

Bis(3-Halogeno α ,5-diMethyl Salicylaldehyde)Ethylenediamine Copper (II) Complexes Synthesis and Characterization

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A series of di-halogeno tetra-Methyl Salen, Schiff base derivatives, and their copper (II) complexes were synthesized and characterized. Their spectral properties and electrochemical behavior were investigated. The copper (II) complexes show a square-planar geometry with cis-N₂O₂ chromophores. The position of d-d band is influenced by the attractive capacity of electron presented by the substituent, X. Halogens and methyl groups grafted on the ligand influence the electrochemical behavior of the complexes.

Keywords: halogeno-Schiff bases; copper (II) complexes; properties

Transition metal complexes containing quadridentate Schiff base ligands have been the subject of several studies [1-3]. Chelates of salen [H₂Salen = bis(salicylaldehyde) ethylenediamine] containing cobalt (II) are known for their dioxygen uptake compatibility, while those of chromium, manganese, copper, iron and nickel act as catalyst for oxidation reactions [4,5].

Copper has been known as an essential bioelement but its biological roles have been recognized only in the last decades. It plays a significant role in interaction between model complexes and protein biochemistry [6].

The present work reports synthesis, and characterization of some copper (II) coordination compounds of di-halogeno tetra-Methyl Salen, Schiff base derivatives. The coordination of copper with Schiff bases has been investigated and a considerable number of obtained complexes have been characterized by the usual spectroscopic methods (UV-VIS, FT IR). The electrochemical properties of the complexes were studied by cyclic voltammetry. It was seen that the aliphatic substituents on the azomethinic groups and the halogens grafted on the ligand molecules modified the redox and catalytic properties of the complexes.

Experimental Part

Solvents and commercial starting materials of analytical grade were used without further purification. Elemental analysis (C, H, N) was performed by the Service de Microanalyses de Gif-sur-Yvette, France. ¹H-NMR spectra for ligands were recorded on a Bruker AM 250 or AC 250 spectrometers operating at 250 MHz. All spectra were obtained in CDCl₃ and chemical shifts calculated in ppm with respect to TMS (d = 0) or solvent residual peak (= 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.

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 mm²); as reference, electrode a saturated calomel electrode (SCE) and as auxiliary electrode, a platinum wire.

Preparation of the ligands

The 2-hydroxy 3-chloro 5-methyl acetophenone has been obtained by Friedel-Crafts substitution of the corresponding dichlorophenols, with acetylchloride [7]. The 2-hydroxy 3-bromo 5-methyl acetophenone was obtained by brominating of 2-hydroxy 5-methyl acetophenone with pyridiniumbromochromate (PBC) [8]. The 2-hydroxy 3-iodine 5-methyl acetophenone was obtained by iodination of 2-hydroxy 5-methyl acetophenone with I₂ in presence of HgO [9].

The ligands were obtained by condensation of 2-hydroxy 3-halogeno 5-methyl acetophenone with ethylene-diamine in 2/1 molar ratio, in EtOH solution at 45°C. The copper (II) complexes were synthesized by general methods, by reaction between ligand, dissolved in EtOH at 40°C, and Cu(OAc)₂·6H₂O solved in H₂O, under vigorous stirring [3,5]. A precipitate was deposited immediately. The mixture is further stirred at 40°C for one hour. After cooling until 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 (yield »60%). *Anal. Calc.* for C₂₀H₂₇N₂O₂Cu: C, 62.24; H, 5.79; N, 7.26. *Found:* C, 62.05; H, 5.86; N, 7.19. *Anal. Calc.* for C₂₀H₂₀N₂O₂Cl₂Cu: C, 58.81; H, 4.43; N, 6.16. *Found:* C, 58.67; H, 4.58; N, 6.19. *Anal. Calc.* for C₂₀H₂₀N₂O₂Br₂Cu: C, 44.18; H, 3.71; N, 5.15. *Found:* C, 43.98; H, 3.82; N, 5.09. *Anal. Calc.* for C₂₀H₂₀N₂O₂I₂Cu: C, 37.67; H, 3.16; N, 4.39. *Found:* C, 37.63; H, 3.25; N, 4.32.

