

# Electronic and steric effects in cobalt Schiff bases complexes: Synthesis, characterization and catalytic activity of some cobalt(II) tetra-halogeno-dimethyl salen complexes

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## Abstract

The synthesis, characterization and catalytic activity of a series of tetra-halogeno-dimethyl salen cobalt (II) complexes are reported in this paper. The investigated complexes of cobalt (II) with Schiff bases are:  $\alpha,\alpha'$ -di-methyl Salen cobalt (II) [Co(dMeSalen)], 3,3',5,5'-tetra chloro  $\alpha,\alpha'$ -di-methyl Salen cobalt (II), [Co(tClIdMeSalen)], 3,3'-di-bromo 5,5'-di-chloro  $\alpha,\alpha'$ -di-methyl Salen cobalt (II), [Co(tBrdMeSalen)], 3,3',5,5'-tetra bromo  $\alpha,\alpha'$ -di-methyl Salen cobalt (II), [Co(tBrdMeSalen)] and 3,3',5,5'-tetra iodo  $\alpha,\alpha'$ -di-methyl Salen cobalt (II), [Co(tIdMeSalen)] (where Salen is bis(salicylaldehyde)ethylenediamine). The characterization of the complexes was performed by elemental analysis, cyclic voltammetry, UV–Vis, IR and EPR spectroscopies. The study was made in DMF, and pyridine was used for coordination as axial base. The redox potential is influenced by the substituent grafted on aromatic ring and in the azomethynic position and also by the molecules coordinating in axial position (solvent, DMF, or pyridine). The catalytic oxygenation of 2,6-di-*tert*-butylphenol by these complexes leads to the obtention of benzoquinone and diphenoquinone products. The cobalt (II) complexes form reversible adducts with molecular oxygen.

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## 1. Introduction

The transition metal complexes with Schiff bases as ligands, are of paramount scientific interest, due to their multiple implications [1–5]. Some of such complexes are able to bind reversibly molecular oxygen, being used as simplified models in the study of dioxygen fixation by its natural transporters because they mimic the biological oxidation. The Co(II) ions form coordinative compounds with Schiff bases, with square planar geometry, capable of reversible binding molecular oxygen [6–8]. According to this principle, cobalt chelate complexes are useful in highly selective catalytic oxidation reactions using molecular oxy-

gen, as models for oxygenases, peroxydases or mono- and dioxygenases. The complex compounds of cobalt with Schiff bases catalyze the oxidation of phenols, alcohols, flavonoides, nitroalkanes, hydrazines or olefins [9–11]. The Schiff bases complexes are also involved in the study of the artificial metalloproteins and metalloenzymes [12,13].

This study aims the obtention new coordinative compounds with similar properties. Therefore, the present paper describes the synthesis, characterization and the catalytic activity of some new *tetra*-halogeno *di*-methyl salen cobalt complex derivatives with the general formula presented in Fig. 1. The influence of halogens (Cl, Br and I) grafted on aromatic ring and of methyl radical from azomethyne group on the chemical properties was studied. The influence of electrochemical potential on

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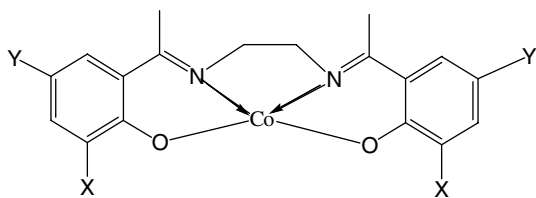


Fig. 1. General formula of the cobalt (II) complexes.

X = Y = H	Di-methyl-Salen	Co(dMeSalen)
X = Y = Cl	Tetra-chloro di-methyl Salen	Co(tClIdMeSalen)
X = Br, Y = Cl	Di-chloro di-bromo di-methyl Salen	Co(dBrdClIdMeSalen)
X = Y = Br	Tetra-bromo di-methyl Salen	Co(tBrdMeSalen)
X = Y = I	Tetra-iodo di-methyl Salen	Co(tIdMeSalen)

the catalytic activity of these compounds was also studied.

## 2. Experimental

### 2.1. Materials and methods

The ligands were obtained, according to the general methods, by the reaction between 2 HO, 3X, 5Y-acetophenone (where X and Y are H, Cl, Br, I) and ethylenediamine in a 2:1 molar ratio [14,15].

