# Synthesis Characterization and Catalytic Activity of Some New Manganese (II) Compounds with Tetra-chloro R-*bis*(salicylaldehyde) Ethylenediamine and R- *bis*(salicylaldehyde) Phenylenediamine Ligands (R= H, $CH_3$, $CH_2$-$CH_3$)

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*The Schiff bases with two chlorine atoms grafted on each salicyl-aldehyde or salicyl-ketone molecules and with -H, -$CH_3$ or $CH_3$-$CH_2$- in the azomethynic-position were synthesized as ligands. The chain between donors N-N atoms is either ethylene or –o-phenylene. The manganese (II) ion forms with such ligands coordinative compounds. The free ligands and manganese compounds were characterized by elemental analysis, UV-VIS, FT IR, NMR spectroscopy and cyclic voltammetry. The semi waves potentials are influenced of nature of substituents (Cl and R) grafted on the molecule of the ligands. These complexes are able to oxidize the 2,6-di-tert-butyl-phenol (DtBuP), in presence of molecular oxygen in DMF solution, with formation of the tetra-tert-butyl-diphenoquinone (TtBuDQ).*

*Keywords: manganese(II) complexes; Schiff bases, catalytic activity*

A series of cations of the transitional metals, such as Co(II), Cu(II), Mn(II), Mn(III), Cr(III) etc., form with quadridentate Schiff bases, metallic complexes which have been the subject of several investigations [1-5]. Some of them are known for their dioxygen uptaking capability, whereas other complexes act as catalysts for oxidation reactions [6-12]. Manganese complexes play an essential role in biological redox chemistry, beginning with manganese superoxide dismutase.

Today, manganese complexes with Schiff bases are involved in catalytic epoxidation of olefins and other substrates and for designing the artificial metaloproteins [1,13-16].

The present paper describes the synthesis, characterization and catalytic activity of some new manganese complexes with *tetra*-chlorinated Schiff bases derivatives of type salen and salophen α-R substituted [salen = bis(salicyliden)ethyenediimine and salophen = bis(salicyliden)-o-phenylenediamine, and R = H, $CH_3$, $CH_2$-$CH_3$]. The general formula of the ligands is presented in fig. 1.

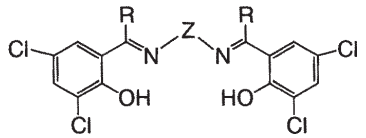


Fig. 1. General formula of the ligands

**Z = - $H_2C$-$CH_2$ -, (en)**

R = H, tetrachloro Salen, (tClSalen)

R = $CH_3$, tetrachloro-dimethyl Salen, (tCldMeSalen)

R = $CH_3CH_2$, tetrachloro-diethyl Salen, (tCldEtSalen)

**Z = o - $C_6H_4$, (ophen)**

tetrachloro Salophen, (tClSalophen)tetrachloro

tetrachloro-dimethyl Salophen, (tCldMeSalophen)

tetrachloro-diethyl Salophen, (tClEtdSalophen)

## Experimental part

All reagents were purchased from Acros or Aldrich and were used without further purification. Elemental analysis (C, H, N) was performed in a specialized laboratory (Service de Microanalyses, Gif-sur-Yvette, France). $^1$H NMR measurements were made on a Brucker AM 250 or AC 250 spectrometer operating at 250 MHz. All spectra were obtained in $CDCl_3$ and chemical shifts were calculated in ppm with respect to TMS (δ = 0) or solvent residual peak (δ = 7.26 for proton). UV-VIS spectra were taken on DES device, operating with SAFAS program. The FT IR spectra were obtained on a Brucker IFS 66 apparatus in KBr pellets.

Cyclic voltammetry experiments were performed on Autlab Eco Chemie equipment. The recordings were made in a 2mM solution in DMF under argon atmosphere, using lithium perchlorate as electrolyte support. The working electrode was a vitreous carbon electrode (4.0 $mm^2$); as reference electrode a saturated calomel electrode (ESC) and as auxiliary electrode a platinum wire were used.

*Preparation of the ligands.*

3,5-dichloro-2-hydroxy-benzaldehyde and 3,5-dichloro-2-hydroxy-acetophenone are commercially available. The 3,5-dichloro-2-hydroxy-acetophenone and 3,5-dichloro-2-hydroxy-propiophenone have been obtained by a Friedel-Crafts procedure of substitution corresponding dichlorophenols, with acetyl- and propionyl chloride respectively.

