Synthesis, Characterizations, and Electrochemical Study of the Electrocatalytic Properties of the Interaction between the Manganese Schiff Base Complex 5,5'-Dibromo N, N'-Bis-(salicylidene)bis-(3-aminopropylamine) and Molecular Oxygen

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Abstract

This work focuses on the synthesis and characterization of a pentadentate Schiff base complex of manganese, 5,5'-dibromo N, N'-bis-(salicylidene)bis-(3-aminopropylamine), and its electrochemical behavior. To understand the effectiveness of manganese complexes in the epoxidation reaction of cyclooctene molecules.

The electrochemical behavior study of the Mn(II)-CIL complex in an organic medium primarily focuses on determining the conditions for homogeneous catalysis. In this regard, cyclic voltammetry was employed as an electrochemical method during this investigation.

This analysis involves studying the electrochemical behavior of the Mn(II)-CIL complex. It includes investigating the catalytic system under nitrogen and oxygen atmospheres on a glassy carbon electrode (CV) in various solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile (AN), while estimating the formation of metaloxo species (MnV=O).

Keywords: Schiff base complexes, transition metals, electrocatalysis, pentadentate Schiff base, Molecular Oxygen.

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Introduction

Schiff base ligands and their complexes represent an important class of chelating agents in coordination chemistry [1]. These compounds have consistently played a significant role in various areas of chemistry [2]. Substantial efforts have been made to systematize synthetic methods for obtaining these compounds [3]. This category of compounds has served as models for porphyrin ligands and their transition metal complexes [4], attracting considerable attention from many researchers over a long period [5]. This attention is based on their biological significance and industrial relevance, as these structures are systematically derived from products found in living systems, particularly in the liver, which is the site of numerous oxidation reactions mediated by cytochromes P-450 [6].

The porphyrin cores and their complexes [7] derived from cytochrome P-450 exhibit very high activity in oxidation reactions within the human body. Based on these interesting properties, numerous research efforts have primarily focused on molecular modeling to develop new types of chelating agents, including multi-dentate Schiff bases in particular [8]. These studies have a dual objective: first, to enhance current knowledge of the functioning of cytochrome P-450 in living systems, and second, to explore a catalytic system as effective as possible for oxidation catalysis, potentially applicable in industrial settings [9].

Finally, one of the essential reasons that motivated us to undertake this research on this category of complexes and ligands is the presence of a nitrogen atom, which facilitates their solubility in water, whether in the form of ligands or complexes.

Manganese complexes constitute a class of chelating compounds commonly studied in coordination chemistry. This widespread interest can be attributed to two essential factors: the simplicity of their syntheses and the diversity of applications.

Biomimetic catalysis is one of the most interesting applications in this research field, primarily due to the structural similarities with cytochrome P-450 [10]. These properties have led to numerous research efforts focused on modeling biochemical reactions that result in the production of industrially important molecules, including the catalytic oxidation and hydrogenation of olefins and alcohols, respectively. Complexes based on porphyrins and Schiff ligands are two widely involved models in the study of reaction mechanisms [11].

Experimental section

The purity of two synthesized compounds was verified by: Ultraviolet-Visible (UV-VIS) Spectroscopy: UV-visible spectra were recorded in chloroform (CHCl₃) at room temperature using a UV-300 UNICOM spectrophotometer connected to a computer with Vision 32 software. The concentration of the products (C) was 10⁻⁴ mol/L, using a quartz cell with a thickness of 1 cm.

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Infrared Spectroscopy (IR): IR spectra of the ligand and its corresponding complexes were obtained using a PERKIN-ELMER series (1000) FTIR instrument. The sample, dispersed in a KBr pellet, had a concentration of 1% in 100 mg of KBr and was subjected to a pressure of 80 tonnes/cm-1.

Proton Nuclear Magnetic Resonance (1H NMR): 1H NMR spectra were acquired on a 400 MHz Bruker AVIII 400 machine, using CDCl₃ as the solvent.

Thin-Layer Chromatography (TLC): The purity of the ligand and its synthesized complexes was assessed by TLC using silica gel plates. The products were revealed using sublimed iodine.

