

Five-coordinated Metal Complexes of Bis(2-hydroxy-1-naphthylideneimine-3-propyl)amine and their Reactivity Towards Dioxygen. Part I. An Electrochemical Investigation on Manganese(II), Iron(II), Cobalt(II), Nickel(II) and Copper(II) Complexes[§]

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The electrochemical behaviour in aprotic solvent of the complexes $\{M[\text{bis}(2\text{-hydroxy-1-naphthylideneimine-3-propyl)amine}]\}$, where $M = \text{Mn(II)}$, Co(II) , Fe(II) , Ni(II) and Cu(II) is reported. The complexes were prepared and characterized by elemental analysis, infrared and visible spectroscopy and magnetic susceptibility measurements. In addition the reactivity towards dioxygen of the Mn(II) , Fe(II) and Co(II) derivatives was investigated, mainly by cyclic voltammetry and gas-volumetric uptake measurements. The results indicate that the Co(II) complexes are able to add dioxygen reversibly, while Mn(II) and Fe(II) compounds undergo an irreversible oxygenation process. The pathway of the dioxygenation processes is tentatively interpreted on the basis of the electrochemical responses. The results confirm that the location of the oxidation potential allows one to predict whether a compound is able to react with dioxygen, but it is not sufficient to predict whether the dioxygenation reaction proceeds reversibly.

Introduction

During the last ten years particular attention has been reserved to metal complexes containing tetradentate and quinquedentate Schiff-base ligands which uptake dioxygen reversibly. Emphasis has been placed on their similarity to biological oxygen carriers [1] and their ability to catalyze the insertion of oxygen into organic molecules [2].

The polarization of the metal–dioxygen bond with a portion of negative charge on O_2 in the 1:1

metal–dioxygen adducts [1] is in agreement with the hydrogen bond formation between the terminal oxygen atom and the distal histidine in oxymyoglobin [3], as well as the distal amide group in some hemoprotein models [4]. On the other hand, in the structure of the reversible dioxygen adduct of $\text{N,N'-(3,3'-dipropylmethylamine)bis(salicylideneaminate)-cobalt(II)}$ the O_2 molecule is surrounded by a hydrophobic “pocket” made both by the salicylic rings of dioxygenated and non-dioxygenated complex molecules facing one another, and by benzene molecules in short contact with terminal oxygen atoms [5, 6].

Electrochemical studies have shown to be useful in the study of reactivity towards dioxygen of metal complexes [7–12]. The present electrochemical investigation on a series of five-coordinated transition metal complexes of the bis(2-hydroxy-1-naphthylideneimine-3-propyl)amine ligand has the aim of evaluating if the aromatic portions of the ligand itself play roles in the dioxygenation process resulting from both electronic and hydrophobic effects.

Experimental

2-Hydroxy-1-naphthaldehyde and manganese(II), cobalt(II), nickel(II) and copper(II) acetates were purchased from Merck and used without any further purification. Iron(II) acetate was obtained by the procedure reported in Ref. 12.

All the metal complexes have been prepared according to the procedure reported for the corresponding derivatives from salicylaldehyde [11, 14]. As manganese(II), iron(II) and cobalt(II) compounds showed reactivity towards dioxygen, all the operations for synthesis were carried out under ultra-pure nitrogen. The complexes were recrystallized from acetone or benzene, and dioxygen reactive species

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were stored under dry argon. The compounds were characterized by elemental analysis, IR and UV–visible spectroscopic measurements and magnetic susceptibility determinations (see below).

IR spectra of the complexes in solution were recorded on a Perkin-Elmer 283B spectrophotometer equipped with a 3600 Data Station. Dimethyl sulphoxide (dmsO) and toluene solutions were put in conventional cells and IR spectra were obtained by compensating with a cell of the same thickness with the solvent in the reference beam. The IR signals were accumulated by suitable software and comparisons with reference spectra were carried out by computer programs. IR spectra of solid complexes were obtained using nujol mull and KBr pellets techniques.

UV–visible absorption spectra were recorded with a Model 200 Perkin-Elmer spectrophotometer. Reflectance spectra were measured on powdered samples with a Beckman DK2 spectrophotometer.

Magnetic susceptibility values were obtained by the Faraday method, applying the appropriate corrections for diamagnetism. The effective magnetic moments μ_{eff} were calculated using the Curie equation: $\mu_{\text{eff}} = 2.83 \times (\chi_{\text{M}}^{\text{corr}})^{1/2} \times T^{1/2}$.

C, H, N analyses were obtained with the elemental analyzer Model 1102 Carlo Erba. Metal analyses were performed by atomic absorption spectroscopy with a Model 303 Perkin-Elmer spectrometer equipped with acetylene-air flame and multielement Perkin-Elmer Lamps.

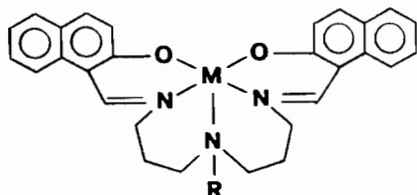
Oxygen uptake measurements were carried out as previously described [11].