Elemental analyses (C, H, N) were performed in the Laboratory of Microanalyses from Gif-sur-Yvette, France.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses were performed by using a Bruker AM 250 or AC 250 spectrometer, operating at 250 MHz. All spectra were obtained in  $\text{CDCl}_3$  and chemical shifts were calculated in ppm with respect to TMS ( $\delta = 0$ ) or solvent residual peak ( $\delta = 7.26$  for proton and 77.1 for carbon). Electronic absorption spectra were recorded with a Safas 190 DES double-mode spectrophotometer. The FT-IR spectra were obtained on a Bruker IFS 66 apparatus in KBr pellets.

Cyclic voltammetry experiments were performed on a Digilab apparatus. The recordings were made in a 2 mM solution in DMF, in argon atmosphere, using lithium perchlorate as electrolyte support. The following material was used for analysis: a vitreous carbon electrode as working electrode ( $A = 3.8 \text{ mm}^2$ ); a saturated calomel electrode as reference electrode and a platinum wire as auxiliary electrode.

EPR spectra were recorded in frozen DMF solution at 10 K, on a Bruker Elexis apparatus. EPR sample was prepared by dissolving 1.2 mg of complex in 2 mL degassed DMF under argon, followed by adding of 0.1 mL of pyridine (py). Approximately, 0.3 mL of complex solution was then syringed into a quartz EPR tube sealed with a septum, under argon atmosphere. Then, the tube was placed in liquid nitrogen, for freezing, and afterwards, in EPR device for being analysed. Oxygenated sample of the complex was obtained by bubbling the molecular oxygen into solution. ESMS spectra were recorded in  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  mixture on an Excalibur device.

The catalytic activity of low amount of complexes was investigated in the oxidation reaction of 2,6-di-*tert*-butylphenol (DtBuP) with molecular oxygen. The reaction was performed in a 100 mL round-bottomed flask sealed with a rubber septum, at room temperature (21–22 °C). The flask was connected via a syringe needle to a gas burette. General catalytic procedure:  $2.5 \times 10^{-2}$  mmols of complex (5% molar to substrate) are dissolved in 5 mL of dry degassed DMF in argon, followed by adding 2.5 mmols of pyridine and 103 mg (0.5 mmols) of DtBP dissolved in 5 mL of DMF. The argon was evacuated under vacuum, the flask was refilled with oxygen, and connected to the burette. The stirring was started, observing the oxygen consumption using a gas burette. After 24 h, the reaction was stopped and the mixture was separated by flash chromatography with dichloromethane/heptane 1/1 (in volume) as eluent. After evaporation of the volatiles, the fractions were analysed by  $^1\text{H}$  NMR and by gas-chromatography on a Bruker AM 250 and a Fison 9000 GLC apparatus, respectively. The conversion and the yields of the products were determined.

### 2.2. Preparation of the ligands and cobalt (II) complexes

The ligands have been prepared by stirring a solution of 2 equiv. of 2-HO, 3X, 5Y-acetophenone derivatives and 1 equiv. of diamine, in MeOH or EtOH at 40 °C for 2–3 h. The ligands were recrystallized from methanol or ethanol and characterized by  $^1\text{H}$  NMR, elemental analyses, UV-Vis and FT-IR spectroscopies [16].

Cobalt complexes were prepared as described in the literature [17,18]. To a solution of 1 equiv. of ligand, dissolved by stirring, in 25 mL of methanol or ethanol, at 40 °C, 1 equiv. of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  dissolved in 5 mL water was added by dropping in argon atmosphere. In the case of less soluble ligands, two equivalents of NaOH were added. The precipitate was deposited immediately. The mixture was further stirred at 40 °C for 1 h. After cooling of the mixture, at room temperature, the solid was filtered and washed with water, ethanol–water mixture and absolute ethanol. After drying in vacuum, the cobalt complexes were isolated and analyzed.

## 3. Results and discussion

The 3,5-di-halogeno derivative of 2-hydroxyacetophenone was obtained using various methods for introducing halogen atoms into the aromatic ring [16]. The ligands were obtained from the reaction between 2HO-, 3X-, 5Y-acetophenone (where X and Y are Cl, Br, I) and ethylenediamine in 2:1 molar ratio [17,18]. The cobalt(II) complexes were obtained by a general method using aqueous solution of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and solutions of ligands in EtOH, under argon [19,20]. The elemental analysis showed the formation of complexes in a 1:1 metal to ligand ratio, Table 1. The ESMS spectrometry also confirmed these data.

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