Differential Scanning Calorimetry (DSC): DSC analyses were conducted using an ERIT – M 0104 apparatus in the temperature range of 40 to 500°C, with a heating rate of 10°C/min under a nitrogen atmosphere.

Cyclic Voltammetry: The study of the electrochemical properties of the ligand and its complexes was performed through cyclic voltammetry in a double-walled glass cell thermostated at 25°C under an inert atmosphere maintained by nitrogen, which served to purge any electroactive oxygen. The cell was equipped with a lid allowing the introduction of three electrodes: Working (Et), Counter (Eau), and Reference (Eref). Electrochemical measurements were conducted using a Tacussel measurement setup, comprising a potentiostat-galvanostat (Tacussel, type PJT 120-06), a pilot unit (pilovite num), and a recording table (SEFRAM type TGM).

The electrochemical cell, with a volume of 5 ml, housed the three electrodes: the working electrode was a vitreous carbon disk with a 3 mm diameter, the counter electrode was a platinum plate with a 2 cm2 surface area, and the reference electrodes used were silver electrodes (Ag/Ag+10-2M). The working electrode was cleaned by polishing with fine-grit emery paper, rinsed with distilled water, then acetone, and finally dried with Josef paper before each manipulation.

For the syntheses described later in this experimental section, all chemicals were obtained from commercial sources and used as received without further purification. Absolute ethanol, 99.5%, methanol 99.9%, and dimethylformamide 99% (DMF) are solvents from Prolabo. Water is bidistilled using a quartz apparatus. Tetra-n-butylammonium perchlorate, 98% (TBAP), is a recrystallized product from Fluka and stored away from moisture. Potassium hydroxide, 99.99% (KOH), is a commercial strong base. Bis-(3-aminopropyl)amine and 5-bromosalicylaldehyde, both 99%, are from Janssen, and hydrated manganese chloride, 98% (MnCl₂·4H₂O) is from Fluka.

Synthesis of Metal Complex = Mn– Schiff Base

The synthesis involves the preparation of a manganese(II) complex with a penta-dentate Schiff base in order to obtain an oxidizing species with satisfactory stability. We conducted the preparation of a penta-dentate ligand and its manganese(II) complex with a Schiff base using the method proposed by Coleman and col [12,13]

Synthesis of Ligand: The ligand (L) is a Schiff base (figure 1), 5,5'-dibromo-N,N'-bis-(salicylidene)bis-(3-aminopropylamine), with a molecular weight of 497 g/mol.

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Figure 1: Structure of the Schiff base ligand L

in a 100 ml three-necked flaskone mmol (0.131 g) of bis(3-aminopropyl)amine dissolved in 5 ml of absolute ethanol. This solution undergoes magnetic stirring. Subsequently, 0.402 g (2 mmol) of 5-bromo-salicylaldehyde, dissolved in 10 ml of absolute ethanol, is added dropwise to the diamine. As soon as the two compounds come into contact, a yellow coloration is observed. The setup is then refluxed for one hour. Afterward, ethanol is removed by evaporation under reduced pressure, and the resulting ligand is obtained as a viscous yellow oil. The reaction yield was estimated to be 78%.

The overall reaction involving the ligands (L) is as follows (figure 2):

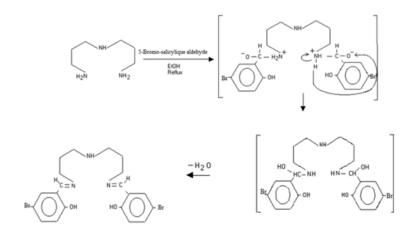


Figure 2: Mechanism of ligand formation

Thin-layer chromatography (TLC): The purity of ligand L was checked using TLC with the same previous eluent; in this case, a retention factor of 0.61 was obtained.

Infrared spectroscopy: The characteristic absorption bands for ligand L are presented in Table 1. An average absorption band for the azomethine group is observed at 1636 cm⁻¹, with a shift towards higher frequencies. This shift suggests a bathochromic effect attributed to the bromine atom of the salicylaldehyde derivative [14,15](see Table 1).

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Table 1: Main IR absorption bands attributed to ligand L.

