Contribution from the « SNAM Progetti - L.S.R. » - S. Donato Milanese, Italy

E.S.R. Study of Cobalt-Oxygen Complexes

C. Busetto, C. Neri, N. Palladino, and E. Perrotti

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On the basis of ESR evidence a mechanism is proposed for the formation of 1:1 oxygen adducts of Cobalt(II) chelates. On the basis of the ESR signals two forms of 1:1 O_2/Co adduct are suggested to be present in the oxygenation process. The evolution from one form of 1:1 adduct to the other probably goes through a diamagnetic 1:2 O_2/Co adduct. The 1:2 O_2/Co adduct formation is a general step in the oxygenation of all Cobalt(II) chelates studied.

Introduction

The solid state oxygenation of Cobalt(II) chelates with Schiff bases generally leading to the formation of an 1:2 adduct of oxygen with cobalt in which the oxygen molecule is a bridging system between the two cobalt atoms, has been extensively studied.[1] More recently the interest has shifted to the liquid phase oxygenation of the same chelates under which conditions, depending on the nature of the chelate ligand and of the solvent, adducts with O_2/Co ratios higher than 1:2 have been isolated.[2,3] Recently we have been interested in the general process of O_2 activation by Co^{II} chelates. This fact stimulated our investigation via ESR on the factors influencing the formation of O_2/Co adducts.

The reactions studied can be indicated schematically as follows, were L indicates a Lewis base in the presence of which the oxygenation is carried out:

$$2Co^{II}_{solid} + O_2 \rightleftharpoons Co^{III}-O-O-Co^{III} \tag{1}$$

$$2Co^{II}_{solut.} + O_2 + 2L \rightleftharpoons LCo^{III}-O-O-Co^{III}L \tag{2}$$

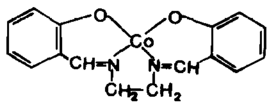
$$Co^{II}_{solut.} + O_2 + L \rightleftharpoons LCo^{II}O_2 \tag{3}$$

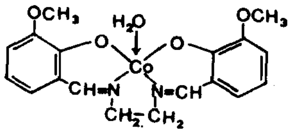
No ESR data* on Co-salen-oxygen adducts are reported in literature apart from a study on the oxygenation of Co-salen in poly(4)vinylpyridine.[7]

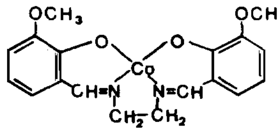
In this work an 8-line ESR signal at 3300 G in the final stage of oxygenation is attributed to a $Co-O_2$ species in which the unpaired electron is partially delocalized on the oxygen. The ESR spectra of the oxygenation product of the $[Co(CN)_5]^{3-}$ anion[8] and of Vitamin B_{12}[9,10,11] were similarly interpreted.

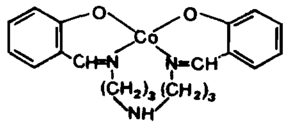
Starting with different Co-chelates and in different solvents we have followed the evolution of the oxygenation reaction carried in an ESR apparatus in order to check if the 1:2 or 1:1 O_2/Co adduct formation were part of the same process and if the final O_2/Co ratio was dependent on other factors than basicity of the ligand in one of the axial positions of the starting square-planar complexes of Co^{II} when the oxygenation was carried in presence of Lewis bases.

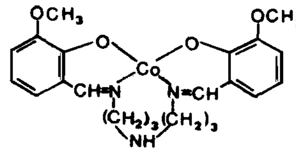
The Co^{II} complexes on which we studied the oxygenation processes are the following:

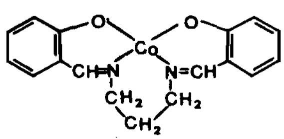

I) Co-salen


II) Co-salen(3—OCH_3) . H_2O


III) Co-salen (3—OCH_3)


IV) Co-sapr


V) Co-sapr (3—OCH_3)


VI) Co-salpropen

Experimental Section

The oxygenation reactions were carried out in a gas-volumetric apparatus in pyridine, piperidine and dimethylsulfoxide as solvents, using concentrations ranging from 10^{-3} to 10^{-2} *M*, and temperatures from 20°C to 50°C.

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* While this paper was being written three papers from Basolo *et al.*[4,5,6] have appeared reporting ESR studies of $Co/O_2 = 1:1$ adducts.