The electrochemical apparatus and procedures have been described elsewhere [11]. When necessary an electrode with periodic renewal of the diffusion layer (DLPRE) was obtained by moving the solid electrode, a platinum sphere or a gold sphere freshly covered with a thin mercury layer, with a time-controlled knocker.

All potential values refer to an aqueous saturated calomel electrode (s.c.e.). The temperature was controlled at 20 ± 0.1 °C.

Results

A number of transition metal complexes [ML] have been prepared from the quinquedentate ligand derived from 2-hydroxy-1-naphthaldehyde and bis(3-aminopropyl)amine [see below: R = H(L¹); R = Me(L²); M = Mn, Fe, Co, Ni, Cu].



Analytical and magnetic data of the complexes are listed in Table I. As expected, the manganese(II), cobalt(II) and nickel(II) complexes are all high-spin at room temperature and the values of magnetic moments are close to those found for the corresponding bis(salicylideneimine-3-propyl)amine complexes [ML'], where R = H(L¹) and R = Me(L²) [14]. Spectrophotometric measurements in the visible region have shown absorption patterns very similar to those of the corresponding [ML'] derivatives, except for small shifts towards longer wavelengths of the frequencies of the peaks. These data allow us to assume all the derivatives under study to have a five-coordinated structure with the metal centers in a high-spin configuration.

In dmsO solution, both [CoL¹] and [CoL²] undergo at a mercury microelectrode an anodic process which in cyclic voltammetry gives responses similar to that reported in Fig. 1.

Controlled potential coulometric tests and cyclic voltammetric data at different scan rates indicate that in both cases an uncomplicated one-electron quasi-reversible charge transfer is involved in the anodic process.

In cyclic voltammetry the two cobalt(II) complexes also display cathodic responses similar to those reported in Fig. 2.

As can be seen two one-electron successive reduction steps are operative, formally attributable to Co^{II}/Co^I and Co^I/Co⁰ redox changes. The analysis of responses at different scan rates indicates that the less cathodic process involves a quasi-reversible charge transfer complicated by coupled following chemical reactions. Experiments at different depolarizer concentrations allow us to state that a first-order irreversible chemical reaction follows the charge transfer. A rough evaluation of the lifetime of the electro-generated Co^I complex can be accomplished from the anodic to cathodic peak current ratio, i_p^a/i_p^c .

The more cathodic process is less reproducible as regards its directly associated re-oxidation peak, hence an accurate analysis of responses at different scan rates has not been performed.

In Table II the electrochemical parameters of the electrode processes relevant to cobalt(II) complexes are reported, together with those for all the complexes studied. Formal electrode potentials E^{o'}, assumed equal to the reversible half-wave potentials, have been computed as the average of the cathodic (or anodic) peak potential and the directly associated anodic (or cathodic) peak potential, in the likely hypothesis that transfer coefficient values range from 0.3 to 0.7.

The electrochemical behaviour of [NiL²] in dmsO solution is qualitatively similar to that reported above for cobalt(II) complexes, in that an uncomplicated one-electron quasi-reversible charge transfer is present in the anodic scan at a platinum microelectrode,

TABLE I. Analytical and Magnetic Data for the [ML] Complexes.

[ML]	% Calculated				% Found				μ_{eff} (B.M.)
	C	H	N	M	C	H	N	M	
[MnL ¹]	68.25	5.53	8.53	11.17	68.37	5.36	8.25	11.60	5.47(18 °C)
[MnL ²]	68.79	5.77	8.30	10.86	68.54	5.70	7.93	11.21	5.56(19.5 °C)
[FeL ¹]	68.13	5.52	8.52	11.32	68.90	5.30	8.10	10.70	
[FeL ²]	68.67	5.76	8.28	11.01	68.41	5.77	7.70	11.40	
[CoL ¹]	67.70	5.48	8.46	11.88	67.03	5.56	7.98	11.42	4.06(18 °C)
[CoL ²]	68.25	5.73	8.23	11.55	67.90	5.53	7.73	11.20	4.18(18 °C)
[NiL ¹]	67.73	5.49	8.47	11.83	67.10	5.32	7.12	11.33	3.09(19.5 °C)
[NiL ²]	68.28	5.73	8.23	11.51	67.94	5.84	7.94	11.88	3.32(19.5 °C)
[CuL ¹]	67.07	5.43	8.38	12.69	67.23	5.74	8.46	12.20	
[CuL ²]	67.63	5.68	8.16	12.35	67.00	5.45	7.80	11.85	

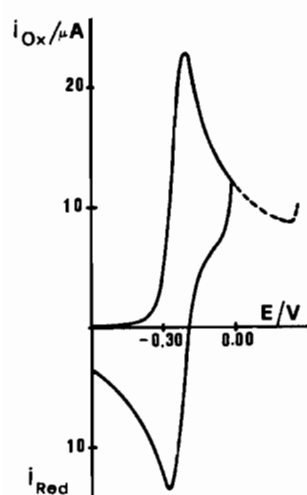


Fig. 1. Cyclic voltammogram response of a dmsol solution containing [CoL²] (1.83×10^{-3} mol dm⁻³) and [NET₄][ClO₄] (0.1 mol dm⁻³). Mercury working microelectrode. Scan rate 0.2 V s⁻¹. Anodic scan.

