

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF THE *tetra*-CHLOROSALEN AND *tetra*-CHLOROSALOPHEN COPPER(II) COMPLEXES

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A series of new copper (II) complexes with *tetra*-chlorinated Schiff base derivatives of the salen and salophen α -R-substituted type were synthesized. Their spectral properties and electrochemical behavior were investigated. The catalytic activity of these complexes was studied in the oxidation of 2,6-di-*t*-butylphenol with molecular dioxygen in DMF solution.

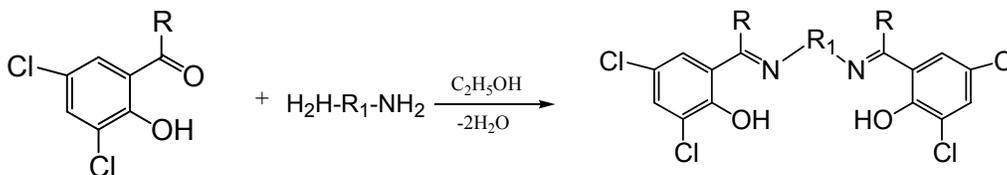
INTRODUCTION

The coordination behavior of transitional metals (Co, Cu, Mn, Fe) with Schiff bases has been investigated and a considerable number of complexes obtained have been characterized by the usual spectroscopic methods (UV-VIS, FT IR, NMR, EPR).¹⁻⁶ For some of these complexes studies concerning their dioxygen uptake ability and their catalytic activity regard oxidation processes were carried out.⁷⁻¹⁰

The present work reports the synthesis, spectral characterization and catalytic activity of new copper (II) coordination compounds with *tetra*-chlorinated Schiff bases derivatives of the salen and salophen [salen = bis(salicyliden)ethylenediamine and salophen = bis(salicyliden)-*o*-phenylenediamine] type. The electrochemical properties of the complexes were studied by cyclic voltammetry. The catalytic activity of the complexes was studied with regards to the oxidation of 2,6-di-*t*-butylphenol. It was seen that the aliphatic substituents on the azomethinic groups and the chloro grafted on the ligand molecules modified the redox and catalytic properties of the complexes.

RESULTS AND DISCUSSION

The ligands (H_2L) have been prepared as reported in the literature, by condensation of the corresponding aldehyde- or keto- derivatives with ethylenediamine or *o*-phenylenediamine according with the general equation presented in Scheme 1.¹¹



Scheme 1 – General equation for the synthesis of the ligands.

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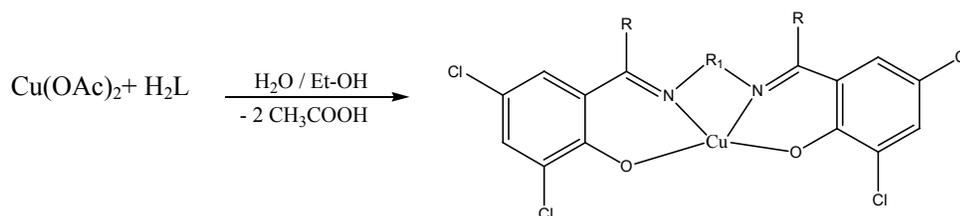
Where:

R₁ = -H₂C-CH₂- , (en)
 R = H, tetrachloro Salen, (tClSalen)
 R = CH₃, tetrachloro-dimethyl Salen,
 (tClMeSalen)
 R = CH₃CH₂, tetrachloro-diethyl Salen,
 (tClEtSalen)

R₁ = o-C₆H₄- , (ophen)
 R = H, tetrachloro Salophen, (tClSalophen)
 R = CH₃, tetrachloro-dimethyl Salophen,
 (tClMeSalophen)
 R = CH₃CH₂, tetrachloro-diethyl Salophen,
 (tClEtSalophen)

The ligands were characterized by elemental analysis, FT IR, UV-Vis and ¹H-NMR techniques. These analyses indicated that the target ligands had been obtained and good purity.

The copper complexes have been prepared by reaction between Cu(OAc)₂ and the ligands, in a 1:1 molar ratio, carried out in a water/ethanol solution according to the equation presented in Scheme 2.¹²



Scheme 2 – General equation for the synthesis of the copper complexes.