[1] (a) M. Calvin, R.H. Bailes, W K. Wilmarth, *J. Am. Chem. Soc.*, *68*, 2254, (1946). (b) C.H. Barkelew and M. Calvin, *J. Am. Chem. Soc.*, *68*, 2257 (1946). (c) W.K. Wilmarth, S. Aranoff, and M. Calvin, *J. Am. Chem. Soc.*, *68*, 2263 (1946). (d) M. Calvin and C.H. Barkelew, *J. Am. Chem. Soc.*, *68*, 2267 (1946). (e) E.W. Hughes, W.K. Wilmarth, and M. Calvin, *J. Am. Chem. Soc.*, *68*, 2273 (1946).

[2] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (A), 1969, 946.

[3] H.P. Fritz and W. Gretner, *Inorg. Nucl. Chem. Lett.*, *3*, 141 (1967).

[4] A.L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, *92*, 55 (1970)

[5] B.N. Hoffman, D.L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, *92*, 61 (1970).

[6] D.L. Diemente, B M. Hoffman, and F. Basolo, private communication, in press.

[7] A. Misono, S. Koda, and J. Uchida, *Bull. Chem. Soc. Jap.*, *42*, 580 (1969).

[8] J.H. Bayston, E.D. Looney, and M.E. Winfield, *Aust. J. Chem.*, *16*, 557 (1963).

[9] J.H. Bayston, N.K. King, E.D. Looney, and M.E. Winfield, *J. Am. Chem. Soc.*, *91*, 2775 (1969).

[10] G.N. Schrauzer and I.P. Lee, *J. Am. Chem. Soc.*, *90*, 6541 (1968).

[11] G.N. Schrauzer and L.P. Lee, *J. Am. Chem. Soc.*, *92*, 1551 (1970).

Oxygen was allowed to react with the solution of Co-chelate in a thermostated vessel under magnetic stirring and samples of the solution were withdrawn at every 5% of total oxygen absorbed as referred to the 1:1 adduct formation. ESR spectra were then taken by freezing the sample at temperatures ranging from 113°K to 297°K, directly in the ESR apparatus. This procedure was carried on until no more oxygen absorption was observed. Before the reaction went to about 50% of oxygenation no ESR spectra could be observed at temperatures higher than the freezing point of the solvent. At the final stage an ESR spectrum can be observed even at room temperature (Figure 1e).

Area measurements on each ESR signal were performed using a double cavity and were compared with a sample of copper sulphate. A Varian V 4502-11 was used. Temperature was controlled through the Varian accessory.

Reagent grade solvents were treated to a water content below 10 p.p.m.

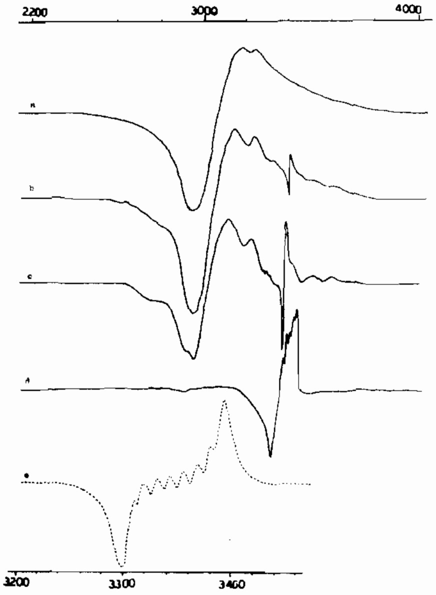


Figure 1. Evolution of Oxygenation process: *a*) Initial spectrum; *b*) Spectrum to about 30% of oxygenation; *c*) Spectrum to about 50% of oxygenation; *d*) Final oxygenation product at 113°K; *e*) Final oxygenation product at 297°K. *Experimental conditions*: *a*) Modulation Amplitude (M.A.) 200; Signal Level (S.L.) 200; Temperature (T) 113°K; *b*) M.A. 320; S.L. 250; T=113°K; *c*) M.A. 400; S.L. 630; T=113°K; *d*) M.A. 100; S.L. 200; T=113°K; *e*) M.A. 160; S.L. 400; T=298°K

Results

The ESR spectra at the various steps of oxygenation are reported in Figure 1: those spectra refer to chelate (II). In the same experimental conditions very similar results were obtained with the other chelates giving an 1:1 adduct with oxygen as the final oxygenation product (see Table I). The ESR spectra of the chelates studied are in agreement with the ESR data reported in literature for other Co^{II} low spin complexes.

No spectra are observable above the freezing point of the solutions. By raising the temperature from 113°K to 220°K the intensity and resolution of the ESR signal are gradually lost. In this temperature range the spectral resolution is concentration dependent. At the lower limit of concentration (10^{-3} *M*) a well resolved 8-line signal is observable (Figure 2) with a $g_{\parallel}$ value of 2.02 and an $A_{\parallel}$ value of 94.4 G due to the interaction of the unpaired electron with the ^{59}Co nucleus.

