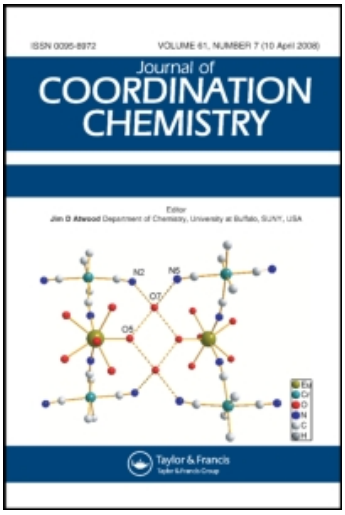

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Aurel Pui[a]; Cristian Dobrota[b]; Jean-Pierre Mahy[c]
[a] Faculty of Chemistry, "Al. I. Cuza" University, 6600 Iasi, Romania [b] Faculty of Chemistry, Department of Organic Chemistry, University of Bucharest, Bucharest, sector 5, Romania [c] Laboratory of Bioorganic and Bioinorganic Chemistry, Institute of Molecular and Materials Chemistry, 91405 Orsay Cedex, France

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Electrochemical and spectroscopic characterization and catalytic activity of Co(II) complexes of tetra-chloro-R-Salen ([tClSalen = *bis*(3,5-di-chloro-α-R salicylidene)ethylenediamine]) and tetra-chloro-R-Salophen ([tClSalophen = *bis*(3,5-di-chloro-α-R salicylidene)-1,2-phenylenediamine]), R = H, CH_3, CH_2-CH_3

AUREL PUI*†, CRISTIAN DOBROTA‡ and JEAN-PIERRE MAHY§

†Faculty of Chemistry, "Al. I. Cuza" University, Bvd. Carol I, No. 11, 6600 Iasi, Romania
‡Faculty of Chemistry, Department of Organic Chemistry, University of Bucharest, 90-92 Panduri Road, 050657, Bucharest, sector 5, Romania
§Laboratory of Bioorganic and Bioinorganic Chemistry, Institute of Molecular and Materials Chemistry, Paris Sud (XI) University, BAT 420, 91405 Orsay Cedex, France

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A series of 3,5-tetra-chloro-R-Salen and 3,5-tetra-chloro-R-Salophen Co(II) complexes, (where R = H, CH_3, and CH_2-CH_3; Salen is *bis*(salicylaldehyde)ethylenediimine; and Salophen is *bis*(salicylaldehyde) *N*,*N*′-*o*-phenylendiimine) have been obtained. The synthesis and characterization of the free ligands and Co(II) complexes and also catalytic activity of the complexes are reported in this article. The characterization of the complexes was performed by elemental analyses, cyclic voltammetry, UV-Vis, FT-IR and EPR spectroscopy, and by elemental analyses, UV-Vis and FT-IR spectroscopy for the free ligands. The catalytic oxygenation of 2,6-di-*tert*-butylphenol, with these complexes, leads to the formation of two products, benzoquinone and diphenoquinone. In this process the Co(II) complexes form reversible adducts with molecular oxygen.

Keywords: tetra-Chloro R-Salen/Salophen; Co(II) Complexes; Catalytic activity

1. Introduction

Transition metal complexes of Schiff bases (imines) are still a subject of intense scrutiny, due to their multiple implications in catalysis [1–5].

Some complexes that are able to fix reversibly molecular oxygen are used as simplified models in the study of dioxygen binding by its natural carriers. In addition,

*Corresponding author. Email: aurel@uaic.ro

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they find use as models for oxygenases, peroxidases, mono- and dioxygenases. Among these complexes, cobalt chelates catalyze the oxidation of phenols, alcohols, flavonoides, nitroalkanes, hydrazines or olefins [6–12]. Mn and Cr Schiff-base complexes have been employed to replace the heme cofactor of, respectively, cytochrome c peroxidase and myoglobin to elaborate new artificial metalloproteins that are able to catalyze the stereoselective sulfoxidation of thioanisole [13, 14].

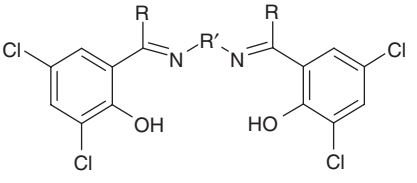
The present article describes the synthesis and characterization of several new chlorinated derivatives of salen (**1**–**3**) and salophen (**4**–**6**) (figure 1), as well as their corresponding new cobalt complexes (scheme 1). The catalytic activity of these complexes in the oxidation of phenol derivatives by O_2 is presented and compared to that of the corresponding non-chlorinated complexes.

The structure of the corresponding Co(II)-complexes is presented in scheme 1.

2. Experimental

2.1. *Materials and methods*

All reagents were obtained from Acros or Aldrich and were used without further purification. Elemental analysis (C, H, N) was performed by the Service de Microanalyses de Gif-sur-Yvette (CNRS, France). ^{1}H NMR spectra were obtained in



R′ = $-H_2C-CH_2-$ (**en**)

R = H tetra-chloro-Salen (tCl Salen)

R = CH_3 tetra-chloro-methyl-Salen (tClMe Salen)

R= CH_2CH_3 tetra-chloro-ethyl-Salen (tClEt Salen)

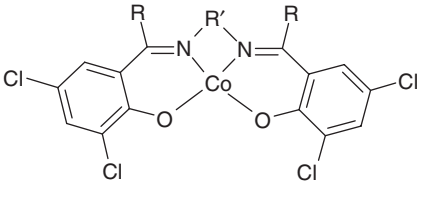
R′ = *o*-Phenylene (**ophen**)

R= H tetra-chloro-Salophen (tCl Salophen)

R = CH_3 tetra-chloro-methyl-Salophen (tClMe Salophen)

R = CH_2CH_3 tetra-chloro-ethyl-Salophen (tClEt Salophen)

Figure 1. Chlorinated salen and salophen derivatives.