Function	Absorption Band υ (cm ⁻¹)	Intensity	
NH, OH	3367	M	
CH aliphatic	2974	m	
C=N	1636	m	
C=C	1584	m	
C-N	1478	m	
C-O	1279	m	
C-Br	627	F	

UV-Visible Spectrophotometry

The electronic spectrum of ligand L shows two main peaks attributed to $n-\pi$ transitions (λ max = 328nm, A = 1.435) and the π - π * transition of the aromatic system (λ max = 246nm, A = 2.056) [16] (See Figure 3).

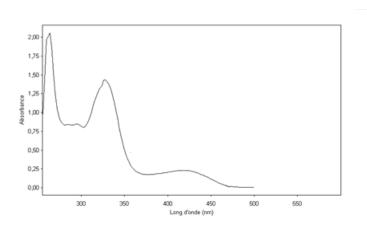


Figure 3: Electronic spectrum of ligand L (10-4M) in DMSO.

Proton Nuclear Magnetic Resonance Spectroscopy (1H NMR):

The results of the 1H NMR spectroscopy of ligand L were indicative, showing that the molecule is symmetrical and exhibiting seven different absorptions.

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$$(c) \quad (b) \quad (e) \quad (e) \quad (f) \quad (e) \quad (f) \quad (f)$$

These absorptions are observed at chemical shifts δH of:12.50 ppm (2H, multiplet), attributed to the two hydroxyl (OH) groups.8.30 ppm (2H, singlet) and 7.12 ppm (6H, multiplet) designated, respectively, for the vinylic protons (CH=N) and (CH=C) of the two aromatic cycles.

The absorptions at 3.65 ppm (4H, triplet, J 4.0 Hz) and 0.90 ppm (4H, quartet of doublets, J 4.0; 2.5 Hz) represent the protons of the groups [-CH₂ (b) and -CH₂ (c)]. However, the absorption observed at 1.85 ppm (4H, multiplet) is related to the two groups [-CH2 (d)]. The absorption of the amino group (NH) appears at 2.75 ppm (1H, multiplet).

Preparation of complexes (Mn (II) Cl–L Schiff base M = 555.69 g/mol.

0.131g of bis(3-aminopropyl)amine is dissolved in 5ml of absolute ethanol in a three-necked flask under stirring. Next, 2mmoles (0.402g) of 5-bromo-2-hydroxybenzaldehyde are dissolved in absolute ethanol, and dropwise added to the diamine solution using a Pasteur pipette. The system is then refluxed under a nitrogen atmosphere. After 3 hours, 1mmole of Manganese salt MnCl₂·4H₂O (0.245g) dissolved in 5ml of deoxygenated methanol is added dropwise to the solution. A green precipitate forms, and after filtration and washing with deoxygenated methanol, the product is dried in a vacuum desiccators (Figure 4). The complex is formed with a mass of 0.140g, yielding 28%.

Figure 4: Structure of the manganese Schiff base complex Mn (II) Cl-L.

Thin-Layer Chromatography Using the same previous eluent, the frontal ratio value assigned to the Mn(II)Cl-L complex is 0.45.

Infrared Spectroscopy The identification of the Mn(II)Cl-L complex structure was carried out through infrared spectroscopy (See Figure 5). The azoimide function underwent a shift towards lower frequencies compared to the ligand L2 (1638 cm⁻¹ to 1624 cm⁻¹) [17], demonstrating its

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involvement in manganese coordination. Table compiles the main characteristic bands of the Mn(III)Cl-L complex:

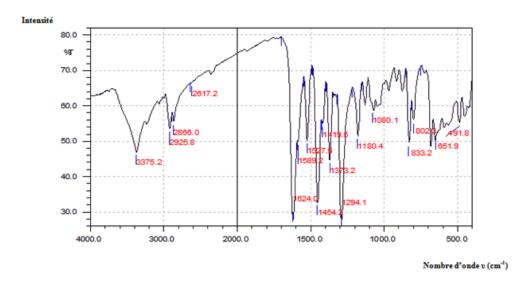


Figure 5: Infrared Spectrum of the Mn(II)-Cl L Complex.