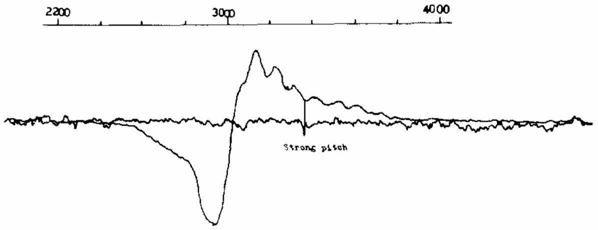


Figure 2. ESR spectrum (113°K) of starting Co^{II} salen at [Co] = 10^{-3} *M*.

Experimental conditions: M.A. 300; S.L. 250; T=113°K. Measurements were performed using a double cavity and referred to the g value of the strong picht.

Co=10^{-3}*M* in pyridine $A_{\parallel}=94.433$ $g_{\parallel}=2.022$

In the case of the d^7 high-spin[1d] compounds (IV and V), a broad signal with a substantial evidence of hyperfine structure is present at 2000 G. Generally the spectra of the initial chelates show no dependence on the nature of solvent. When the reaction is followed by taking the ESR spectra at the end of each intermediate oxygenation step, as reported in the experimental section, a progressive decrease of the intensity of the 3000 G signal is initially observed (Figures 1,a,b,c) together with an increase of spectral resolution.

In the intermediate steps of oxygenation two signals appear: a) an 8-line signal at 3300 G which can be observed also at room temperature ($g_{iso}=2.027$, $A_{iso}=$ 13 G) and b), a narrow singlet signal of amplitude of about 10 G and $g_{iso}=2.00$; the intensity of the latter signal decreases when the temperature is raised in the range 113°K - 220°K.

The narrow signal reaches a maximum (Figure 3b) at oxygenation levels of about 50% (referred to the 1:1 ratio) to decrease continously at higher oxygen percents. At the final step (100% oxygenation, 1/1 ratio) the only signal present is the new 8-lines at 3300 G (Figures 1,d,e). Area measurements show the same intensity for both the initial and the final signal.

The appearing of the narrow intermediate signal seems to be conditioned by the presence of exchangeable protons either in the ligands or in the solvents. In fact in the case of (III), for which no narrow signal is present in anhydrous solvent, the addition of small quantities of water, t-butyl alcohol, piperidine, causes the radical form to appear.

Table I lists the cases in which the narrow singlet and the 8-lines 3300 G signals are observed, together with the O_2/Co ratios in the final oxygenated products, as deduced from independent gas-volumetric determin-

Table I. Oxygenation of Cobalt(II) Chelate Compounds and and ESR Results

Compound	Solvent	Final Ratio O_2/Co	Co(3300)G_{signal})	Radical
Co(Salen)(I)	Py	0.5	Present	—
	py—$(CH_3)_3COH$	0.5	Present	—
	Pipd	1	Present	Present
Co-salen(3,OCH_3)—H_2O(II)	Py	1	Present	Present
Co—salen(3,OCH_3)(III)	Py	1	Present	—
	py—$(CH_3)_3COH$	1	Present	Present
	Pipd	1	Present	Present
	DMSO—H_2O	1	Present	Present
Co Sapr(IV)	Py	1	Present	—
	DMSO—H_2O	1	Present	Present
Co Sapr—H_2O	Py	1	Present	Present
Co Sapr(N—D) (*)	Py		Present	—
Co—sapr(3,CH_3O)(V)	Py	1	Present	—
	Py—$(CH_3)_3COH$	1	Present	Present
Co—Salpropen(VI)(—N—CH_2—CH_2—CH_2—N)		0.5	—	

Except for compound(VI) this pattern is observed for all of the Cobalt(II) complexes studied. Spectra recorded at 113°K. (*) Deuterated on the secondary nitrogen atom.

ations. In Figure 4 the evolution of the ESR spectra is reported vs. the absorbed oxygen. As observed by other authors[2] the O_2—Co bond can be broken by gentle warming of the solution of the oxygenated adduct to about 50°C.

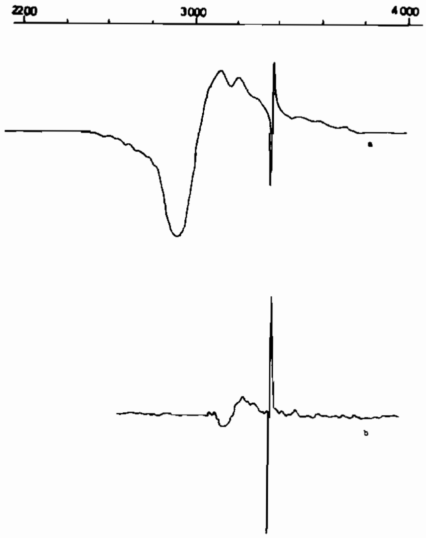


Figure 3. Evolution of the final species by warming to 323÷333°K under nitrogen. *a*) Spectrum obtained dissolving 1 : 2 O_2/Co adduct in pyridine plus *t*-butylalcohol.
Experimental conditions: *a*) M.A. 400; S.L. 620; T=113°K; *b*) M.A. 400; S.L. 600; T=113°K.