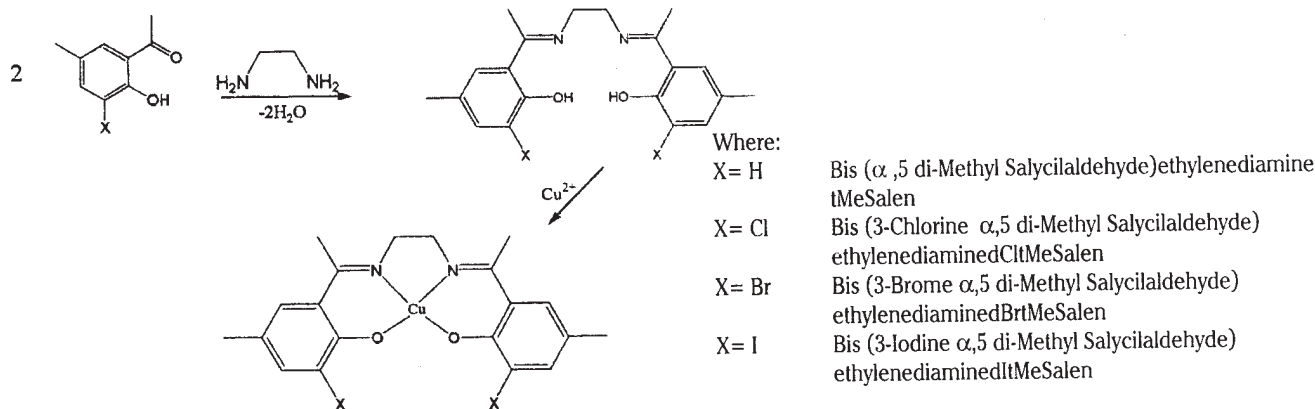
Results and Discussion

The ligands (H₂L) have been prepared as reported in literature, by condensation of the corresponding 2-OH, 3-X, 5-Me, acetophenone derivatives with ethylene-diamine, in 2/1 molar ratio. Then, the obtained Schiff bases (ligands) react with copper (II) ions, in 1/1 molar ratio (scheme 1).

All ligands were characterized by elemental analysis, FT IR, UV-VIS and ¹H-NMR techniques. These analyses confirm the structure of the ligand presented in scheme 1. The complexes were characterized by elemental analyses, UV-VIS and FT IR. The elemental analyses indicate the formation of the complexes in a 1:1 molar ratio (CuL).

The electronic spectra are measured at room temperature in DMF due to the low solubility of the complexes in other organic solvents. The complexes

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Scheme 1. General equations for the synthesis of the ligands and copper (II) complexes

Table 1
ELECTRONIC SPECTRAL DATA FOR THE COPPER COMPLEXES IN DMF

Compounds	λ_1 , nm (ϵ , l/mol·cm)	λ_2 , nm (ϵ , l/mol·cm)	λ_3 , nm (ϵ , l/mol·cm)	λ_4 , nm (ϵ , l/mol·cm)
Cu(tMeSalen)	556 (1.96)	386 (3.16)	348 (3.13)	288 (3.16)
Cu(dCltMeSalen)	564 (1.95)	398 (3.18)	358 (3.12)	284 (3.14)
Cu(dBrtMeSalen)	566 (1.98)	402 (3.18)	360 (3.12)	282 (3.15)
Cu(dItMeSalen)	593 (2.15)	404 (3.21)	363 (3.87)	266 (4.12)

Table 2
SIGNIFICANT FT IR ABSORPTION BANDS (CM⁻¹) FOR THE COPPER COMPLEXES

Compounds	ν_{C-N}		New bands	
	Complexes	Ligands	ν_{M-N}	ν_{M-O}
Cu(tMeSalen)	1580	1618	608	433
Cu(dCltMeSalen)	1584	1612	564	508
Cu(dBrtMeSalen)	1587	1610	666	506
Cu(dItMeSalen)	1593	1610	580	440

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).