UV-Visible Spectroscopy The coordination of manganese within the ligand L is confirmed by the appearance of an absorption band in the visible region at 398nm (A=0.879) (See Figure 6). The two shoulders located at 269nm, with absorbance values of 0.745, are attributed to π - π * transitions of the iminic function and the benzene ring of the Mn(II)Cl-L complex.

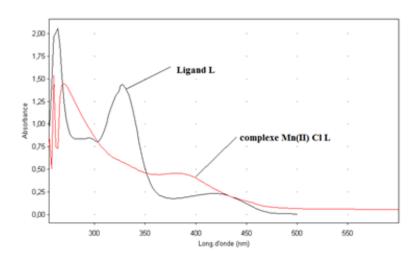


Figure 6: Electronic Spectrum of the Schiff base ligand L and its Mn(II)Cl-L complex (10⁻⁴M) in DMSO.

Differential Scanning Calorimetry (DSC)

The DSC curve for the Mn(II)Cl-L complex shows an endothermic peak at 214° C, corresponding to the dehydration of water molecules, and another exothermic peak at 397° C, corresponding to the decomposition of the manganese complex through the loss of [18] Mn₂O₅

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molecules. When comparing the DSC curve of this complex to that of the non-substituted Mn(II)Cl-L, a significant stabilizing effect is observed due to the bromine atom substituent in the para position relative to the phenol function in the salicylaldehyde derivative (See Figure 7).

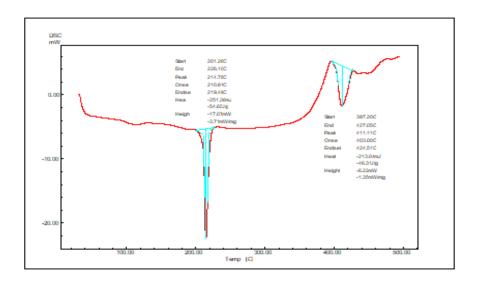


Figure 7 : Courbe DSC pour le complexe Mn (II)Cl- L base de schiff

The electrochemical behavior study of the Mn(II)-Cl L complex in an organic medium primarily focuses on determining the conditions for homogeneous catalysis. In this study, cyclic voltammetry was employed as the electrochemical method.

This analysis is centered around investigating the electrochemical behavior of the Mn(II)-Cl L complex. It involves studying the catalytic system under nitrogen and oxygen atmospheres, using different solvents (AN, DMF, DMSO), and employing cyclic voltammetry (CV) on various electrodes. This aims to illustrate the influence of these factors on the catalytic properties of the Manganese complex.

Before delving into this electrochemical study, it is crucial to determine the electroactivity domain plots of the environments. This is essential for observing the behavior of these catalysts within the investigated domain.

Electrochemical behavior of the Schiff base complex (Mn(II)-Cl L) Determination of electroactivity domains

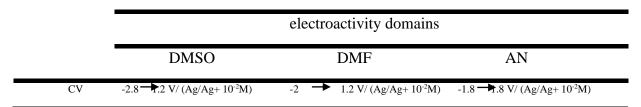
Cyclic voltammograms were recorded from negative to positive potentials with a scan rate of 100 mV/s on the working electrode, a glassy carbon disk CV (dia = 3 mm).

We used organic solvents such as AN 10⁻¹M in TBAP, DMF 10-1M in TBAP, and DMSO 10⁻¹M in TBAP. The reference electrode was Ag/Ag⁺ (10⁻² M), and a platinum auxiliary electrode (2 cm² plate) was employed.

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A potential scan was conducted from -2.8 to +2.4 V (Ag/Ag⁺ 10⁻² M). The presence of currents increasing with the potential at the limits of the anodic and cathodic paths corresponding to the solvent walls was observed. In the voltage range -1.8 to 1.8 V (Ag/Ag⁺ 10⁻² M) (Figure), no peaks were noted. This preliminary step is performed before each electrochemical study of the products.

The electroactivity domain on different electrodes in the three media is represented in the following table (See Figure 8).