Scheme 1. The general formula of cobalt complexes.

$CDCl_3$ and chemical shifts calculated in ppm (TMS as reference); analysis were made on a Brucker AM 250 or on a Brucker AC 250 spectrometer operating at 250 MHz. UV-Vis spectra were recorded in DMF solution ($c = 10^{-4}$ M) on DES device, operating with a SAFAS program. The FT-IR spectra were obtained on a Brucker IFS 66 apparatus in KBr pellets.

Cyclic voltammetry experiments were performed on a Autlab apparatus, in a glass cell incorporating a conventional three-electrode configuration using a vitreous carbon electrode ($A = 4.0\,mm^2$) as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. Cyclic voltammograms were recorded at 293 K, for 2 mM solutions of Co complexes in DMF, under argon, using lithium perchlorate as supporting electrolyte. Potentials are reported *versus* SCE, using the ferrocenium/ferrocene couple (Fc^+/Fc) as internal standard ($E_{Fc^+/Fc} = 0.47$ V, under these experimental conditions: scan rate $= 0.1\,V\,s^{-1}$, concentration 2 mM).

EPR spectra were recorded in frozen DMF solution at 10 K, on a Brucker Elexis apparatus.

2.2. *Ligand synthesis*

2.2.1. Synthesis of carbonyl compounds. The 3,5-dichloro-2-hydroxy-acetophenone and 3,5-dichloro-2-hydroxy-propiophenone were obtained by a Friedel-Crafts substitution of corresponding dichlorophenols, respectively, with acetyl- and propionyl chloride [15]. The 3,5-dichloro-2-hydroxy-benzaldehyde was commercially available.

2.2.2. General procedure for the preparation of salen ligands. The salen-derived ligands were prepared by heating a solution of 2 equivalents of carbonyl derivative and 1 eq. diamine in MeOH at 40°C (A typical procedure is described below) [16].

Preparation of *bis*(3,5-dichloro-salicylaldehyde)ethylenediamine (tCl Salen). 0.75 g (0.84 mL, 1 eq.) of ethylenediamine diluted with 2 mL of methanol are added dropwise under stirring to a solution of 4.77 g (0.025 mmol) of 3,5-dichloro-2-hydroxy-benzaldehyde in 40 mL of methanol at 40°C. A yellow precipitate appears immediately. The mixture is further stirred for 2 h under the same conditions. It is then allowed to stand overnight at room temperature. The solid is filtered and washed well with methanol. The crude product is recrystallized from methanol to give 4.65 g (92% yield) of yellow crystals. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.00 (s, 4H, CH_2-CH_2); 7.15 (s, 2H, ArCH); 7.40 (s, 2H, ArCH); 8.28 (s, 1H, N=CH); 12.96 (s, 2H, 2OH). Elemental analysis: found (calculated) C, 47.40 (47.32); H, 2.97 (2.98); N, 6.88 (6.90).

***bis*(3,5-Dichloro-α-CH_3-salicylaldehyde)ethylenediamine (tCldMeSalen).** Yellow solid (90% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.42 (s, 6H, CH_3); 4.04 (s, 4H, $2CH_2$); 7.26 (s, 2H, ArCH); 7.42 (s, 2H, ArCH); 12.89 (s, 2H, OH). Elemental analysis: found (calculated) C, 49.78 (49.80); H, 3.67 (3.71); N, 6.39 (6.45).

***bis*(3,5-Dichloro-α-CH_2-CH_3-salicylaldehyde)ethylenediamine (tCldEtSalen).** Yellow solid (93% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.28 (t, 6H, CH_3); 2.82 (q, 4H, CH_2); 4.05 (t, 4H, $2CH_2$); 7.39 (s, 2H); 7.43 (s, 2H); 12.85 (s, 2H, 2OH). Elemental analysis: found (calculated) C, 51.92 (51.97); H, 4.31 (4.36); N, 5.98 (6.06).

2.2.3. General procedure for the preparation of salophen ligands. The *bis*(3,5-dichloro-salicylaldehyde)-*o*-phenylenediamine (tCl Salophen) ligand was prepared by the procedure described below [17].

A mixture of 3,5-dichloro-salicylaldehyde (1.91 g, 10 mmol, 2 eq.) and o-phenylenediimine (0.054 g, 5 mmol, 1 eq.), in 20 mL ethanol, are stirred for 3 h (40°C) and an orange product precipitated. The reaction mixture was cooled at room temperature and allowed to stand overnight. The precipitate obtained was filtered and washed well with ethanol (1.53 g, 67% yield). The ligand was recrystallized from methanol. Elemental analysis: found (calculated) C, 53.06 (52.90); H, 2.59 (2.66); N, 6.12 (6.17); m.p. = 215–217°C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.22 (m, 2H, ArCH); 7.30 (m, 2H, ArCH); 7.44 (m, 2H, ArCH); 8.55 (m, 2H, HC=N); 13.59 (s, 2H, 2OH).

The other ligands: *bis*(3,5-dichloro-α-CH_3-salicylaldehyde)-*o*-phenylenediamine (tCl-dMe-Salophen) and *bis*(3,5-dichloro-α-CH_2-CH_3-salicylaldehyde)-*o*-phenylenediamine (tCl-dEt-Salophen), were prepared according to the method described by Boghaei and Mohebi [18]. The reaction of the carbonyl derivative and *o*-phenylenediamine in a 1 : 1 molar ratio yielded the unsymmetrical monosubstituted imine, which was separated and reacted further with another equivalent of carbonyl, to give the desired ligand with fair yields. A general procedure is presented as follows:

***bis*(3,5-Dichloro-α-CH_3-salicylaldehyde)-*o*-phenylenediamine.** A mixture of 3,5-dichloro-α-CH_3-salicylaldehyde (1.025 g, 5 mmol, 1 eq.) and *o*-phenylenediamine (0.054 g, 5 mmol, 1 eq.) were stirred for 3 h in 25 mL ethanol at room temperature. The precipitate formed was filtered and washed well with ethanol (red products, 1.3 g, 93% yield). Then, 1.18 g (4 mmol) of the previously filtered solid was dissolved in EtOH and treated with another equivalent of 3,5-dichloro-α-CH_3-salicylaldehyde (0.764 g, 4 mmol), added dropwise with stirring for 4 h at 5°C, and then allowed to stand overnight. Then, the product was filtered under vacuum and washed several times with cold methanol and dried. An orange solid was obtained (38% yield), m.p. 90–92°C. Elemental analysis: found (calculated) C, 54.92 (54.80); H, 3.33 (3.34); N, 5.79 (5.81). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.67 (s, 6H, $2CH_3$); 6.85 (m, 2H, ArCH); 7.57 (m, 2H, ArCH); 7.94 (m, 2H, ArCH); 12.74 (s, 2H, 2OH).

***bis*(3,5-Dichloro-α-CH_2-CH_3-salicylaldehyde)-*o*-phenylenediamine(tCl-dEt-Salophen).** This complex was made by a similar procedure, but at a lower temperature: 0–5°C. A dark-yellow product was obtained (21% yield), which was very soluble in EtOH and MeOH, with a melting point of 92–94°C. Elemental analysis: found (calculated) C, 56.46 (56.49); H, 3.98 (3.95); N, 5.42 (5.49). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.22–1.30 (m, 6H, CH_3); 2.65 (m, 4H, CH_2); 7.03 (m, 2H, ArCH), 7.30 (m, 2H, ArCH), 7.44–7.45 (m, 2H, ArCH), 7.69 (m, 2H, ArCH), 12.81 (s, 2H, 2OH).

2.3. *Synthesis of the cobalt complexes*

Cobalt complexes were prepared using the general procedure described below [17, 19].

2.3.1. Preparation of Co(tClSalen). To a solution of 0.812 g (0.2 mmol) of tClSalen in 25 mL of methanol, were added 0.498 g (0.2 mmol) of $Co(OAc)_2 \cdot 4H_2O$ dissolved in 5 mL of water at 40°C, with stirring, under an argon flow. A red-brick solid immediately precipitated. The mixture was further stirred at 40°C for one hour.

After cooling at room temperature, the solid was filtered and washed successively with water, ethanol–water 1/1 (v/v) and absolute ethanol. After drying at 80°C *under vacuum*, 467 mg (50.4%) of the cobalt complex was isolated; elemental analysis: found (calculated) C, 41.37 (41.41); H, 2.45 (2.39); N, 6.02 (6.04).

The other Co complexes of the series were isolated using the same procedure: Co(tCldMeSalen): brown solid, isolated 0.65 g (66%), elemental analysis: found (calculated) C, 43.95 (44.03); H, 2.95 (2.87); N, 5.63 (5.70); Co(tCldEtSalen): brown solid, isolated 0.685 g (66%), elemental analysis: found (calculated) C, 46.14 (46.27); H, 3.62 (3.49); N, 5.37 (5.40); Co(tClSalophen): orange solid, isolated 0.737 g (62%) elemental analysis: found (calculated) C, 50.59 (50.73); H, 3.41 (3.37); N, 5.01 (4.93); Co(tCldMeSalophen): isolated 0.351g (45%), elemental analysis: found (calculated) C, 48.78 (49.01); H, 2.70 (2.62); N, 5.19 (5.20); Co(tCldEtSalophen): isolated 0.265 g (31%), elemental analysis: found (calculated) C, 47.02 (46.91); H, 2.30 (2.17); N, 5.45 (5.47).

2.4. *Catalytic activity studies*

To investigate the catalytic activity of the cobalt complexes, the oxidation of 2,6-di-*tert*-butyl-phenol (DTBP) with molecular oxygen, was performed in the presence of catalytic amounts of Co complex in the presence of pyridine (Py). The reaction was performed in a 100 mL round-bottomed flask sealed with a rubber septum, at room temperature. The flask was connected *via* a syringe needle to a gas burette.

2.4.1. General catalytic procedure. 2.5×10^{-2} mmol of Co complex (5% molar with respect to the substrate) were dissolved in 5 mL of dry degassed DMF under argon, followed by the addition of 2.5 mmol pyridine and 103 mg (0.5 mmol) of DTBP dissolved in 5 mL of DMF. The argon was removed under vacuum and the flask was then refilled with oxygen and connected to the burette.

Stirring was then started and the oxygen consumption was monitored during the course of the reaction. After 24 h, the reaction was stopped and the mixture was separated by flash column chromatography with dichloromethane/heptane 1/1 (v/v). After evaporation of the volatiles, the fractions were analysed by ^{1}H NMR and GC (on a Bruker AM 250 and Fison 9000 GLC apparatus, respectively), in order to determine the conversion and yields of products.

3. Results and discussion

Chlorinated derivatives of salen (**1**–**3**) and salophen (**4**) were synthetized upon reaction of 2-hydroxy-3,5-dichlorophenyl substituted aldehyde or ketone (figure 1) with, respectively, ethylenediamine or *o*-phenylenediamine in methanol at 40°C, according to an already described procedure [17]. However, when this procedure was used for preparation of the other ligands, *bis*(3,5-dichloro-α-CH_3-salicylaldehyde) *o*-phenylenediimine (tCl-dMe-Salophen) **5**, and *bis*(3,5-dichloro-α-C_2H_5-salicylaldehyde)-*o*-phenylenediamine (tCl-dEt-Salophen) **6**, but at lower temperature (5–10°C and 0–5°C, respectively), only a mixture of mono- and *bis*-imines could be