The salen type ligands have been prepared by stirring for 2-3 h a solution of 2 equivalents carbonyl derivative and 1 eq. diimine in MeOH or EtOH at 40 °C. The salophen type ligands have been prepared by stirring a solution of 2 eq. carbonyl derivatives and 1 eq. diimine in MeOH or EtOH at room temperature or at cold. The ligands were recrystallized from methanol.

For the other ligands: bis(3,5 di-chloro α-$CH_3$-salycilaldehyde)o-phenylenediimine (tCl-dMe- Salophen) and bis(3,5 di-chloro δ-$CH_2$-$CH_3$- salicylaldehyde) o-

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**Table 1**

ELECTRONIC SPECTRAL DATA FOR LIGANDS AND COMPLEXES IN DMF

| Compounds | $\lambda_1$, nm (ε, L/(mol·cm)) | $\lambda_2$, nm (ε, L/(mol·cm)) | $\lambda_3$, nm (ε, L/(mol·cm)) | $\lambda_4$, nm (ε, L/(mol·cm)) |
|---|---|---|---|---|
| Mn(tClSalen) | 483 (1.85) | 432 (3.63) | 324 (3.56) | 262 (3.14) |
| Mn(tCldMeSalen) | 582 (2.68) | 400 (3.28) | 340 (3.58) | 226 (3.13) |
| Mn(tCldEtSalen) | 568 (2.34) | 430 (3.31) | 310 (3.61) | 212 (3.60) |
| Mn(tClSalophen) | 550 (2.96) | 436 (3.83) | 326 (3.73) | 235 (3.52) |
| Mn(tCldMeSalophen) | 512 (2.02) | 400 (3.27) | 320 (3.47) | 230 (2.83) |
| Mn(tCldEtSalophen) | 482 (1.91) | 418 (3.46) | 358 (3.38) | 240 (2.84) |

phenylenediamine (tCl–dEt-Salophen), the reactions were made by the same procedure, but at low temperatures, only (5-10 °C and 0-5 °C respectively). Since the products were impure (mono- and bis-imines) and the coupling yields low, the method described in [17] has been tested. The reaction of the carbonyl derivative and *o*-phenylenediimine in a 1:1 molar ratio yielded the unsymmetrical monosubstituted imines, which were separated and reacted further with another equivalent of carbonyl derivate, in order to obtain the desired ligand with satisfactory yields.

*Preparation of the complexes*

The manganese(II) complexes were synthesised by general procedures. Owing to their air-sensitivity, the manganese(II) Schiff bases complexes were prepared under argon with strict exclusion of air. To a solution of 1 equivalent of ligand dissolved in 25 mL of methanol, or ethanol was added 1 equivalent of $Mn(OAc)_2 \cdot 4H_2O$ dissolved in 5 mL water at 40 °C, by stirring. The precipitate is immediately deposed. The mixture is further maintained under stirring at 40°C for one hour. After cooling at room temperature, the solid is filtered and successively washed with water, ethanol-water mixture and absolute ethanol. After drying *in vacuo*, the manganese complex was isolated and analyzed. Mn(tClSalen), Found (Calculate): C, 38.78 (38.82); H, 2.87 (2.85); N, 5.65 (5.66); $Mn(C_{16}H_{14}Cl_4N_2O_4)(H_2O)_2$. Mn(tCldMeSalen), Found (Calculate): C, 41.23 (41.33); H, 3.50 (3.47); N, 5.31 (5.36); $Mn(C_{18}H_{18}Cl_4N_2O_4)(H_2O)_2$. Mn(tCldEtSalen), Found (Calculate): C, 43.61 (43.58); H, 3.98 (4.02); N, 5.01 (5.08); $Mn(C_{20}H_{22}Cl_4N_2O_4)(H_2O)_2$. Mn(tClSalophen), Found (Calculate): C, 44.14 (44.23); H, 2.71 (2.60); N, 5.18 (5.16); $Mn(C_{20}H_{14}Cl_4N_2O_4)(H_2O)_2$. Mn(tCldMeSalophen), Found (Calculate): C, 46.31 (46.26); H, 3.21 (3.18); N, 4.89 (4.90); $Mn(C_{22}H_{18}Cl_4N_2O_4)(H_2O)_2$. Mn(tCldEtSalophen), Found (Calculate): C, 47.99 (48.11); H, 3.83 (3.70); N, 4.65 (4.68); $Mn(C_{24}H_{22}Cl_4N_2O_4)(H_2O)_2$.