The copper complexes show a broad d-d transition band at 556-600 nm. This d-d transition is in the region of that observed for structurally well-characterized complexes of copper (II) Schiff bases with square-planar geometry with C_{2v} symmetry [11, 12]. The bands in the spectral range 266-404 nm are assigned as $\pi-\pi^*$ or $n-\pi^*$ transitions from ligand molecules and have become blue shifted upon complexation. Although the electronic spectra of the complexes are similar, the d-d band position is shifted to the highest energy side with the diminution of electron attractive capacity of the substituent (X) in order $Cl < Br < I$.

The ligands and their copper (II) complexes exhibit characteristic IR absorption in which the differences from ligands and complexes correspond to the change of status of donor atoms. For instance, the ligands show a broad band characteristic to OH groups at 3300-3400 cm^{-1} . After complexation, the bands in that region disappear, indicating that OH groups are without proton to give Cu-O bonds. The ligand molecules have also an intra-molecular hydrogen bonding, which originates in the interaction between the phenoxyl and iminic-groups (O-H...N=C). That is strongly affected by substituents of the phenyl ring because of direct conjugation with the ring. After complexation, the $\nu_{C=N}$ band is correspondingly shifted because of the lost of hydrogen bonding and formation of

new chelate ring in which the C=N nitrogen serves as a donor atom; e.g. the $\nu_{C=N}$ band, which is at over 1600 cm^{-1} for ligands is shifted under 1600 cm^{-1} by coordination.

Other bands from 1500 cm^{-1} are assigned to ring vibration, 1280 cm^{-1} assigned to OH phenolic deforming outside, 1230 assigned to ν_{C-N} and 1050 cm^{-1} assigned to ν_{C-O} . Also, by coordination, these bands are shifted. The characteristic ligand bands for 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 center. The formation of the metal-oxygen σ bond and metal-nitrogen p-bond determines the apparition of new absorption bands in the region 420-685 cm^{-1} [13,14]. The principal FT IR absorption frequencies of the copper complexes are listed in table 2.

In these complexes, azomethine, carbonyl and phenoxyl groups, which are involved in interaction with the copper ion, serve as tetra-dentate ligand that gives *cis*- N_2O_2 coordinated chromophore around the central ion, with a C_{2v} symmetry [15].

The electrochemistry of the complexes was investigated, because the redox potential is an important parameter in electron transfer processes in general and also in catalytic systems. The redox potentials for the complexes were measured by cyclic voltammetry (CV) using a working platinum electrode in DMF solution, containing 0.1 M $LiClO_4$ as the supporting electrolyte in the range of -1.2 to 1.2 V versus SCE. The cyclic voltammograms do not show

Table 3
ELECTROCHEMICAL DATA FOR COMPLEXES #

Compounds	E _{pa}	E _{pc}	ΔE
Cu(tMeSalen)	0.701	-0.951	1.652
Cu(dCltMeSalen)	0.801	-1.005	1.806
Cu(dBrMeSalen)	0.804	-0.977	1.761
Cu(dItMeSalen)	0.006	-0.564	0.570

c_[CuL] = 2x10⁻³ M; scan rate 0.1 V/sec; E_{pa} and E_{pc} are the anodic and cathodic peaks potentials respectively. ΔE is E_{pa} - E_{pc} in 0.1M LiClO₄ in DMF. E_{1/2} = (E_{pa} + E_{pc})/2

reversible peaks. The free ligands do not show oxidation or reduction peaks in the investigated range. The electrochemical data, the peak values E_{pa}, E_{pc}, the difference from values E_{pa}, E_{pc} and ΔE potentials for the copper complexes are presented in table 3.

Examining the data presented in table 3 we can observe that the complexes present an irreversible behavior, according with other copper (II) complexes [16]. This behavior can be explained by the electrical influence determined by halogens and methyl groups in the complexes [17].

Conclusions

Grafting of various substituents on the aromatic ring and in the azomethinic group of Salen type ligands, lead to the obtaining of some new ligands. In reaction with Cu(II) ions, they form coordinative compounds with square planar geometry. Their properties are influenced by methyl groups and halogen grafted on the molecule of ligand. Such compounds are of interest in oxygen reversible fixation and catalytic activity.

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