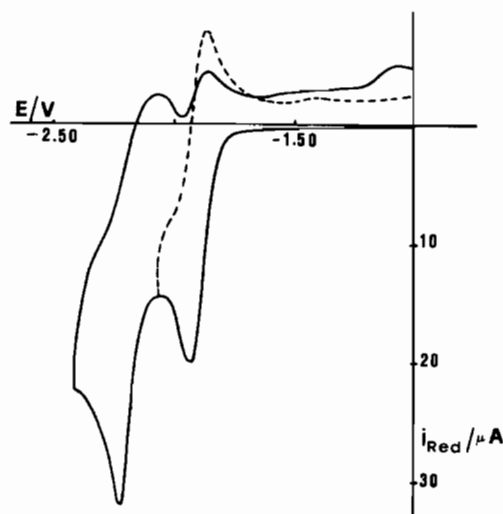


Fig. 2. Cyclic voltammograms recorded on a dmsol solution containing [CoL²] (1.83×10^{-3} mol dm⁻³) and [NET₄][ClO₄] (0.1 mol dm⁻³). Mercury working microelectrode. Scan rate 0.2 V s⁻¹. Cathodic scan.

TABLE II. Significant Parameters for Cathodic and Anodic Behaviour of Complexes [ML].

[ML]	$E_{\text{III/II}^{\circ'}}$ /V	$E_{\text{II/I}^{\circ'}}$ /V	$t_{1/2}[\text{M(I)complex}]/\text{sec}$	$E_{\text{PI}0}/\text{V}$
[CoL ¹]	-0.37	-1.97	1	-2.25*
[CoL ²]	-0.23	-1.90	5	-2.15*
[NiL ¹]	+0.35	-1.78	0.5	-2.18*
[NiL ²]	+0.40	-1.76	4	-2.36*
[CuL ¹]	+0.75*	-1.11	—	-1.30**
[CuL ²]	+0.86*	-1.16	—	-1.24**
[MnL ¹]	-0.31	-2.09	—	-2.29*
[MnL ²]	-0.31	-2.08	—	-2.23*
[FeL ¹]	-0.32			
[FeL ²]	-0.27			

*Peak potential value at 0.2 V s⁻¹.

**Peak potential value at 2 V s⁻¹.

and two subsequent one-electron charge-transfer steps are operative in the cathodic scan at a mercury microelectrode. Also in this case an irreversible first-order chemical reaction follows the less cathodic process, but in this case from the cyclic voltammetric picture it is possible to identify free Ni^{I} ions as a product of this reaction [15].

$[\text{NiL}^{\text{I}}]$ gives rise to the same cathodic behaviour, but the anodic behaviour is somewhat different. In fact on the basis of both cyclic voltammetric responses at different scan rates and controlled potential coulometry it must be concluded that an anodic process is involved in which a chemical reaction is interposed between two one-electron charge transfers (e.c.e. mechanism). It seems plausible that both the metal center and the ligand are involved in the anodic process. It is however sufficient to use scan rates of $1-2 \text{ V s}^{-1}$ to prevent the complications following the first charge transfer.

Table II reports the redox parameters of nickel(II) complexes.

In dmsO solution, the anodic cyclic voltammetric responses of both $[\text{CuL}^{\text{I}}]$ and $[\text{CuL}^{\text{II}}]$ at a platinum electrode show an oxidation peak, to which no re-reduction peak is directly associated even at the highest scan rate (50 V s^{-1}). In addition the electrochemical features are typical for a totally irreversible one-electron charge transfer.

In the cathodic scan at a mercury electrode, the behaviour of such complexes shows a single reduction peak attributable to a two-electron process at slow scan rates, which however splits into two cathodic peaks at increasing scan rates ($v > 1 \text{ V s}^{-1}$). In these conditions it is possible to note that the first charge transfer (formally attributable to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ step) is quasi reversible in character, while the more cathodic one (formally due to the $\text{Cu}^{\text{I}}/\text{Cu}^0$ reduction) is irreversible. The different degree of reversibility of the two processes accounts for the splitting of the peak at high scan rates. The closeness of the two processes prevents any accurate computation of the half-life of the Cu^{I} complex species primarily electro-generated.

The significant parameters for copper(II) complexes are reported in Table II.

The anodic oxidation at a mercury microelectrode of dmsO solutions of both $[\text{MnL}^{\text{I}}]$ and $[\text{MnL}^{\text{II}}]$ shows in cyclic voltammetry an oxidation peak to which a reduction peak is directly associated.