*Catalytic activity studies*

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 complexes. The reaction is performed in a 100 mL round-bottomed flask sealed with a rubber septum, at room temperature. General catalytic procedure was the following: $2.5 \times 10^{-2}$ mmols of complex (5% molar to substrate) is dissolved in 5 mL of dry degassed DMF under argon, and 103 mg (0.5 mmols) of DtBP dissolved in 5 mL of DMF were added. The argon is evacuated under vacuum and the flask is refilled with oxygen. The flask is connected *via* a syringe needle to a gas burette that contain pure $O_2$ at p = 1 atm. The stirring is started, by monitoring the oxygen consumption. After 24 h, the reaction is stopped and the mixture is separated by flash chromatography with dichloromethane/heptane 1/1 (in volume). After evaporation of volatiles, the fractions are analysed by $^1H$ NMR and by gas-chromatography, on a Bruker AM 250 and Fison 9000 GLC apparatus, respectively.

## Results and discussion

The purities of the ligands and the complexes synthesized, checked by elemental analysis, FT IR, UV-VIS and NMR techniques are high and these confirm the proposed structure. The elemental analysis of the complexes indicates the formation of the complexes in a 1:1 molar ratio (MnL). The electronic spectra of the free ligands in DMF show two strong absorption bands in the UV-Vis region (300-450 nm), attributed to the π-π* and n-π* transitions [18]. Complexes spectra present modifications in the position and intensity of the bands characteristic to free ligands, as well as the occurrence of new bands (although sometimes not very well-defined) attributed to the d-d or d-π* transition.

The UV-Vis bands for the Mn(II) complexes and their intensity are presented in table 1.

The manganese (II) complexes show, low intensity broad bands in UV-VIS range assigned to the d-d transition, spin-forbidden, or charge-transfer d-π* transition [19,20].

The bands present in the region 200-450 nm can be attributed to the intraligand transitions, modified by the

**Table 2**

SIGNIFICANT FT IR SPECTRAL BANDS ($cm^{-1}$) FOR THE MANGANESE COMPLEXES

| Compounds | $\nu_{H2O}$ | $\nu_{C=N}$ | | New bands | |
|---|---|---|---|---|---|
| | | Complexes | Free ligands | $\nu_{M-N}$ | $\nu_{M-O}$ |
| Mn(tClSalen) | 3426 | 1628 | 1636 | 583 | 443 |
| Mn(tCldMeSalen) | 3404 | 1603 | 1611 | 556 | 450 |
| Mn(tCldEtSalen) | 3423 | 1601 | 1610 | 548 | 434 |
| Mn(tClSalophen) | 3441 | 1608 | 1617 | 508 | 402 |
| Mn(tCldMeSalophen) | 3413 | 1641 | 1648 | 540 | 413 |
| Mn(tCldEtSalophen) | 3421 | 1632 | 1645 | 538 | 423 |

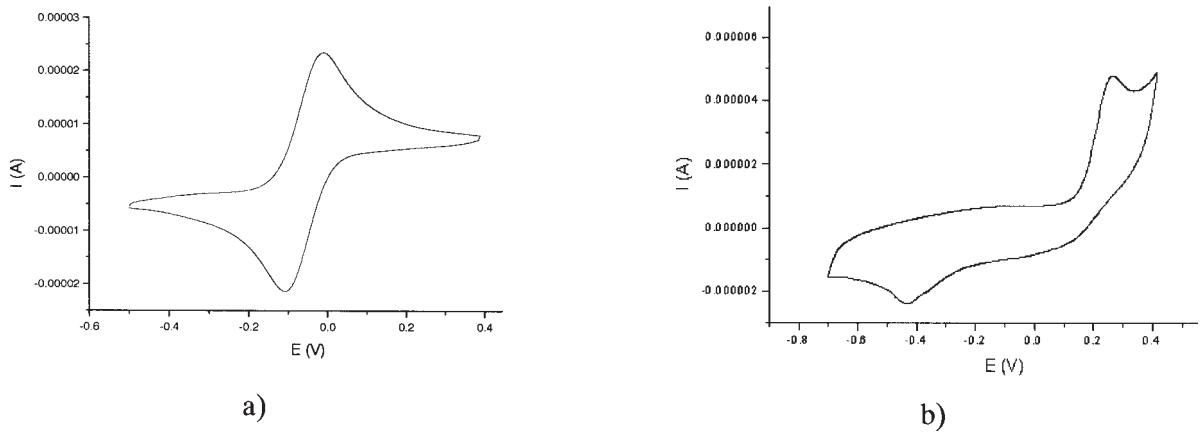



Fig. 2. Cyclic voltammograms for the Mn(tCldMeSalen) a), and for the Mn(tCldEtSalophen) b). $C_{MnL}$ = 2·10$^{-3}$M, in DMF, scan rate = 0.1V/s, potential vs. the saturated calomel electrode (SCE)