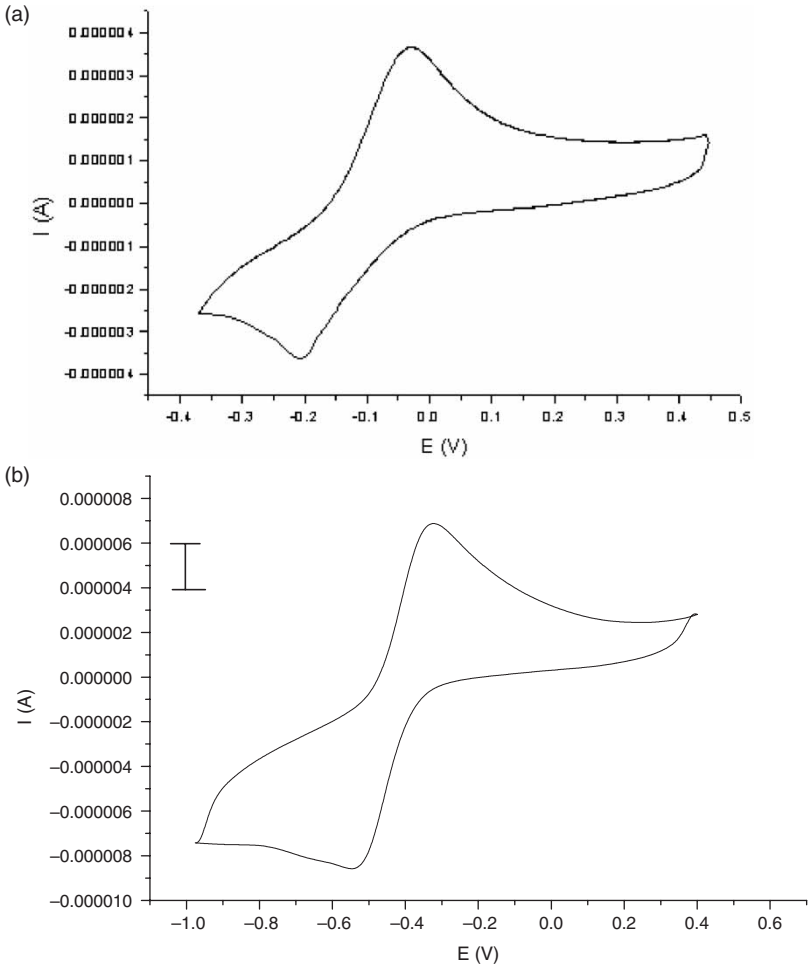


Figure 2. Cyclic voltammogram for Co(tCldEtSalen); $C_{CoL} = 2 \times 10^{-3}$ M, in DMF, scan rate = 0.1 V s^{-1}, *vs.* the saturated calomel electrode (SCE): (a) initial, under argon atmosphere, (b) after adding of pyridine, $c_{py} = 0.2$ M.

obtained with low coupling yields. Consequently, the method described by Boghaei and Mohebi was used [18]. The reaction of the carbonyl derivative and *o*-phenylenediimine in a 1 : 1 molar ratio yielded the nonsymmetrical, monosubstituted imine, which was isolated and reacted further with another equivalent of carbonyl derivative to give the desired ligands, **5** and **6** with fair yields. Further reaction with Co(II) acetate in methanol at 40°C led to the corresponding 1/1 Co^{II}/ligand complexes (figure 2).

The salen and salophen ligands were fully characterized by ^{1}H NMR, FT-IR and UV-Vis spectroscopy, as well as by elemental analysis. FT-IR, UV-Vis and EPR spectroscopy was used to determine the characteristics of the cobalt complexes and their redox properties have been studied by cyclic voltammetry.

Table 1. Significant FT-IR bands (cm^{-1}) for the tetra-chloro-R-Salen (**1**–**3**) and tetra-chloro-R-Salophen (**4**–**6**) ligands and the corresponding Co complexes.

Compounds	$\nu_{C=N}$	$\delta_{(Ar\text{-}OH)}$	ν_{C-N}	ν_{C-O}	ν_{Co-N}	ν_{Co-O}
TClSalen (**1**)	1636	1276	1205	1043	–	–
TCldMeSalen (**2**)	1611	1268	1240	1058	–	–
TCldEtSalen (**3**)	1610	1261	1229	1052	–	–
TClSalophen (**4**)	1617	1295	1200	1056	–	–
TCldMeSalophen (**5**)	1648	1305	1236	1088	–	–
TCldEtSalophen (**6**)	1645	1252	1254	1074	–	–
Co(tClSalen) **1**-Co	1601	–	1179	1089	670	442
Co(tCldMeSalen) **2**-Co	1603	–	1184	1085	685	420
Co(tCldEtSalen) **3**-Co	1605	–	1189	1103	551	426
Co(tClSalophen) **4**-Co	1610	–	1193	1032	537	483
Co(tCldMeSalophen) **5**-Co	1638	–	1226	1081	658	422
Co(tClSalen) **6**-Co	1633	–	1241	1085	642	476

3.1. *Infrared spectroscopy*

The main IR absorption frequencies of the salen and salophen ligands and their cobalt complexes are listed in table 1. The FT-IR spectra of the ligands and of the Co^{II} complexes all show major bands around 1601–1650 cm^{-1} ($\nu_{C=N}$), 1560 and 1500 cm^{-1} (phenyl ring vibrations), 1250–1300 cm^{-1} (deformation of the Ar-OH bond outside the plane of the Ar-OH moiety), 1180–1240 cm^{-1} (ν_{C-N}), and 1040–1100 cm^{-1} (ν_{C-O}). In addition, in the spectra of the Co^{II} complexes, two new bands appear in the 690–400 cm^{-1} region, that can be assigned to the Co–O and Co–N vibrations [20, 21].