On the basis of coulometric tests and cyclic voltammetric data at different scan rates this anodic process must be attributed to an uncomplicated one-electron quasi-reversible charge transfer.

The cathodic scan at a mercury electrode shows two reduction processes very close to each other, which cannot be studied accurately. These processes, as shown in Table II, have been formally assigned to $\text{Mn}^{\text{II}}/\text{Mn}^{\text{I}}$ and $\text{Mn}^{\text{I}}/\text{Mn}^0$ reduction steps.

As in the case of the above described compounds, $[\text{FeL}^{\text{I}}]$ and $[\text{FeL}^{\text{II}}]$ undergo an anodic oxidation process in dmsO solution at a mercury electrode which involves a one-electron quasi-reversible charge transfer. On the contrary, ill-defined cathodic processes are present at potential values more negative than -2.1 V .

Discussion

On the basis of the reduced basicity of tertiary amines it is expected that the II/III metal ion oxidation will be favoured and the II/I reduction disfavoured for $[\text{ML}^{\text{I}}]$ derivatives compared to $[\text{ML}^{\text{II}}]$ derivatives. Table II shows this to be true, except for the oxidation of Mn^{II} derivatives and the reduction of Cu^{II} derivatives. In the latter case it is possible that the evaluation of the formal potentials is affected by the cited closeness of the two cathodic steps. In the former case the insensitivity of Mn^{II} derivatives within 10 mV to the substitution of the proton of the 3,3'-diaminodipropylamine backbone with a methyl group may be supported by the fact that for similar compounds such as $[\text{Mn}^{\text{II}}\text{L}'^{\text{II}}][\text{NCS}]$ and $[\text{Mn}^{\text{II}}\text{L}'^{\text{I}}][\text{NCS}]$ the effect also lies within $10-20 \text{ mV}$ [16].

In this connection, since the ligands studied here can be considered as the product of the fusion of an aromatic six-membered ring to the L'^{I} and L'^{II} ligands, it is interesting to compare the electrochemical parameters of the complexes of the two classes of ligands.

Table III reports the data relevant to $[\text{ML}'^{\text{I}}]$ derivatives [11, 12].

As can be noted the same trends as for $[\text{ML}]$ derivatives hold, except for Ni^{II} compounds where unexpectedly $[\text{NiL}'^{\text{I}}]$ is more reducible than $[\text{NiL}'^{\text{II}}]$.

The comparison of Tables II and III indicates that the complexes $[\text{ML}]$ are more easily oxidized than $[\text{ML}'^{\text{I}}]$, in agreement with the fact that an aromatic ring is electron-donating compared to hydrogen, electron-donating substituents favouring the oxidation of the central metal(II) ion [11, 12].

It must also be noted that in both cases the M^{I} complexes of L'^{II} ligand are more stable than those of the corresponding L'^{I} ligand.

A comparison of the redox process $+2/+3$ in the gas-phase and in solution can be performed by comparing the third ionization energy of the elements with the above reported oxidation potentials.

Figure 3 shows that third ionization energies* of the metal and oxidation potentials of the corresponding $[\text{ML}^{\text{II}}]$ derivatives do not correlate linearly (dashed line, correlation coefficient = 0.67). However by applying the appropriate corrections for the gain

*Throughout this paper: $1 \text{ eV} \approx 1.60 \times 10^{-19} \text{ J}$.

TABLE III. Significant Parameters for the Anodic and Cathodic Behaviour of Complexes [ML'].

[ML']	$E_{III/II}^{\circ}/V$	$E_{II/I}^{\circ}/V$	$t_{1/2}[M(II)complex]/sec$	$E_{pI/O}/V$
[CoL ¹]	-0.27	-2.08	1	-2.40*
[CoL ²]	-0.14	-1.95	5	-2.32*
[NiL ¹]	+0.41	-1.68	0.05	-2.50*
[NiL ²]	+0.44	-1.76	1	-2.53*
[CuL ¹]	+0.84*	-1.06	3	-1.50*
[CuL ²]	+0.71	-1.02	8	-1.46*
[MnL ¹]	-0.21 ^a			
[MnL ²]	-			
[FeL ¹]	-0.29			
[FeL ²]	-0.25			

*Peak potential value at 0.2 V s^{-1} . ^aRef. 17.

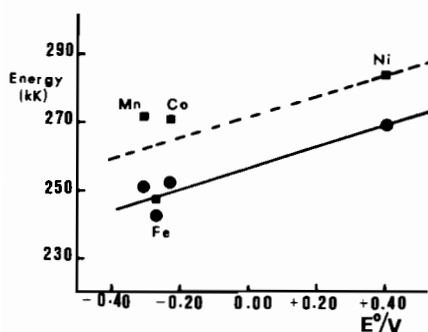


Fig. 3. Third ionization energies vs. the oxidation potentials of [ML²] derivatives, where M = Fe, Co, Mn, Ni (■). Values corrected for c.f.s.e. (●).