**Table 3**
ELECTROCHEMICAL DATA FOR COMPLEXES

| Compounds | $E_{pa}$ (V) | $E_{pc}$ (V) | $\Delta E$ (V) | $E_{1/2}$ (V) |
|---|---|---|---|---|
| Mn(tClSalen) | 0.107 | 0.006 | 0.101 | 0.056 |
| Mn(tCldMeSalen) | -0.146 | -0.267 | 0.121 | -0.206 |
| Mn(tCldEtSalen) | -0.125 | -0.340 | 0.215 | -0.232 |
| Mn(tClSalophen) | 0.485 | -0.043 | 0.523 | 0.221 |
| Mn(tCldMeSalophen) | 0.468 | -0.167 | 0.635 | 0.151 |
| Mn(tCldEtSalophen) | 0.261 | -0.422 | 0.683 | -0.341 |

c = 2x10$^{-3}$ M in DMF and 0.1M $LiClO_4$; scan rate 100mV/s; $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials respectively. $\Delta E = E_{pc} - E_{pa}$; $E_{1/2} = (E_{pa}+E_{pc})/2$

complexation process. Over the π-π* or n-π* transitions of the ligands, from 400-450 nm range the d-d and d-π* transitions are superposed. The formation of the complexes is shown in appearing of the new bands over 450 nm that can be attributed also to the d-d or d-π* transitions characteristic the divalent manganese (II). Sometimes the d-d bands transition is not very well defined being presented as a shoulder.

The FT IR spectra of the ligands show major bands around 1600 cm$^{-1}$ assigned to $\nu_{C=N}$, around 1560 cm$^{-1}$ and 1500 cm$^{-1}$ assigned to ring vibrations, around 1280 cm$^{-1}$ assigned to OH phenolic deforming outside, around 1230 cm$^{-1}$ assigned to $\nu_{C-N}$, and around 1050 cm$^{-1}$ assigned to $\nu_{C-O}$. In the spectra of the complexes, the C=N stretching mode shifted to a lower frequency and additional shifts in the bands correspond 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 occurrence of new absorption bands in the region 400-590 cm$^{-1}$ [21]. The most important FT IR absorption frequencies of the manganese complexes and $\nu_{C=N}$ for the corresponding ligands are listed in table 2.

The recorded FT IR spectra support the formation of the complexes by the coordination of manganese to the azomethinic nitrogen and to the phenolic oxygen [22].

According with elemental analysis, UV-VIS and FT IR data we can admit that the manganese (II) can coordinate two water or solvent molecules in axial position.

The redox potential is an important parameter in electron transfer processes, in general, and also in catalytic studies. Figure 2 shows the cyclic voltammograms, in DMF (vs SCE), in argon atmosphere, for the Mn(tCldMeSalen) and Mn(tCldEtSalophen) complexes.

The values of the anodic and cathodic peaks (Epa, Epc), and semi waves potentials ($E_{1/2}$), for the manganese complexes are listed in table 3.

The studies of cyclic voltammetry show a *quasi*-reversible behaviour for the salen type ligands and irreversible behaviour for the other. This behaviour can be explained by steric hindrance of chain o-phenilendiamine between nitrogen donors atoms [23,24].

The presence of chlorine grafted on the aromatic rings, with attractive effects –I, leads to diminish the electric charge on metallic ion of manganese(II) and a shift towards more positive values for the semi waves; e.g. $E_{1/2}$ for Mn(tClSalen) is 0.056 comparative with -0.314 for Mn(Salen).

The presence of some substituents with donor or attractive electronic effect, grafted on the ligand molecule, influences the electrochemical behaviour of metallic ion. By examining the trend of the experimental semi waves values, we can observe that the $E_{1/2}$ in the Mn-complexes is influenced by the nature of the substituents R from azomethinic groups. Indeed, the semi waves values $E_{1/2}$ are shifted to lower positive values with the increase of inductive effect (+I) of the substituents from azomethinic groups. This can be explained by the fact that an increase of the +I effect determines the increase of the electronic density on the metallic centre, Mn(II) ion, and thus became more oxidable.