The bands corresponding to the azomethinic groups in the cobalt complexes are shifted to lower frequencies with respect to those observed for the free ligand, as a result of complexation. Also, the bands that are characteristic for the deformation of the Ar-OH bond outside the Ar-OH plane in the ligand are absent in the cobalt complexes, as a consequence of the involvement of the phenolate oxygen anion into a σ bond with the metal center. In addition, in the spectra of the Co complexes, the C=N stretching mode is shifted to a lower frequency as well as the band corresponding to the C–N bond, whereas the band corresponding to the C–O bond is shifted to a higher frequency, when compared to those observed in the spectra of the free ligands. The formation of a metal-oxygen σ-bond and a metal-nitrogen π-bond also causes the appearance of new absorption bands, respectively, around 420–480 cm^{-1} (ν_{Co-O}) and 540–685 cm^{-1} (ν_{Co-N}). The FT-IR spectra recorded fully support the formation of Co complexes by the coordination of Co to the azomethinic nitrogen and to the phenolic oxygen of the new tetra-chloro-R-Salen (**1**–**3**) and tetra-chloro-R-Salophen (**4**–**6**) ligands [22, 23].

3.2. *Electronic spectra*

The electronic spectra of the free ligands **1**–**6** in DMF (table 2) show two strong absorption bands in the UV-Vis region, between 322 and 350 nm and between 408 and 440 nm, that can be attributed to the π–π^* and n–π^* transitions, respectively. The free ligands also exhibit a UV band between 224 and 266 nm that can be attributed to the n–σ^* and n–π^* transitions (table 2) [24, 25].

Table 2. Electronic spectral data for ligands in DMF.

Ligands	λ_1 (nm) (ε, L mol^{-1} cm^{-1})	λ_2 (nm) (ε, L mol^{-1} cm^{-1})	λ_3 (nm) (ε, L mol^{-1} cm^{-1})
TClSalen (**1**)	253 (3.59)	334 (3.52)	430 (3.35)
TCldMeSalen (**2**)	258 (3.05)	340 (3.46)	418 (3.54)
TCldEtSalen (**3**)	266 (2.89)	346 (3.78)	432 (3.49)
TClSalophen (**4**)	264 (3.19)	322 (3.81)	440 (3.89)
TCldMeSalophen (**5**)	236 (2.83)	342 (3.63)	410 (2.95)
TCldEtSalophen (**6**)	224 (2.95)	350 (3.38)	408 (2.86)

Table 3. Electronic spectral data for cobalt complexes in DMF.

Compounds	λ_1 (nm) (ε, L mol^{-1} cm^{-1})	λ_2 (nm) (ε, L mol^{-1} cm^{-1})	λ_3 (nm) (ε, L mol^{-1} cm^{-1})	λ_4 (nm) (ε, L mol^{-1} cm^{-1})
Co(tClSalen) Co-**1**	298 (3.45)	372 (3.96)	442 (3.74)	548 (2.68)
Co(tCldMeSalen) Co-**2**	268 (3.03)	330 (3.39)	438 (3.47)	516 (2.53)
Co(tCldEtSalen) Co-**3**	276 (3.45)	328 (3.51)	426 (3.57)	486 (2.03)
Co(tClSalophen) Co-**4**	260 (3.06)	308 (3.68)	404 (3.97)	536 (2.18)
Co(tCldMeSalophen) Co-**5**	242 (3.32)	302 (3.51)	414 (3.91)	534 (1.54)
Co(tCldEtSalophen) Co-**6**	244 (3.19)	320 (3.14)	416 (3.54)	526 (2.78)

Insertion of Co(II) into ligands **1**–**6** leads to new electronic spectra in which the bands that are characteristic of the free ligand are shifted to higher wavelengths and their intensity is slightly modified. In addition, a new band located around 490–540 nm appears (table 3).

The bands located in the 404–438 nm region are attributed to the π–π^* or n–π^* transitions of the ligands which overlap the d–π^* charge–transfer transitions. The new band appearing between 486 and 548 nm can be attributed to the d–d transitions of the divalent cobalt in octahedral field, in DMF solution [25, 26]. These alterations in shifts and intensity for the absorption bands support the coordination of the ligand to the Co(II) ion.

Examining the trend of experimental wavelength, one can observe that the energy of the octahedral field in the Co complexes is influenced by the nature of the *meta* groups. Indeed, a decrease in λ_4 (d–d transitions) (e.g. an increase in energy) is observed for both Co-tCl-R-Salen and Co-tCl-R-Salophen complexes when the size of the R substituent of the starting aldehyde or ketone increases (λ_4 (**1**, R = H) < λ_4 (**2**, R = CH_3) < λ_4 (**3**, R = C_2H_5) and λ_4 (**4**, R = H) < λ_4 (**5**, R = CH_3) < λ_4 (**6**, R = C_2H_5) respectively). This can be explained by the fact that an increase in the bulkiness of the R substituent induces higher rigidity of the molecule and accordingly an increase the energy of the octahedral field.

The IR and UV-Vis spectra and elemental analysis data suggest a square-planar donor atom (ONNO) in the solid state. In solution, two solvent (or pyridine) molecules are axial coordinated [26].

3.3. *Cyclic voltammetry*

The redox potential is an important parameter as it characterizes the ability of the redox center to transfer electrons and also to act as a redox catalyst. This value is strongly

Table 4. Electrochemical data for complexes.[a]

Compounds	E_{pa} (V)	E_{pc} (V)	ΔE (V)	$E_{1/2}$ (V)	$E'_{1/2}$ (V)	$\Delta G'$ (kJ mol^{-1} K)
Co(tClSalen), py	−0.15	−0.37	0.22	−0.26	0.21	−20.26
Co(tCldMeSalen), py	−0.29	−0.47	0.18	−0.38	0.09	−9.68
Co(tCldEtSalen), py	−0.33	−0.54	0.21	−0.44	0.03	−2.89
Co(tClSalophen), py	−0.01	−0.28	0.27	−0.14	0.33	−31.83
Co(tCldMeSalophen), py	0.03	−0.39	0.42	−0.18	0.29	−27.97
Co(tCldEtSalophen), py	0.25	−0.49	0.74	−0.12	0.34	−32.79