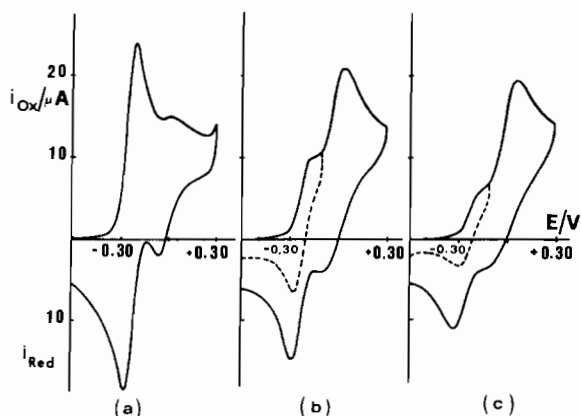


Fig. 4. Cyclic voltammetric behaviour of a dmso solution of [CoL²] ($1.83 \times 10^{-3} \text{ mol dm}^{-3}$) and [NET₄][ClO₄] (0.1 mol dm^{-3}) upon oxygenation. After bubbling air for: 3 min (a), 15 min (b), 30 min and longer (c). Mercury working microelectrode. Scan rate: 0.2 V s^{-1} .

in energy due to crystal field stabilization a reasonably good linear trend holds (solid line, correlation coefficient = 0.93), although solvation energies of the divalent and trivalent ions have not been taken in consideration.

These results seem to suggest that in complexes of trigonal bipyramid stereochemistry the gain in crystal field stabilization energy (c.f.s.e.) experienced in redox changes follows the order $d^7/d^6 \approx d^5/d^4 > d^8/d^7 \gg d^6/d^5$ [12].

The Oxygenation Reaction Studied Electrochemically

One of the aims of the electrochemical studies on complexes potentially able to uptake dioxygen is to correlate the oxidation potentials with the capability to react with dioxygen [1, 17].

On the basis of previous studies on five-coordinate complexes with O₂N₃ donor set in dmso solution [11, 12, 17], it is possible to state that metal(II) complexes with II/III oxidation potentials more positive than about 0 V do not react with dioxygen. A further step should be to identify a range of oxidation potentials where the complexes add dioxygen reversibly.

In agreement with the previous statement neither [NiL¹] and [NiL²] nor [CuL¹] and [CuL²] react with dioxygen. On the contrary cobalt(II) complexes in dmso solution do react with dioxygen.

The effect of addition of dioxygen to [CoL²] solution on the anodic cyclic voltammetric behaviour is schematically represented in Fig. 4.

As can be seen the starting Co^{II}/Co^{III} peak system is replaced by a new anodic system located at $E_p = 0.05 \text{ V}$. After bubbling air for 30 min. the reaction is at equilibrium; in fact, changes in the voltammetric picture are no longer detectable. By bubbling nitrogen for 30 min. the initial anodic voltammetric picture is substantially restored.[§] After the bubbling of air, the peak height of the unreacted amount of cobalt(II) complex (or its limiting current in d.c. voltammetry at DLPRE) allows the calculation of the equilibrium constant for the oxygenation reaction if

[§] Indeed d.c. voltammetry at DLPRE shows that about 7% of the starting cobalt(II) complex is oxidized at the corresponding cobalt(III) form.

such an equilibrium is infinitely slow with respect to the voltammetric time scale [11]. The closeness of the two anodic systems prevents an accurate analysis at different scan rates. However in consideration of the time required to reach the equilibrium and of the behaviour of the structurally similar $[\text{CoL}^2]$ [11], it seems reasonable to assume the oxygenation reaction to be infinitely slow with respect to the voltammetric oxidation. At 20 °C, experiments performed by using both air ($p_{\text{O}_2} \cong 152$ Torr) and a 10% mixture of N_2/O_2 ($p_{\text{O}_2} = 76$ Torr) gave a K_{O_2} value of $(1.0 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$. As expected [11], the value is higher than that of $[\text{CoL}^2]$ [$(3.1 \pm 0.4) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$] in view of the electron-donating property of the fused aromatic ring.

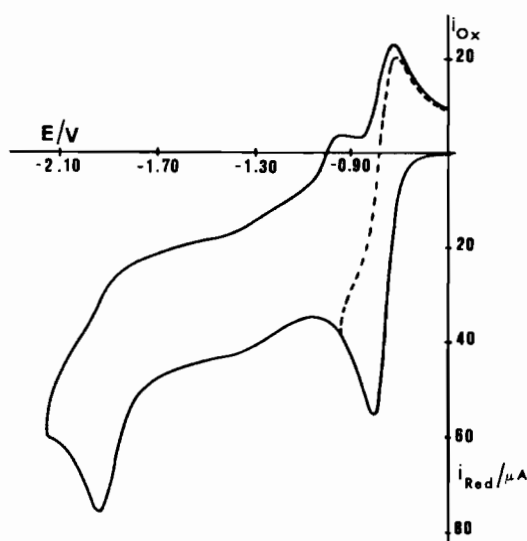


Fig. 5. Cyclic voltammograms recorded at a mercury micro-electrode on a dmsol solution containing $[\text{CoL}^2]$ ($1.83 \times 10^{-3} \text{ mol dm}^{-3}$) and $[\text{NEt}_4][\text{ClO}_4]$ (0.1 mol dm^{-3}) after bubbling air for 30 min. Cathodic scan at 0.2 V s^{-1} .