The catalytic activity of the complexes was studied in the reaction of 2,6-di-*tert*-butyl-phenol (DtBuP) with molecular oxygen, in DMF solution. The DtBuP is easily oxidable with molecular oxygen in the presence of metallic complexes. The reaction gives mainly two products: 2,6-di-*tert*-butyl-1,4-benzoquinone (QN) and 2,6,2',6'-tetra-*tert*-

butyl-1,1'-diphenobenzoquinone (TtBuDQ) respectively, figure 3 [25-27].

Table 4 shows the yields and relative proportions of these two products, determined by $^1$H NMR and GC as described in Experimental part when DtBuP, 0.1 M in dry DMF was oxidized by $O_2$ with 0.5 $10^{-2}$ M (5% molar with respect to the substrate) Mn-salen complex as catalyst. The increase of the catalyst/substrate ratio did not lead to any significant increase in the yield (1-2% at the most).

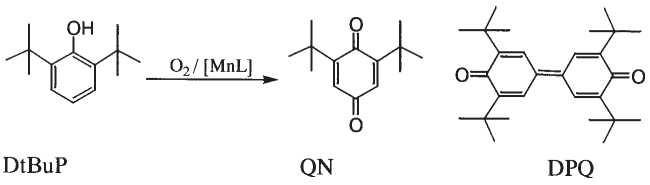



Fig. 3. General reaction of oxidation of the 2,6-di-*tert*-butyl-phenol (DtBuP)

**Table 4**
CATALYTIC OXIDATION RESULTS OF THE DTBUP WITH MANGANESE (II) COMPLEXES

| Compounds | Conversion[a] % | TtBuDQ | QN |
|---|---|---|---|
| Mn(Salen) | 100 | 98 | 2 |
| Mn(tClSalen) | 100 | 100 | - |
| Mn(tCldMeSalen) | 100 | 100 | - |
| Mn(tCldEtSalen) | 100 | 100 | - |
| Mn(tClSalophen) | 76 | 100 | - |
| Mn(tCldMeSalophen) | 68 | 100 | - |
| Mn(tCldEtSalophen) | 56 | 100 | - |

[a] Error ±0.5%

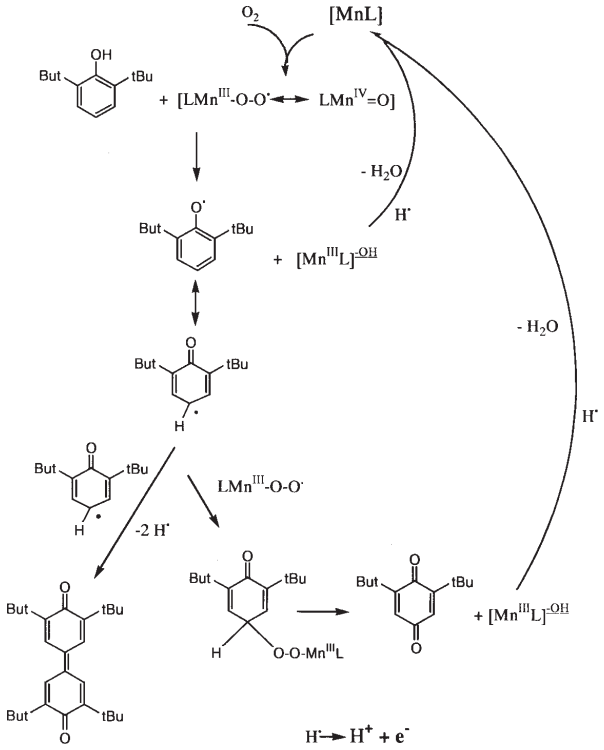
It appears from table 4, that the highest conversion degree is obtained with Mn(tClRSalen) as catalysts. The maximum selectivity in favour of the formation of TtBuDQ was reacted for all complexes, except MnSalen. This can be correlate with steric hindrance for the tetra-chloro Schiff bases complexes [28]. The conversion degree decreased within Salpohen complexes *vis a vis* of Salen complexes and when R are ethyl or methyl (in Mn(II)tClRSalphen complexes), as results of steric hindrance also.