[a]$c_{[CoL]} = 2 \times 10^{-3}$ M; $c_{py} = 2 \times 10^{-1}$ M; scan rate 100 mV s^{-1}; E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively, $\Delta E = E_{pa} - E_{pc}$ in 0.1 M $LiClO_4$ in DMF, $E_{1/2} = (E_{pa} + E_{pc})/2$, $E'_{1/2}$ is $E_{1/2}$ reported to the potential of the couple Fc^+/Fc, where Fc = ferrocene, $E_{Fc^+/Fc} = 0.47$ V; $\Delta G' = -nFE'_{1/2}$; $F = 96{,}458$ C mol^{-1}; $T = 293$ K.

influenced by the nature of the axial ligand of the metal. Accordingly, the addition of pyridine to a solution of cobalt complex leads to a severe decrease in the half-wave potential $E_{1/2}$ [$E_{1/2} = (E_{pa} + E_{pc})/2$], and also to an increase in the ΔE ($\Delta E = E_{pa} - E_{pc}$) value. This decrease of the half-wave potential is due to the replacement of the axial solvent molecules by strong donating pyridine ligands, which enhance the electron density on the metal [27–29]. For instance, figure 2 shows the cyclic voltammograms recorded in DMF, under argon, for the Co(tCldEtSalen) complex in the absence (figure 2a) and in the presence of 0.2 M pyridine (figure 2b). It is clear that for this complex, the addition of pyridine leads to a decrease of the $E_{1/2}$ value from −0.11 to −0.44 V, and to an increase of ΔE from 0.17 to 0.21 V.

The observed peaks display a ratio of anodic to cathodic peak currents (i_{pa}/i_{pc}) of approximately one unit, which corresponds to a simple one-electron process, $Co(II) \rightleftharpoons Co(III) + 1e^-$.

These investigations were repeated at various scan rates and concentrations (data not shown), and the best electrochemical data obtained under the aforementioned conditions are shown in table 4. It is noteworthy that the half-wave potential ($E_{1/2}$) can be converted into Gibbs free energies according to $\Delta G' = -nFE'_{1/2}$.

All the cyclic voltammograms for the Co-salen (**1**–**3**) and salophen (**4**–**6**) complexes were recorded in the presence of 0.2 M pyridine and the anodic (E_{pa}), cathodic (E_{pc}) and half-wave ($E_{1/2}$) potentials as well as the (ΔE) values measured for each Co(II) complex are reported in table 4. In order to compare the half-wave potential values more easily to literature data, they are also reported to those of the ferrocenium/ferrocene (Fc^+/Fc) couple (i.e. $E'_{1/2}$) [30, 31]. Examining the data collected in table 4 one can observe that the first four complexes have aquasi-reversible behavior, while the last two are irreversible. These properties may be explained if one considers the steric hindrance in the complexes due to the methyl or ethyl radicals in the vicinity of *o*-phenylenediamine. When compared to the E_{pa} and E_{pc} values measured for the Co(II) complex of non chlorinated salen ($E_{pa} = -0.32$ V and $E_{pc} = -0.55$ V) all the E_{pa} and E_{pc} values reported in table 4 are higher, in agreement with the attracting effect of the chlorine substituents.

In the case of the salen complexes, the half-wave potential also decreases when the salen ligand is substituted by an alkyl group: $E_{1/2}$ (**1**-Co, R = H) > $E_{1/2}$ (**2**-Co, R = CH_3) > $E_{1/2}$ (**3**-Co, R = C_2H_5), this correlates with the increasing donating effect of

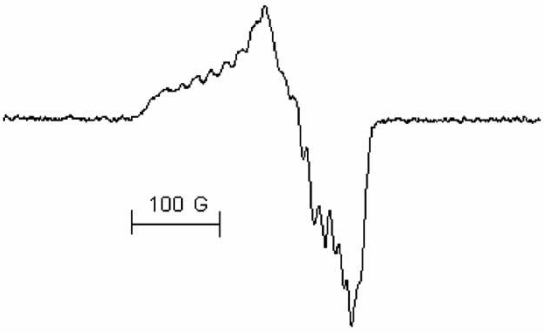


Figure 3. EPR spectra of [Co(tClSalen)], in DMF solution at 10 K.

the R substituent which causes an increase of the reducing power of the Co-salen complexes. On the contrary, in the case of the salophen complexes, substitution of the ligand by an alkyl group has almost no effect on the $E_{1/2}$ value, which may be due to the fact that in this case the conjugation of the ligand is the main factor determining the redox potential of the corresponding Co complex.

3.4. *EPR studies*

EPR spectra of non-oxygenated Co(II) complexes were measured at 10 K as a frozen DMF solution in the presence of excess pyridine. All the spectra were similar to that of Co(tClSalen) **1**-Co shown in figure 3. This spectrum exhibits a signal centered around $g = 2$, characteristic of a low-spin Co(II) complex, with a rhombic distortion from ideal axial symmetry, with g_3 ($g_{//}$) = 2.1 and ($g_{\perp}$) = 2.03. The perpendicular component of the spectrum appears as a clearly identifiable 8 line signal corresponding to the ^{59}Co ($I = 7/2$) hyperfine splitting ($A = 9.4G$) (figure 3). In addition, in the presence of pyridine, the eight-line signal corresponding to the parallel component ($g_{//}$) is further split into three or five lines due to the coupling of the Co(II) center with one or two axially coordinated pyridine nitrogen atoms [32, 33].

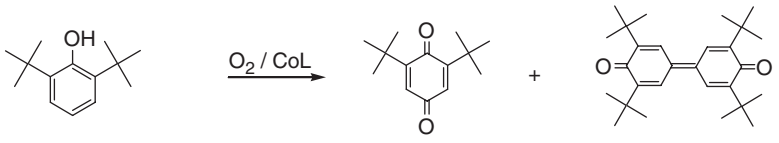
3.5. *Catalytic activity*

2,6-Di-*tert*-butylphenol (DTBP, **7**) can be oxidized by molecular oxygen in the presence of metal complexes as catalysts, to give mainly two products: 2,6-di-*tert*-butyl-1,4-benzoquinone (benzoquinone, QN – **8**) and 2,6,2′,6′-tetra-*tert*-butyl-1,1′-diphenobenzoquinone (dibenzoquinone, DPQ – **9** (scheme 2) [34, 35].