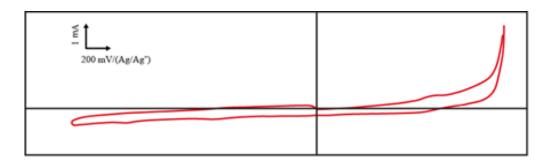


Figure 8: Cyclic voltammetry curve on a Pt electrode (dia. = 6 mm) in a 0.1 M acetonitrile solution with TBAP at a scan rate of 100 mV/s, under N_2 (Reference electrode: Ag/Ag⁺ 10^{-2} M).

A study of cyclic voltammetry was conducted in a solution of AN 10^{-1} M in TBAP, DMF 10^{-1} M in TBAP, and DMSO 10^{-1} M in TBAP, containing the Mn(II)-Cl L complex at a concentration of 10^{-3} M in both the anodic and cathodic regions (positive and negative) with a scan rate of 100 mV/s, in the presence of N_2 .

Observing the voltammogram of the Mn(II)-Cl L complex, three oxidation waves are noted at potentials of -0.1, -0.5, and -1.2 V (vs. Ag/Ag^+ 10^{-2} M), respectively. Among these three oxidation waves, only the first exhibits a reduction wave during the reverse scan, thus forming the MnIII / MnII redox couple. This is in contrast to the other two waves, which correspond to irreversible systems.

On the cathodic side, only the reduction peak corresponding to the solvent wall is observed, limiting the electroactivity of the medium from -1.4 to 0.5 V (vs. Ag/Ag^+ 10^{-2} M). (See electroactivity of the medium in the figure 9).

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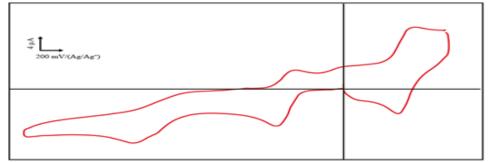


Figure 9: Cyclic voltammetry curve of the Mn(II)-Cl L complex in acetonitrile (AN) 5 mL, containing 10^{-3} M of the Mn(II)-Cl L complex and 10^{-1} M tetrabutylammonium perchlorate (TBAP). The working electrode is a glassy carbon electrode (CV) with a diameter of 3 mm. The reference electrode is Ag/Ag⁺ 10^{-2} M, and the auxiliary electrode is a platinum plate with an area of 2 cm². The experiment was conducted under a nitrogen atmosphere with different scan rates at 50 mV/s. Influence of the scan rate

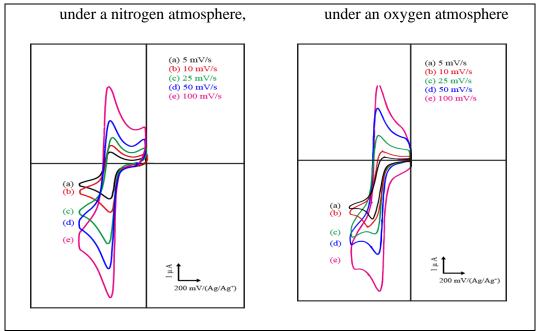


Figure 10: Cyclic voltammetry curves of the Mn(II)-Cl L complex in acetonitrile (AN) 5 mL, containing 10^{-3} M of the Mn(II)-Cl L complex and 10^{-1} M tetrabutylammonium perchlorate (TBAP). The working electrode is a glassy carbon electrode (CV) with a diameter of 3 mm. The reference electrode is Ag/Ag⁺ 10^{-2} M, and the auxiliary electrode is a platinum plate with an area of 2 cm². The experiment was conducted under nitrogen and oxygen atmospheres, with various scan rates.

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Table 2: Electrochemical characteristics of the Mn(II)-Cl L complex at 10⁻³ M in different solvents at various scan rates on the CV electrode (dia. = 3mm) (Reference electrode: Ag/Ag⁺ (10⁻² M)).

