</sup>H<sub>2</sub> ligands are partially deprotonated and two equivalent imine groups of each ligand are bonded to the copper ion.

The spectrum of complex 7 exhibits the presence of water and the deprotonation of the ligand. The bands are slightly shifted with respect to the  $L^{3}H_{2}$ , indicating that the ligand is bonded to the copper ion through four nitrogen atoms.

#### 3.2.2. Electronic spectra

The electronic spectra of complexes in the solid state are very similar. Both of them show a band at a position which agrees with a pentacoordination for the copper, so the solvent molecules are bonded to the copper ion.

# 3.3. Complexes derived from $L^{3}H_{2}$

Direct reactions of the macrocyclic ligand with copper chloride and nitrate give complexes 8 and 9, respectively. The analytical and spectroscopic data indicate that they are adulterated with the ligand, although it was necessary to work under stronger conditions than with the mesocyclic ligand  $L^2H_2$ , probably owing to its inherent rigidity.

# 3.4. Cyclic voltammetry

The study of the electrochemical behaviour of the complexes was carried out in the range from +1 to -1.5 V. In the positive range, +1 to 0 V, the oxidation processes Cu(III)/Cu(II) can be observed. Cyclic scanning between 0 and -1.5 V permits study of the copper reduction centred processes and the ligand reductions; the potential reduction of the Cu(II)/Cu(I) process is related to the potential SOD mimetic activity. Both ranges of potentials were studied independently. The electrochemical response in the total range studied (Figs. 6–8) showed a pattern that can be considered as the sum of the individual responses.

The cyclic voltammogram of  $L^1H_6$  in DMSO shows irreversible reduction waves in the more negative region (Fig. 9(b)) [26,35].

The voltammetric response of all  $L^{1}H_{6}$  complexes exhibits oxidation and reduction metal centred processes, as for complexes previously published [27]. Cyclic voltammograms between +1 and 0.0 V show a redox couple associated with the Cu(III)/Cu(II) process (Table 5). In addition, in the range 0.0 to -1.5 V, peaks which can be assigned to Cu(II)/ Cu(I) and Cu(I)/Cu(0) processes appear [1].

Cyclic scanning of complex 1 (Fig. 6(a)) between +1 and 0 V shows in the cathodic scan a peak at +0.625 V. In the forward scan a poorly defined wave at +0.410 V can be observed and an anodic peak at +0.680 V associated with



Fig. 6. Cyclic voltammograms for complexes: (a) complex 1, [CuL<sup>1</sup>H<sub>5</sub>Cl]; (b) complex 3, [CuL<sup>1</sup>H<sub>6</sub>Cl<sub>2</sub>];  $\nu$ =100 mV s<sup>-1</sup>.



Fig. 7. Cyclic voltammograms for (a) complex **4**,  $[CuL^{1}H_{5}NO_{3}]$ , (b) complex **5**,  $[CuL^{1}H_{6}CH_{3}OH]SO_{4}$ , (c) complex **2**,  $[CuL^{1}H_{4}]$ ,  $\nu = 100$  mV s<sup>-1</sup>.



Fig. 8. Cyclic voltammogram of complex 3, [CuL<sup>1</sup>H<sub>6</sub>Cl<sub>2</sub>], in DMSO after the addition of HCl (2 M),  $\nu$  = 100 mV s<sup>-1</sup>.

the cathodic peak at +0.625 V. The  $\Delta E_{\rm p}$  values fall in the range 50–70 mV, when the scan rate is varied between 100–800 mV s<sup>-1</sup>, with peak current ratio constant (0.8). Also the ratio between the cathodic peak current and the square root of the scan rate ( $I_{\rm pc}/\nu^{1/2}$ ) is practically constant. All of these data are diagnostic of a quasireversible one-electron transfer controlled by diffusion following the equation

#### $[Cu(III)L] + e^{-} \Leftrightarrow [Cu(II)L]$

Cyclic scans of **1** in the range 0 to -1.5 V reveal peaks at -0.470 and -0.930 V in the cathodic scan and in the forward scan a peak at -0.390 V associated with the more negative cathodic peak. These peaks can be assigned to successive Cu(II) reduction processes.

The voltammogram of complex **3** (Fig. 6(b)) is very similar to that of complex **1**. The cyclic voltammogram of **3** shows, between + 1.5 and 0 V, a cathodic peak at +0.680 V and an anodic peak at +0.740 V associated with the cathodic peak. The  $\Delta E_p$  and the current peak ratio of this couple of peaks are as expected for a quasireversible Cu(III)/Cu(II) process.

In the cathodic scan, in the range 0 to -1.5 V, peaks at -0.400 V and -1.030 V are observed. In the anodic scan there is a peak at -0.380 V, associated with the more negative cathodic peak. The first wave is attributed to Cu(II)/Cu(I) reduction and the other peaks correspond to the Cu(II)/Cu(0) reduction processes.

Cyclic voltammograms of complexes **4** and **5** (Fig. 6(a,b)) are very similar. The electrochemical response of complex **4** in the cathodic scan shows a peak at +0.600 V and in the reverse scan an anodic peak at +0.675 V associated with the cathodic peak. The variation of the redox parameters of the redox couple is indicated in Table 6, so it is associated with a quasireversible Cu(III)/Cu(II) process. The voltammogram between 0 and -1.5 V shows peaks at -0.520 V and -0.960 V, which can be attributed to the reductions Cu(II)/Cu(I) and Cu(I)/Cu(0), respectively. The electrochemical parameters for complex **5** are included in Table 6.