The formation of one product or the other depends on the nature of the metallic ion present in the complex. The mechanism of this oxidation has been thoroughly studied [12, 36] and involves the following reactions:

(a) The Co(II)-Schiff base complex first forms an [L(py)Co-O_2] adduct with O_2:

$$[(Py)2LCo^{II}] + O_2 \rightleftharpoons [(Py)LCo^{II}-O_2 \leftrightarrow (Py)LCo^{III}-O-O^{\bullet}] + Py$$



7 (DTBP) **8** (BQ) **9** (DPQ)

Scheme 2. Oxidation of 2,6-di-*tert*-butylphenol (DTBP) with molecular oxygen in presence of CO(II) complexes (CoL).

(b) The adduct formed is able to abstract a hydrogen atom from DTBP, leading to a phenoxyl radical and to $H_2O^{\bullet}$ which further dismutates into H_2O and O_2:

$$\left[(\mathrm{Py})\mathrm{LCo^{II}}-\mathrm{O_2} \leftrightarrow \mathrm{Py})\mathrm{LCo^{III}}-\mathrm{O}-\mathrm{O}^{\bullet}\right] + \mathrm{DTBP}$$
$$\rightleftharpoons \mathrm{DTBP}^{\bullet} + \left[(\mathrm{Py})\mathrm{LCo^{III}}-\mathrm{O}-\mathrm{O}-\mathrm{H}\right]$$
$$\left[(\mathrm{Py})\mathrm{LCo^{III}}-\mathrm{O}-\mathrm{O}-\mathrm{H}\right] \rightarrow \left[(\mathrm{Py})\mathrm{LCo^{II}}\right] + \mathrm{HO_2^{\bullet}}$$
$$\left(2\mathrm{HO_2^{\bullet}} \rightarrow \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2}\right)$$
$$\left[(\mathrm{Py})\mathrm{LCo^{II}}\right] + \mathrm{O_2} \rightarrow \left[(\mathrm{Py})\mathrm{LCo^{II}}-\mathrm{O_2} \leftrightarrow (\mathrm{Py})\mathrm{LCo^{III}}-\mathrm{O}-\mathrm{O}^{\bullet}\right]$$

(c) The phenoxyl radical may then either dimerize, which leads to the formation of the oxidative coupling product, DPQ (**9**) (c_1), or add to the metal-oxygen adduct which leads to a peroxidic intermediate complex, which is the precursor of benzoquinine (**8**) (c_2):

$$\text{(c1)} \quad \mathrm{DTBP}^{\bullet} + \mathrm{DTBP}^{\bullet} \rightarrow \mathrm{DPQ}$$
$$\text{(c2)} \quad \mathrm{DTBP}^{\bullet} + \left[(\mathrm{Py})\mathrm{LCo^{II}}-\mathrm{O_2}\right.$$
$$\left. \leftrightarrow (\mathrm{Py})\mathrm{LCo^{III}}-\mathrm{O}-\mathrm{O}^{\bullet}\right]\left\{\left[\mathrm{DTBP}-\mathrm{O}-\mathrm{O}-\mathrm{Co^{III}L(Py)}\right]\right\}$$

(d) The hydrolysis of this complex leads to formation of BQ (**8**) and a Co^{III}-hydroxo complex, [L(Py)Co(OH)].

$$\left\{\left[\mathrm{DTBP}-\mathrm{O}-\mathrm{O}-\mathrm{Co^{III}L(Py)}\right]\right\} \xrightarrow{\mathrm{H_2O}} \mathrm{BQ} + \left[(\mathrm{Py})(\mathrm{OH})\mathrm{LCo^{III}}\right]$$

The hydroxo complex thus formed oxidizes the phenol derivative into a new phenoxyl radical, with reduction of Co(III) into Co(II). Thus, the phenoxyl radical is the direct precursor of diphenoquinone, while the cobalt-peroxidic complex leads to quinone. Then, the hydroxo ligand of the Co(II) complex obtained can be substituted by pyridine to lead to $[(Py)_2LCo^{II}]$.

Table 5 presents the results obtained with the new complexes.

As can be seen, the complexes Co(tClSalen), Co(tCldMeSalen), Co(tCldEtSalen), Co(tClSalophen) have very good catalytic activity, giving excellent total yields (93–97%). Even more, they lead to almost exclusive formation of the monoquinone. In the case of the other complexes (Co(tCldMeSalophen) and Co(tCldEtSalophen),

Table 5. Catalytic oxidation of 2,6-di-*tert*-butyl-phenol with Co(II) complexes.

Compounds	Yield%	QN (**8**)%	DPQ (**9**)%	**8**/**9**
Co(tClSalen)	98	96	4	24.00
Co(tCldMeSalen)	96	94	6	15.66
Co(tCldEtSalen)	97	93	7	13.29
Co(tClSalophen)	93	92	8	11.50
Co(tCldMeSalophen)	37	65	35	1.86
Co(tCldEtSalophen)	22	32	68	0.47

the conversion and yield are low (37% and 22% yield, respectively). This can be explained by the effect of the steric hindrance of the ligand, which prevents participation of the metal centre in the oxidation process.

The coordination of molecular oxygen to the cobalt complexes has been monitored by cyclic voltammetry and UV-Vis spectroscopy.

In the presence of molecular oxygen, absorption maxima of the complexes shift from values below 450 nm to values above 450 nm, indicating the formation of an $[(Py)LCo^{II}–O_2 \leftrightarrow (Py)LCo^{III}–O–O^{\bullet}]$ adduct. Upon adding the substrate, the maximum shifted again toward 500 nm, suggesting the formation of a peroxo species like $[DTBP\text{-}O–O\text{-}Co^{III}L(Py)]$ [20].