Vitesses(Solvants mV/s)			N	72		O_2				I
	Solvants	-Epa(mV)	-Epc(mV)	Ipa(µA)	-Ipc(μA)	-Epa(mV)	-Epc(mV)	Ipa(µA)	-Ipc(μA)	I _{pc} (O2)/I _{pc} (N2)
	DMSO	500	600	17.6	19.6	480	600	18.8	28.4	1.44
100	DMF	480	440	47.2	45.6	520	500	32.8	45.6	1
	AN	380	420	6.8	8.1	320	320	6.6	7	0.86
	DMSO	520	600	12.8	15.2	500	600	13.2	21.6	1.42
50	DMF	480	470	34.8	34	480	540	22	34.8	1.02
	AN	380	400	4.5	6.1	320	320	6	5.7	0.93
	DMSO	500	600	9.2	10.8	500	600	8.4	16	1.48
25	DMF	480	450	25.2	25.6	480	530	14.4	25.6	1
	AN	360	420	3.2	4.5	320	360	3.5	4.4	0.97
	DMSO	500	600	6	7.6	500	600	4.4	10.4	1.36
10	DMF	460	450	16.8	16.4	460	500	10	17.2	1.04
	AN	360	420	2.4	3.1	300	460	2.8	4	1.29
	DMSO	500	600	3.6	5.6	500	560	3.4	7.6	1.35
5	DMF	460	450	12.8	12.4	440	540	8	12.8	1.03
	AN	340	420	2	2.5	280	420	2.5	3.6	1.44

Table 3: Electrochemical characteristics of the Mn(II)-Cl L complex at 10^{-3} M in different solvents at various scan rates on the CV electrode (dia. = 3 mm) (Reference electrode: Ag/Ag⁺ (10^{-2} M)).

Vitesses(mV/s)	•	N_2					
	Solvants	ΔE (mV)	Ipa/Ipc(μA	E 1/2 (mV)	ΔE(mV)	Ipa/Ipc(μA	E 1/2(μA)
	DMSO	100	0.89	550	120	0.66	540
100	DMF	40	1.03	460	20	0.71	510

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	AN	40	0.83	400	0	094	320
	DMSO	80	0.84	560	100	0.61	550
50	DMF	10	1.02	475	60	0.63	510
	AN	20	0.73	390	0	1.05	320
	DMSO	100	0.85	550	100	0.52	550
25	DMF	30	0.98	465	50	0.56	505
	AN	60	0.71	390	40	0.79	340
	DMSO	100	0.78	550	100	0.42	550
10	DMF	30	1.02	455	40	0.58	480
	AN	60	0.77	390	160	0.7	380
	DMSO	100	0.64	550	60	0.44	530
5	DMF	10	1.03	455	100	0.62	490
	AN	80	0.80	380	140	0.69	350

After this comprehensive study on the electrochemical properties of the Mn(II)-Cl L complex, we focused our attention on the MnIII/MnII redox couple. In this case, we plotted the voltammograms at different scan rates, such as 100 mV/s, 50 mV/s, 25 mV/s, 10 mV/s, and 5 mV/s (See Figure 10), to better understand the electrochemical and electrocatalytic properties of this catalyst. For example, we observed perfect reversibility of the MnIII/MnII systems, as indicated by ΔE values ranging between 70 and 100 mV (vs. Ag/Ag⁺ 10⁻² M) (see the table 2,3), meeting the conditions for Nernstian reversibility. Additionally, the ratio of the complex giving the oxidation current (Ipa) to the reduction current (Ipc) yields a unitary value, confirming the reversibility phenomenon. As for the half-wave potential (E½), it appears not to vary significantly with changes in the scan rate.

the study of complexes under homogeneous catalysis conditions

Under an oxygen atmosphere:

The introduction of molecular oxygen into the reaction medium leads to a clear modification of the cyclic voltammetry curves for these complexes. An increase in the reduction peak (equation 1) is observed, accompanied by a loss of reversibility in the Mn(III)/Mn(II) system.

 $Mn(III) + 1e \rightarrow Mn(II)$ (Equation 1)

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This behavior is well explained by the reaction between the Mn(II) species and molecular oxygen, along with the consumption of a second electron to form the superoxo intermediate, as shown in the catalytic cycle presented in the following scheme:

$$L Mn(II) + O_2 + e \rightarrow [L Mn(III) - O - O] - 2$$
 (Equation 2)

Influence of solvents (AN, DMSO, DMF) Acetonitrile (AN):

The electrocatalytic behavior of the Mn(II)-Cl L complex shows that IPC (O_2) is larger compared to IPC (N_2) in the low-speed domains of 5 mV/s to 25 mV/s. This is consistent with a reaction mechanism following an ECE process, where the limiting step is the reaction with oxygen. However, from 25 mV/s to 100 mV/s, IPC (O_2) becomes lower than that obtained under a nitrogen atmosphere. This can probably be attributed to the formation of insoluble μ -oxo dimers, which are generally not soluble in acetonitrile [19], as observed in IPC (N_2) .