Figure 5 reports the cathodic cyclic voltammetric response after the reaching of the oxygenation equilibrium.

A significant feature is that the cathoanodic system relevant to the $\text{O}_2 \xrightleftharpoons{+e^-} \text{O}_2^-$ process ($E_{1/2} \cong -0.76 \text{ V}$) gives an i_p^a/i_p^c ratio equal to 0.87. This indicates that in solution are present species able to react to some extent with electrogenerated superoxide ions.

By bubbling nitrogen the initial cathodic response regenerates.

The addition of oxygen to $[\text{CoL}^1]$ solutions causes somewhat different effects. In the same experimental conditions described above the following features were observed:

(a) after bubbling air the cathoanodic system O_2/O_2^- shows an i_p^a/i_p^c ratio of about 0.5, which

indicates an involvement of superoxide ions notably higher than that observed in the case of $[\text{CoL}^2]$;

(b) the subsequent bubbling of nitrogen to purge from uncoordinated dioxygen does not restore completely the initial voltammetric picture, in that the starting cobalt(II) complex regenerates only to an extent of about 30%; the remaining oxygenated product undergoes an oxidation process at $E^{\circ'} = -0.01 \text{ V}$ and a few reduction processes, the best shaped of which is located at $E^{\circ'} = -0.91 \text{ V}$.

Manganese(II) complexes are also able to uptake dioxygen in dmsol solution.

In the cited experimental conditions, the addition of dioxygen to $[\text{MnL}^1]$ shows that:

a) after bubbling of dioxygen the electrogenerated superoxide ions notably react with species from the oxygenation reaction, since the i_p^a/i_p^c ratio for the cathoanodic system O_2/O_2^- reaches the value of 0.44;

(b) the subsequent bubbling of nitrogen does not restore the starting voltammetric picture. D.C. voltammetry at a mercury DLPRE gives a cathodic wave at an $E_{1/2}$ value of -0.31 V , equal to the anodic one of $[\text{MnL}^1]$, having a limiting diffusion current about one-half of the latter one. The remaining oxygenated product undergoes anodic oxidation at $E^{\circ'} = +0.01 \text{ V}$ and an ill-defined cathodic reduction at $E_p \cong -0.7 \text{ V}$.

$[\text{MnL}^2]$ behaves in the same manner. In fact electrogenerated superoxide ions are involved to the same extent ($i_p^a/i_p^c = 0.45$); as final products one can identify $[\text{MnL}^2]^+$ for about 50%, the remaining being a product oxidizable at $E^{\circ'} = -0.02 \text{ V}$ and reducible at $E^{\circ'} = -0.80 \text{ V}$.

Finally iron(II) complexes also react with dioxygen. In the above cited oxygenation conditions it can be observed that:

a) after addition of air, the i_p^a/i_p^c ratio relevant to the O_2/O_2^- process is respectively equal to unity in the case of $[\text{FeL}^2]$, and to 0.74 in the case of $[\text{FeL}^1]$. This indicates that in the case of $[\text{FeL}^2]$, species in solution are not able to react with electrogenerated superoxide ions in the voltammetric time scale;

b) the subsequent bubbling of nitrogen shows that in both cases neither the starting iron(II) complex is restored nor are appreciable amounts of the corresponding iron(III) complex formed. Figure 6 illustrates the anodic behaviour of the oxygenated compound of $[\text{FeL}^2]$ at a platinum microelectrode.

As can be noted the oxygenated compound oxidizes at $E_p = +0.62 \text{ V}$ ($+0.63 \text{ V}$ in the case of $[\text{FeL}^1]$) with a charge transfer followed by a chemical reaction leading to $[\text{FeL}^2]^+$. It is interesting to note that the reduction process of the oxygenated compound also occurs, both at a platinum and a mercury electrode, with a quasi-reversible charge transfer process located at $E_{1/2} = -1.03 \text{ V}$ (-1.28 V in the case of $[\text{FeL}^1]$) followed by a chemical reaction lead-