The complexes were characterized by elemental analyses, UV-VIS, FT IR and EPR spectroscopy. The elemental analyses indicate the formation of the complexes in a 1:1 molar ratio (CuL).

Electronic spectra

The UV-VIS spectra of the ligands and complexes were recorded in DMF due to the low solubility of the complexes in other organic solvents. The complexes spectra present modifications in the position and intensity of the bands characteristic to free ligands, as well as the apparition of new absorptions bands (Table 1).

Table 1

Electronic spectral data for the copper complexes in DMF

Compounds	λ_3 , nm (ϵ , l/mol·cm)	λ_2 , nm (ϵ , l/mol·cm)	λ_1 , nm (ϵ , l/mol·cm)
Cu(tClSalen)	296 (3.98)	378 (4.02)	520 (2.78)
Cu(tClMeSalen)	298 (3.51)	376 (3.67)	525 (2.27)
Cu(tClEtSalen)	302 (3.65)	386 (3.57)	573 (2.03)
Cu(tClSalophen)	312 (3.67)	422 (3.58)	550 (3.01)
Cu(tClMeSalophen)	340 (3.57)	450 (2.69)	566 (1.84)
Cu(tClEtSalophen)	326 (3.42)	424 (3.51)	576 (2.18)

The absorptions in 296-340 nm range and 370-450 nm range are assigned as π - π^* or n - π^* transitions. The absorptions from 370-450 nm range include intraligand bands overlapped with ligand-metal charge transfer, d - π^* transition. The new bands appeared to the lowest energy absorption, in 520-570 nm range, can be assigned as d - d transition for Cu(II) in C_{2v} symmetry.^{13,14} The results obtained from the electronic spectra are suggesting a square planar coordination geometry around the Cu(II).

Infrared spectra

The FTIR spectra of the ligands show major bands around of 1600 cm^{-1} assigned to $\nu_{\text{C=N}}$, 1560 cm^{-1} and 1500 cm^{-1} assigned to ring vibration, 1280 cm^{-1} assigned to OH phenolic deforming outside, 1230 cm^{-1} assigned to $\nu_{\text{C=N}}$, and at 1050 cm^{-1} assigned to $\nu_{\text{C-O}}$. The spectra of the complexes present, the C=N stretching mode is shifted to a lower frequency and additional shifts in the bands corresponding to C-N and C-O grouping compared with free ligands. Also, the characteristic ligands bands for the deforming outside the Ar-OH plan (around 1280 cm^{-1}) are absent in the case of complexes, as a consequence of the involvement of the

oxygen anion into a σ bond with the metallic centre. The formation of the metal-oxygen σ bond and metal-nitrogen π -bond determines the apparition of new absorption bands in the region $420\text{-}685\text{ cm}^{-1}$.^{14,15} The principal FT IR absorption frequencies of the copper complexes are listed in Table 2.

Table 2
Significant IR absorption bands (cm^{-1}) for the copper complexes

Compounds	$\nu_{\text{C=N}}$		New bands	
	Complexes	Ligands	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
Cu(tClSalen)	1624	1636	581	482
Cu(tClMeSalen)	1601	1611	551	472
Cu(tClEtSalen)	1587	1604	548	476
Cu(tClSalophen)	1608	1617	536	457
Cu(tClMeSalophen)	1605	1648	556	474
Cu(tClEtSalophen)	1593	1645	552	490

The FT IR spectra recorded support the formation of the complexes by the coordination of Cu to the azomethinic nitrogen and to the phenolic oxygen.^{2,14}

Electrochemistry

The electrochemistry of the complexes was investigated, as the redox potential is an important parameter in electron transfer processes in general and also in our catalytic systems. The studies of cyclic voltammetry show a *quasi-reversible* or *irreversible* behaviour for the more of complexes (Figure 1). The free ligands not show oxidation or reduction peaks in the investigated range.