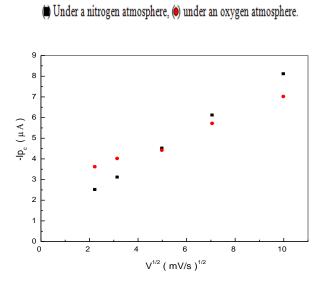


Figure 11: Variation of the cathodic peak current (Ipc) as a function of the square root of the scan rate (v1/2) for Mn(II)-Cl L 10⁻³ M, TBAP 0.1 M in CH₃CN 10⁻² M on the CV electrode (dia = 3 mm).

Dimethylformamide (DMF): The study of the electrochemical kinetics of the Mn(II)-Cl L complex reveals that the intensity of the cathodic peak IPC (O_2) is slightly higher than that of the cathodic peak IPC (N_2) , confirming the formation of superoxo species (Mn=O) in the reaction medium (see figure 11).

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Under a nitrogen atmosphere, ounder an oxygen atmosphere.

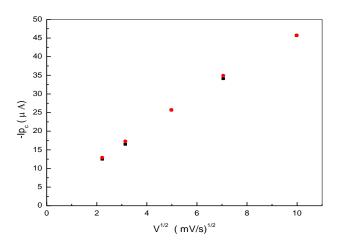


Figure 12: Variation of the cathodic peak current (Ipc) as a function of the square root of the scan rate (v1/2) for Mn(II)-Cl L 10⁻³ M, TBAP 0.1 M in DMF on the CV electrode (dia = 3 mm).

Dimethyl sulfoxide (DMSO):

The electrocatalytic study of the Mn(II)-Cl L complex in dimethyl sulfoxide (DMSO) exhibits a behavior similar to that observed with dimethylformamide (DMF) but with a noticeably higher solubilizing power. Thus, the IPC (O2) peak is higher than that obtained under nitrogen (IPC (N2)). This is attributed to the additional effect played by dimethyl sulfoxide (DMSO) as an axial ligand, accelerating the formation of the superoxide species in Equation 2.

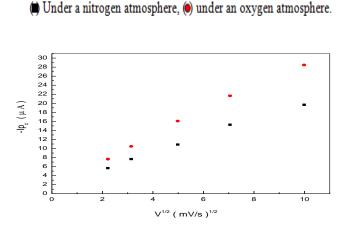


Figure 13: Variation of the cathodic peak current (Ipc) as a function of the square root of the scan rate (v1/2) for Mn(II)-Cl L 10^{-3} M, TBAP 0.1 M in DMSO on the CV electrode (dia = 3 mm).

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Conclusion

The completion of this research work allows us to summarize its main contributions in the following points: Ligands and complexes were characterized using spectroscopic analysis methods such as UV-visible, infrared, NMR, and mass spectrometry. These ligands and complexes were also studied through cyclic voltammetry to determine their electrochemical characteristics. Manganese complexes were additionally investigated through cyclic voltammetry in the presence of molecular oxygen to assess their performance in the hydrocarbon oxidation reaction, following the cytochrome P-450 model.

The study by cyclic voltammetry of our complexes, especially those of manganese, revealed greater solubility in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), with partial solubility noted in acetonitrile. Thus, AN appears to be very interesting as it shifts the half-wave potential (E1/2) values towards anodic potentials, providing a broader utilization of the electrochemical technique using molecular oxygen as a source of oxygen atoms, given that the latter is reduced at approximately 0.8 V/(Ag/Ag+(10-2 M)). The introduction of a fifth coordination site of the (NH) type on tetradentate Schiff base complexes did not yield the expected results, as the activation of molecular oxygen was only slightly enhanced.

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