The same phenomenon is observed in the cyclic voltammetry experiments: bubbling oxygen into a solution of complex results (as seen by voltammetry) in the formation of a $Co^{II}–O_2$ species, the shape of the voltammogram becoming irreversible. Argon proved to have a regenerating effect when bubbled through oxygenated complexes. The voltammograms became reversible, demonstrating that the primarily formation of the $Co^{II}–O_2$ adduct in the presence of molecular oxygen is reversible (figure 4). This process can be illustrated by the following reaction:

$$[CoL(py)_2] + O_2 \rightleftharpoons [CoL(py)(O_2)] + py$$

The new shoulder, which appeared after the oxygen–argon cycle, at −0.64 V (figure 4c), can be assigned to a remaining trace of the oxygenated form of the complex.

Analyzing the experimental data, one can observe that there is a correlation between the half-wave potential and the catalytic activity of the complex. The lower the potential value, the higher is the catalytic activity. As far as the complexes Co(tCldMeSalophen) and Co(tCldEtSalophen) are concerned, although they possess a small value for the $E_{1/2}$ (comparable with that of other members of the series), their catalytic activity is low. This is due to the steric effects that determine a (very) slow rate in the equilibrium $Co^{II} \rightleftarrows Co^{III}$. Furthermore, access of dioxygen to the cobalt ion is limited (for the same steric reason) preventing to some extent the formation of the μ-peroxo phenolic complex, an intermediate in the production of quinone.

4. Conclusion

The 3,5-di-chloro α-R substituted Schiff bases form complexes with Co(II) with square-planar or octahedral structure. These complexes with molecular oxygen form reversible

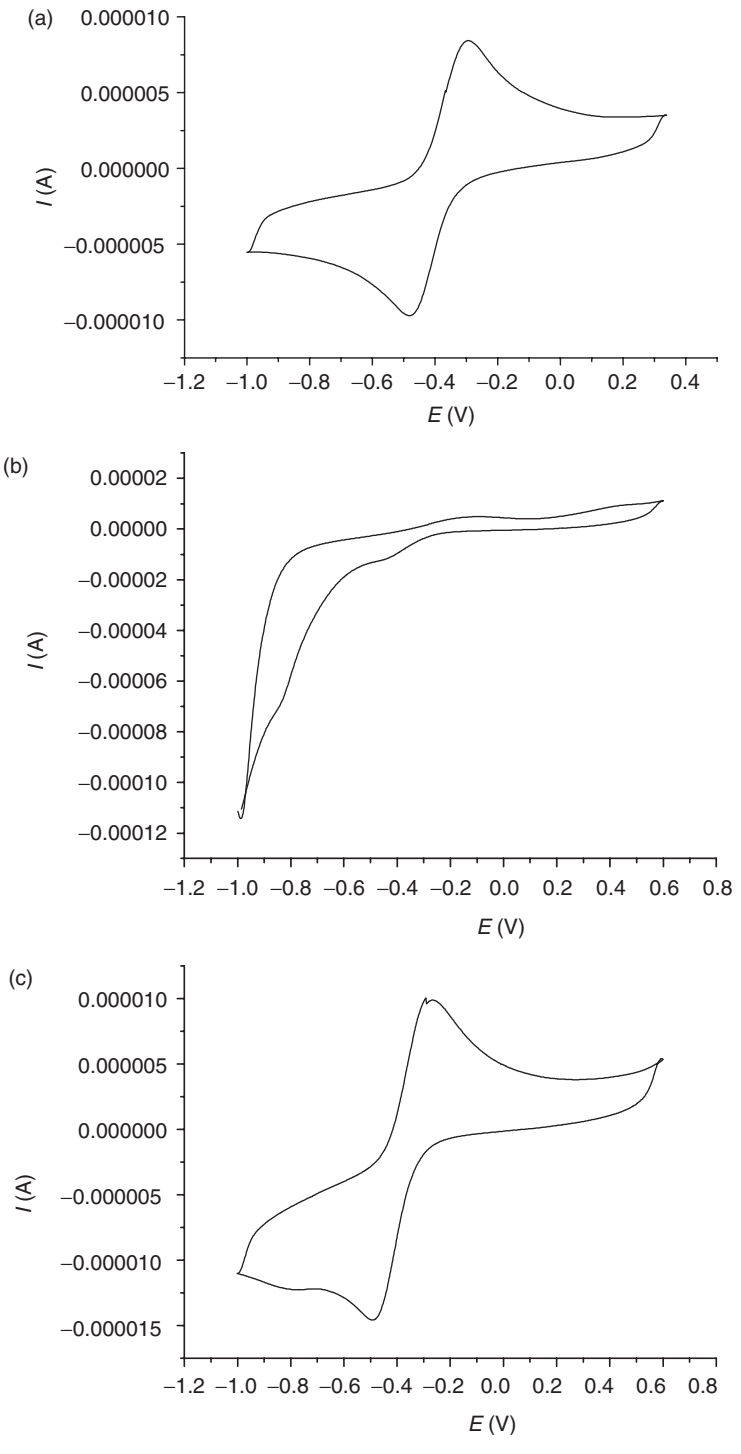


Figure 4. Cyclic voltammograms for Co(tCldMeSalen); $C_{CoL} = 2\,mM$, in DMF; $v = 100\,mV\,s^{-1}$: (a) initial, under argon atmosphere; (b) in the presence of O_2; c) after elimination of O_2 (argon bubbling), under argon atmosphere.

adduct which may oxidize various organic substrates. In case of Salophen complexes steric hindrance occurs. Compared to the unsubstituted Co(Salen) complexes, the presence of chlorine substituents on the aromatic moiety do not influence significantly the catalytic behavior of the new complexes.

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