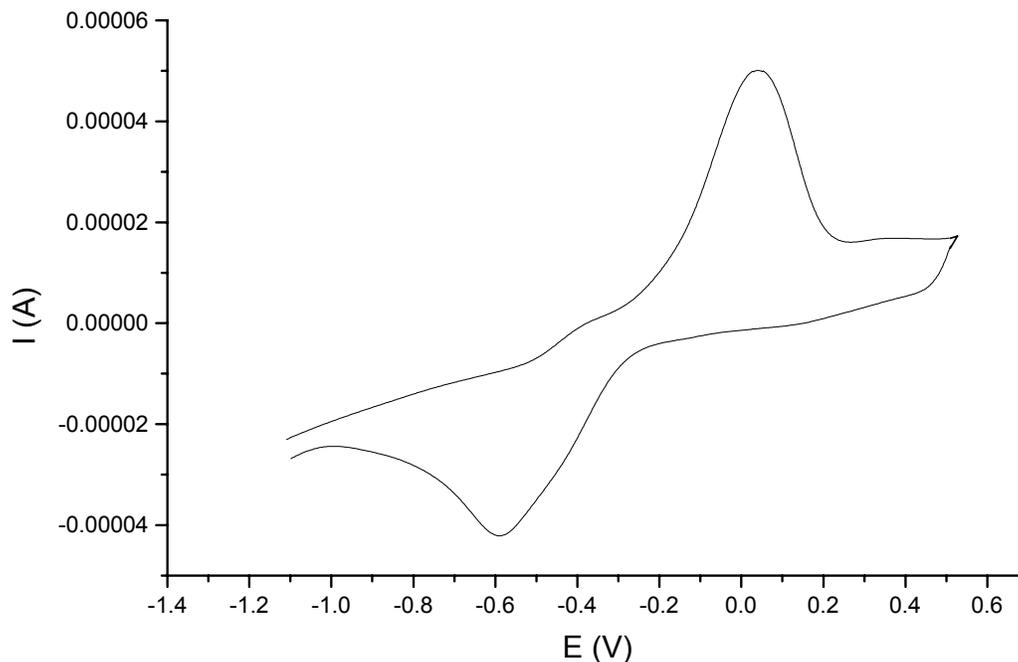


Fig. 1 – Cyclic voltammogram of the Cu(tClMeSalophen) complexes in DMF, $\nu = 0.1\text{ V/s}$.

The electrochemical data, the peaks values E_{pa} , E_{pc} , the difference from values E_{pa} , E_{pc} , ΔE , and semi-wave, $E_{1/2}$ potentials for the copper complexes are presented in Table 3.

Examining the data collected in the Table 3 one can observe that the first two complexes and four and five have a quasi-reversible behavior, while the three and six present an irreversible behavior. This behavior may be explained by the steric hindrance in the complexes with the ethyl radicals.

The intensities and the peak's area, available from both $^1\text{H-NMR}$ spectra and chromatograms, permit the evaluation of the transformation degree, and the quinone (QN) and diphenoquinone (DPQ) contents. The results obtained are listed in Table 4. Analysis of the evidence in the Table shows that for all the oxidation product is only DPQ. The yields are between 53% and 100%. This is in good correlation with redox potential and steric hindrance.

Table 4

Results of DtBuP oxidation with O_2 in presence of the Cu(II) complexes

Compounds	Yield %	QN %	DPQ %
Cu(tClSalen)	99		100
Cu(tClMeSalen)	100	-	100
Cu(tClEtSalen)	94	-	100
Cu(tClSalophen)	100	-	100
Cu(tClMeSalophen)	74	-	100
Cu(tClEtSalophen)	53	-	100

The formation of the DPQ in high yield involves the reversible formation of some $[\text{CuL-O}_2]$ adducts and CuL complexes are implicated in the stage of oxidation reaction, in formation of phenoxyl radicals.¹⁶⁻¹⁸

EXPERIMENTAL PART

Elemental analysis (C, H, N) was performed by the Service de Microanalyses de Gif-sur-Yvette. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM 250 or AC 250 spectrometers operating at 250 MHz. All spectra were obtained in CDCl_3 and chemical shifts calculated in ppm with respect to TMS ($\delta = 0$) or solvent residual peak ($\delta = 7.26$ for proton). UV-Vis spectra were taken on DES device, operating with the SAFAS program. The FT IR spectra were obtained on a Bruker IFS 66 apparatus in KBr pellets. EPR spectra were recorded in frozen DMF solution at 100K, on a Bruker Elexis apparatus.