To explain the formation of TtBuDQ or DtBuQ it is necessary to consider the mechanism of the reaction, scheme 1. The mechanism involves reactions of manganese (II) complexes with molecular oxygen when one solvent molecule is substituted by $O_2$ and one adduct is formed. Then, the adduct reacts with DtBuP and one electron is transferred from manganese complexes to phenol, and one phenoxyl radical is formed. The phenoxyl radical is able to dimerize, and manganese complexes are reformed [29-31].

Conversion rate from table 4 can be correlated with the value of DE peak separation in voltammograms, (fig. 4).

These data are in concordance with steric hindrance determined by the *o*-phenylenic chain to nitrogen donors atoms and with the value of ΔE. High values for ΔE involve an irreversible electrochemical behaviour of the compounds and, as consequence, a small yield of transformation. On the other hand, the obtained product is only TtBuDQ. This involves the reversible formation of some [LMn-$O_2$] adducts.

The formation of reversible [LMn-$O_2$] adduct can be studied by cyclic voltammetry. For this, we analyzed the behaviour of the complexes in the absence of oxygen (in argon atmosphere), in presence of oxygen and also, after removal of oxygen from the system (fig. 5).




Scheme 1. Mechanism for oxygenation of DtBuP with molecular oxygen, in the presence of Mn(II) complexes

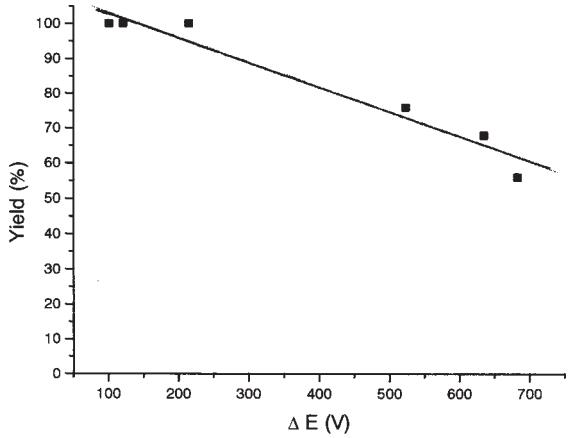



Fig. 4. Correlation between ΔE and transformation yield

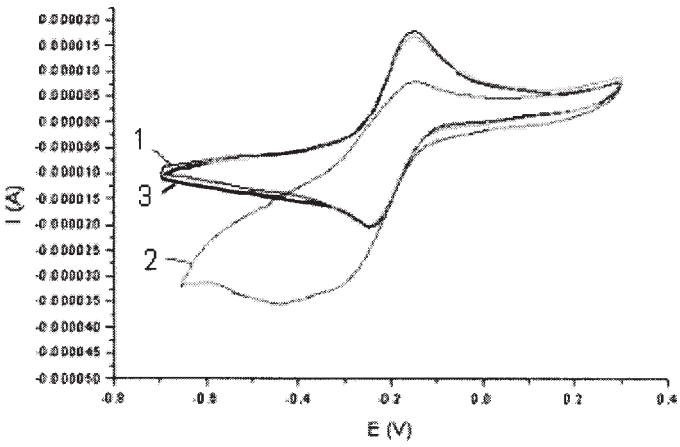



Fig. 5. Cyclic voltammograms for the Mn(tClSalen): 1- initial (in argon atmosphere), 2- in presence of oxygen, and 3- after elimination of oxygen; $C_{MnL}$ = 2·10$^{-3}$M, in DMF, scan rate = 0.1V/s, vs. the saturated calomel electrode (SCE)

These voltammograms indicate that the manganese complexes, in presence of molecular oxygen, form [LMn-$O_2$] adduct, according to the following equilibrium [32, 33].

$$[LMn^{II}] + O_2 \rightleftharpoons [LMn^{III}\text{-}O_2] \quad (1)$$

This adduct is able to attract a hydrogen atom from DtBP, in order to form the phenoxyl radical which leads to diphenoquinone by dimerisation.

## Conclusions

The manganese (II) cations coordinate tetradentate Schiff bases and form Mn (II) six-coordinated complexes with two water or solvent molecules in the axial positions. The UV-VIS and FT IR spectra show the modifying bands of the free ligands and the occurrence of some new bands characteristic for the metallic ion and for the metal-donor atoms from ligands bonds. The data from cyclic voltrammetry indicate a reversible or irreversible electrochemical behaviour according to the structure of the complexes. The semiwaves potentials are influenced of the chlorine atoms and R radical grafted on the molecule of the ligands and these are in concordance with their electronic effect (-I or +I).

The catalytic activity is in correlation with redox behaviour and with the effects of the steric hindrance.

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