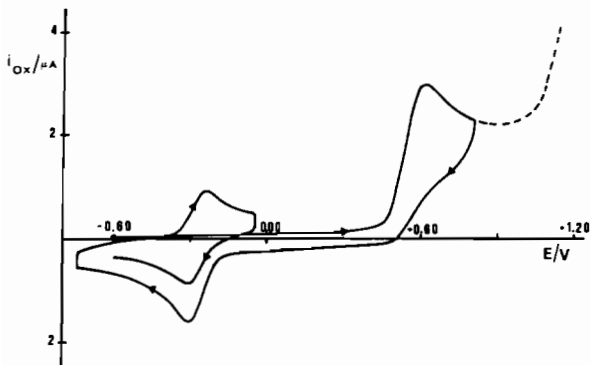
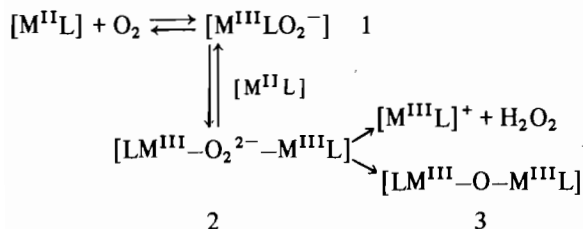


Fig. 6. Cyclic voltammetric response of a dmsO solution containing $[\text{FeL}^2]$ ($7.2 \times 10^{-4} \text{ mol dm}^{-3}$) and $[\text{NEt}_4][\text{ClO}_4]$ (0.1 mol dm^{-3}) after bubbling air for 30 min and subsequent bubbling of nitrogen for 30 min. Platinum working microelectrode. Anodic scan. Scan rate: 0.2 V s^{-1} .

ing to the starting $[\text{FeL}^2]$ species. In addition an irreversible charge transfer at $E_p = -1.80 \text{ V}$ is also present (-1.85 V in the case of $[\text{FeL}^1]$).

Let us assume that metal complexes M(II)L react with dioxygen according to the following scheme [18]:



although the formalism involved in the superoxo species 1 is unknown [19].

This scheme together with volumetric dioxygen uptake measurements may help in a tentative interpretation of the electrochemical results.

As regards manganese(II) complexes the presence of $[\text{Mn}^{\text{III}}\text{L}]^+$ has been checked and may be responsible for the reaction with electrogenerated superoxide ions [20, 21]. In addition the species which undergoes both oxidation and reduction processes would be roughly identified as the μ -peroxo species $[\text{LMn}^{\text{III}}-\text{O}_2-\text{Mn}^{\text{III}}\text{L}]$, where the oxidation involves the peroxo group and the reduction involves the Mn^{III} moiety. In this connection a μ -peroxo manganese(III) product has been assumed to form in the oxygenation of $[\text{Mn}(5\text{-NO}_2)\text{L}^1]$ [17].

As in the case of $[\text{MnL}^1]$ complexes [22], gas volumetric measurements cannot help in the identification of the oxygenated product since the uptake of O_2 continues indefinitely, indicating that the μ -peroxo compound, if formed, is a transient species.

In the case of iron(II) complexes no appreciable presence of $[\text{Fe}^{\text{III}}\text{L}]^+$ species has been revealed. This

could agree with the observed insensitivity to electrogenerated superoxide ions in the case of $[\text{FeL}^2]$.

However in the case of $[\text{FeL}^1]$ the slight effect on superoxide ions, also noted in the case of $[\text{FeL}^1]$ complexes [12], seems to indicate the formation of some amounts of $[\text{Fe}^{\text{III}}\text{L}]^+$. The electrode activity of oxygenated compounds could be assigned to one of the most common oxygenation products of iron(II) complexes, the μ -oxo dimer $[\text{Fe}^{\text{III}}\text{L}-\text{O}-\text{Fe}^{\text{III}}\text{L}]$ [23], in which the anodic oxidation of the oxo group is followed by breakage of the molecule with formation of $[\text{Fe}^{\text{III}}\text{L}]^+$, as well as the cathodic reduction of Fe^{III} center followed by breakage of the molecule with formation of $[\text{Fe}^{\text{II}}\text{L}]$.

The cathodic process at higher potentials, at least in principle, may be attributed to the second Fe^{III} center [12]. The attribution of the anodic oxidation to the oxo center rather than to the peroxo one could be justified both by the high potentials involved ($+0.62 \text{ V}$) with respect to those involving the previously supposed μ -peroxo oxidation ($\sim 0.0 \text{ V}$), and by the fact that it lies near to the potential at which hydroxide ions oxidize in dmsO ($+0.75 \text{ V}$) [24]. In addition oxygen-uptake measurements indicate that 0.22 mol of O_2 per mol of iron are consumed, confirming the dominant formation of the μ -oxo derivative (Fig. 7).