The cyclic voltammogram of complex **2** (Fig. 7(c)) shows a different electrochemical response and it is close to that published previously [27]. The most important characteristic is the quasireversible waves associated with the Cu(II)/ Cu(I) process (Table 6).

For all complexes, redox processes associated with oxidation to Cu(III) are observed, probably because the  $L^1H_6$  is

Table 5 Oxidation potential values (V) of  $L^1H_6$  complexes

Compound	$E_{1/2}$ <sup>a</sup> Cu(III)/Cu(II)
$C_{16}H_{15}N_{6}S_{2}CuCl(1)$	0.652
$C_{16}H_{14}N_6S_2Cu(2)$	0.645
$C_{16}H_{16}N_{6}S_{2}CuCl_{2}$ (3)	0.710
$C_{16}H_{15}N_6S_2CuNO_3(4)$	0.635
$CuC_{16}H_{16}N_6S_2SO_4 \cdot 2CH_3OH(5)$	0.640

 $\overline{E_{1/2}} = (E_{\text{pa}} + E_{\text{pc}})/2, \nu = 100 \text{ mV s}^{-1}.$ 



Fig. 9. Evolution of the cyclic voltammogram of  $CuCl_2 \cdot 2H_2O$  in DMSO (a); with successive additions of  $L^1H_6$  (b); after 0.4 ml (c); after 1.4 ml (d); after 2.4 ml (e).

Table 6 Summary of electrochemical data for complexes <sup>a</sup>

Complex	+1.5 to 0 V	7		0 to -1.5 V			
	$E_{\rm pc}$	$E_{\rm pa}$	$\Delta E_{\rm p}$	$I_{\rm pc}/I_{\rm pa}{}^{\rm b}$	$E_{\rm pc}$	$E_{\mathrm{pa}}$	$E_{ m pc}$
1	0.625	0.680	0.055	0.800	-0.470	-0.390	-0.930
2	0.620	0.670	0.050	0.860	-0.600	-0.500	
3	0.680	0.740	0.060	1.000	-0.400	-0.380	-1.030
4	0.600	0.675	0.075	0.980	-0.520		-0.960
5	0.610	0.670	0.060	0.820	-0.510		-0.990

<sup>a</sup> Redox potential (V) at 298 K, scan rate 100 mV s<sup>-1</sup>. Cyclic voltammograms registered in the range from +1 to -1.5 V.

<sup>b</sup> Scan rate in the range 100–800 mV s<sup>-1</sup>.

an open chain ligand and in its complexes the oxidation of copper is favoured since this ligand can adopt a different conformation to fit the small copper(III). The change from the Cu(II) to the Cu(III) state ( $d^8$  low spin) involves a drastic reduction of the metal ion radius. In addition, this process does not involve changes in the geometries of the copper(II) complexes in DMSO solution. The oxidation values in Table 5 agree with that, because more positive values

and more difficulty in stabilizing the copper(III) oxidation state are observed for complexes **1** and **3** [36,37].

On the other hand, the values of the reduction potential fall in the range -0.400 to -0.520 V, indicating difficulty in reducing the copper(II) ion in these complexes. This fact can be interpreted in terms of less favourable fitting of the Cu(II)/Cu(I) ion, because this reduction is related to the level of tetrahedral distortion in the complexes and in our case in solution they seem to be almost planar. In accordance with these reduction potentials and the electronic spectra of  $L^1H_6$  complexes, they do not seem to be suitable SOD mimetics.

The electrochemical response of complexes 1 and 3 with successive additions of hydrochloric acid (2 M) was also studied. The voltammogram changes immediately with the first addition, the more positive potential peaks are modified and a new peak couple arises. These changes increase with the successive additions of acid or with time until 1 cm<sup>3</sup> is added. The voltammogram (Fig. 8) now shows two peaks at +0.280 and -1.00 V in the cathodic scan and an anodic peak at +0.360 V associated with +0.280 V, indicating a significant change in the complex structure under these conditions. These results agree with those from the visible spectra in the same solvent described in the previous section.

Reaction of copper(II) chloride with  $L^{1}H_{6}$  in DMSO was studied by cyclic voltammetry. Cyclic voltammograms of  $CuCl_{2} \cdot 2H_{2}O$  solutions in DMSO, in which  $L^{1}H_{6}$  was added gradually until a 1:3 molar ratio was reached, were recorded (Fig. 9(a,b)). Changes in the colour and in the electrochemical response were shown from the first addition. The changes increase when the ligand proportions increase (Fig. 9(c,d)), but the cyclic voltammogram does not reproduce the cyclic voltammogram of isolated complex until a 1:2.5 molar ratio. These results indicate that the complexation reaction is slow. The donor character of the solvent may be the reason for that, owing to the difficult substitution by the ligand as was shown for the visible spectra of complexes.

Cyclic voltammograms of macrocyclic complexes **6** and **7** are very different to those of the open chain complexes. They do not show waves corresponding to a Cu(III)/Cu(II) process; this agrees with the behaviour of similar copper macrocyclic complexes [27]. The voltammograms only exhibit reduction waves at negative potentials which could be related to the reduction process of the copper ion and the unsaturation of the ligand [38].

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