Cyclic voltammetry experiments were performed on an Autlab apparatus. The recordings were made in a 2mM solution in DMF under argon atmosphere, using lithium perchlorate as electrolyte support. The following material has been used for analysis: as working electrode a vitreous carbon electrode ($A = 4.0 \text{ mm}^2$); as reference electrode, a saturated calomel electrode and as auxiliary electrode a platinum wire.

The catalytic activity was studied followed the oxidation of 2,6-di-*tert*-butyl phenol (DtBuP) with molecular oxygen, on employing the synthesized compound as catalysts. The reaction products have been separated by elution on a silica column with $\text{CH}_2\text{Cl}_2\text{-C}_7\text{H}_{16}$ (1/1) as eluent. The analysis of the oxidation products has effected by $^1\text{H-NMR}$ and by gas-chromatography on a Bruker AM 250 and Fison 9000 GLC apparatus, respectively. The reagents used were obtained from Acros or Aldrich and used without further purification.

3,5-dichloro-2-hydroxybenzaldehyde and 3,5-dichloro-2-hydroxyacetophenone are commercially available. The 3,5-dichloro-2-hydroxyacetophenone and 3,5-dichloro-2-hydroxypropiophenone have been obtained by Friedel-Crafts substitution of the corresponding dichlorophenols, with acetyl- and propionyl chloride, respectively. The salen type ligands and tClSalophen have been prepared by heating a solution of 2 eq. carbonyl derivative and 1 eq. diamine in MeOH at 40 °C.

For the preparation of the other ligands, tClMeSalophen and tClEt-Salophen, the reactions was carried out by the same procedure, but at cold (5-10 °C and 0-5 °C respectively). Since the products were impure (mono- and bis-imines) and coupling yields low, the method described by Boghaei and Mohebi has been used.¹⁹ The reaction of the carbonyl derivative and *o*-phenylenediamine in a 1:1 molar ratio yielded the unsymmetrical monosubstituted amine, which was separated and reacted further with another equivalent of carbonyl, to give the desired ligand with fair yields.

The Cu(II) complexes were synthesized by general methods.²⁰ To a solution of 1 equivalent of ligand dissolved in methanol or ethanol (25 mL) was added $\text{Cu}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (1 equivalent) dissolved in water (5 mL) at 40 °C, with stirring. A precipitate was deposited immediately. The mixture is further stirred at 40°C for one hour. After cooling to room temperature, the solid is filtered and washed successively with water, ethanol-water mixture and absolute ethanol. After drying *in vacuo*, the copper complex is isolated and analyzed.

The catalytic activity was investigated in the oxidation of 2,6-di-*tert*-butyl-phenol with molecular oxygen, in the presence of catalytic amounts of complex. The reaction is performed in a 100 mL round-bottomed flask sealed with a rubber septum, at room temperature. The flask is connected *via* a syringe needle to a gas burette. General catalytic procedure: complex (2.5×10^{-2} mmols, 5% molar to substrate) are dissolved in dry degassed DMF (5 mL) under argon, and of DtBuP (103 mg, 0.5 mmols) dissolved in DMF (5 mL) was added. The argon is evacuated under vacuum and the flask is refilled with oxygen and connected to the burette. The stirring is started, with monitoring of the oxygen consumption. After 24 h, the reaction is stopped and the mixture is separated by flash chromatography eluting with dichloromethane-heptane 1:1 (v:v). After evaporation of volatiles, the fractions are analyzed by NMR and GC, determining conversion and yields of products.

CONCLUSIONS

Grafting of various substituents on the aromatic ring and in the azomethinic group of Salen and Salophen type ligands, lead to the obtaining of some new ligands. In reaction with Cu(II) ions, they form

coordinative compounds with square planar geometry. Such compounds are of interest in oxygen reversible fixation and catalytic activity.

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