Finally the slight formation of $[\text{Co}^{\text{III}}\text{L}^2]^+$ from the oxygenation of $[\text{CoL}^2]$ accounts for the low reactivity towards electrogenerated superoxide ions. However the dominant formation of the 1:1 adduct is supported by the substantial reversibility of the oxygenation reaction and from volumetric dioxygen uptake measurements (Fig. 7). It is difficult from the electrochemical behaviour to draw some conclusions

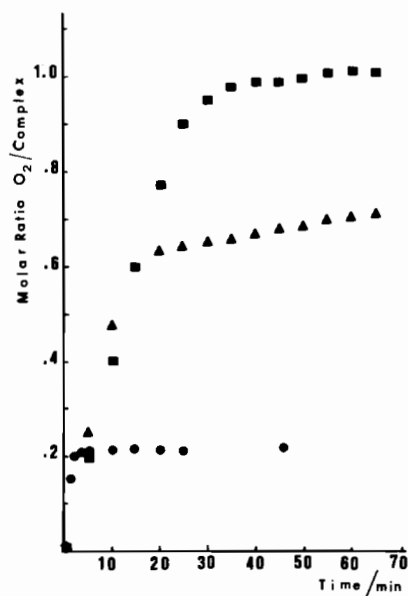


Fig. 7. Oxygen uptake measurements in dmsO solution at $21 \text{ }^\circ\text{C}$ and $P_{\text{O}_2} = 800 \text{ mmHg}$. (●) FeL^1 ; (▲) CoL^1 ; (■) CoL^2 .

on the nature of this 1:1 adduct. In fact the new anodic peak in Fig. 4 can be ascribed to the oxidation of either the cobalt(II) centre in a $[\text{Co}^{\text{II}}\text{L}^2\cdot\text{O}_2]$ formulation or to the O_2^- group in a $[\text{Co}^{\text{III}}\text{L}^2\text{O}_2^-]$ formulation; even if in the latter case one would expect to find the reduction peak relevant to the cobalt(III) centre [24] unless it is obscured by the oxygen reduction systems. However the oxygenation of the complex $[\text{CoL}^2]$ was investigated also by IR spectroscopy (other complexes showed generally too poor solubility for analytical purposes) both in dmsO and toluene solvents. The reversibility of the dioxygen uptake was monitored by running IR spectra of oxygenated and de-oxygenated solutions. Neat, medium intensity absorptions at 1139 cm^{-1} (dmsO) and 1130 cm^{-1} (toluene) were found in oxygenated solutions and completely disappeared when dioxygen was removed by bubbling nitrogen or by evacuation of the solutions. The above frequencies, which were regenerated with approximately the same intensity upon re-oxygenation of the solutions, were in agreement with O–O stretching frequencies of superoxide ion [1].

In the case of $[\text{CoL}^1]$ the formation of the following species could be inferred: the 1:1 adduct from the partial reversibility of oxygenation; $[\text{Co}^{\text{III}}\text{L}^1]^+$ (even if not put in evidence) from the reactivity towards electrogenerated superoxide ions; $\text{L}^1\text{Co}^{\text{III}}-\text{O}_2-\text{Co}^{\text{III}}\text{L}^1$ from both anodic and cathodic electrode activity of the above discussed type. In this case the 1:0.65 cobalt to oxygen ratio measured volumetrically is less significant but indicative of the formation of a mixture of oxygenated compounds. Further information on the oxygenation process will be gained by an ESR study which is now in progress. The results of this investigation will be published in Part II of this paper.

Assuming an irreversible pseudo-first order chemical reaction with respect to superoxide ions to be involved in the consumption of electrogenerated superoxide ions, from the cyclic voltammetric responses one can compute the lifetime of superoxide ion when it reacts with the above discussed species. Table IV reports the results. $[\text{Co}^{\text{III}}\text{L}^2]^+$ and $[\text{Fe}^{\text{III}}\text{L}^2]^+$ have the lowest affinity for superoxide ions. In the last case it must be noted that no significant difference holds with respect to $[\text{FeL}^1]$ and $[\text{FeL}^2]$ complexes ($t_{1/2} = 1.7\text{ sec}$) [12].

The present study together with previous reported ones [11, 12] indicate that oxygenation potentials alone do not allow us to accurately forecast the reversibility of oxygenation reactions, at least for the studied pentadentate ligands. Structural parameters are also important, in addition to the type of metal center. In fact the only oxygen carriers are the cobalt(II) complexes of the L^2 and L'^2 ligands, while those of L^1 and L'^1 ligands give partially reversible adducts, although some oxidation potentials of the

TABLE IV. Lifetime of Superoxide Ion in the Presence of $[\text{M}^{\text{III}}\text{L}]^+$ Complexes.

Species assumed to react with O_2^-	$t_{1/2}(\text{O}_2^-)/\text{sec}$
$[\text{Co}^{\text{III}}\text{L}^1]^+$	0.9
$[\text{Co}^{\text{III}}\text{L}^2]^+$	5
$[\text{Mn}^{\text{III}}\text{L}^1]^+$	0.8
$[\text{Mn}^{\text{III}}\text{L}^2]^+$	0.7
$[\text{Fe}^{\text{III}}\text{L}^1]^+$	2.3
$[\text{Fe}^{\text{III}}\text{L}^2]^+$	—

two classes are superimposable. It seems certain however that the easier the electrochemical oxidation, the stronger the tendency towards irreversible oxidation [25].

Although Fe^{II} and Mn^{II} complexes have oxidation potentials in the same range as Co^{II} ones, they do not reversibly uptake dioxygen either in the L^2 and L'^2 forms or in the L^1 and L'^1 ones.

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