This reverse process can be followed by taking ESR spectra of intermediate steps of deoxygenation. In these conditions we observe the decrease of the 3300 G 8-lines signal, and the build up of the narrow singlet line, that reaches a maximum (Figure 3b) to desappear in the final deoxygenation stage. When the deoxygenation is complete only the 8-lines spectrum at 3000 G of the deoxygenated chelate can be observed in the ESR spectra.

We have also verified by ESR measurements the reactions:

$$LCo^{II}O_2 + LCo^{II} \rightleftharpoons LCo^{III}\text{—O—O—}Co^{III}L \tag{4}$$

$$LCo^{III}\text{—O—O—}Co^{III}L + O_2 \rightleftharpoons 2LCo^{II}O_2 \tag{5}$$

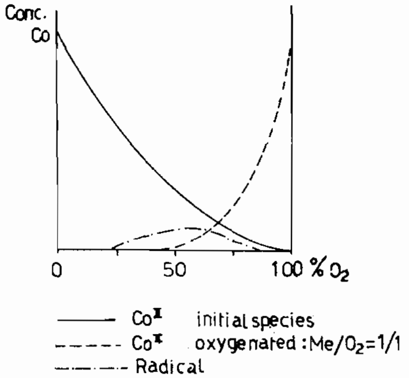


Figure 4. Evolution of the various species as function of absorbed, oxygen.

In the case of reaction (4) the formation of the narrow signal is observed together with the decrease of the Co^{II} signals at 3000 G and 3300 G of the reacting species. The appearence of the narrow signal from species whose ESR spectra does not show other signals besides the initial 8-lines at 3000 and 3300 G respectively and in absence of other oxygen sources, is a further confirmation of the relevant nature of the singlet in the oxygenation process. Reaction (5) was followed gas-volumetrically and absorption of another mole of oxygen per mole of compound was found thus showing that under the experimental conditions equilibrium (5) is largely shifted to the right.

In order to exclude further the presence of side reactions we have dissolved the 1:2 adduct in anydrous pyridine under N_2 in presence of traces of t-butyl alcohol. According to the equilibrium relation (b) we observed both the signal of the radicalic species and of the starting Co^{II} complex (Figure 3a).

Over the period of a week no spectral variations are observed showing that if the radical species is due to the solvent it is then a very stable one unlikely to be present in our system. If at the end of this period we resume the oxygenation there is absorption corresponding to the quantity just needed to reach the 1:1 adduct formation, showing no consumption of oxygen for other reactions at the expense of impurities; the final ESR spectra is the same as obtained in the normal oxygenation process.

Discussion

The following considerations on the singlet narrow signal:

1) When it reaches the maximum intensity its area is comparable with that of the 8-line signal.

2) Its lifetime (a very long one).

3) Its behaviour during the direct and reverse oxygenation processes and in the course of reaction (4), lead us to believe that, more than to an impurity, the narrow singlet signal must be attributed to a different form of O$_2$/Co adduct.

We assume then that two O$_2$/Co adducts in the 1:1 ratio are present. One, giving rise to the narrow signal, can be indicated as Co^{III}–O–O$^\bullet$, in which the Cobalt is in the +3 valency state and in which the unpaired electron is completely delocalized on the oxygen, as shown by the absence of any hyperfine structure due to the Co-nucleus. The other, giving rise to the 8-line 3300 G signal, is indicated as Co^{II}O$_2$, in which the unpaired electron is only partially localized on the Co atom. This species is observed in the final stage of oxygenation (O$_2$/Co ratio 1:1) and corresponds to the species found by other authors[7] and discussed by Basolo and coworkers.[4,5,6] We suppose that the oxygenation of the Co^{II} complexes takes place according to the following scheme:

$$LCo^{II} + O_2 \rightleftharpoons LCo^{III}–O–O^\bullet \qquad (a)$$

$$LCo^{III}–O–O^\bullet + LCo^{II} \rightleftharpoons LCo^{III}–O–O–Co^{III}L \qquad (b)$$

$$LCo^{III}–O–O–Co^{III}L + O_2 \rightleftharpoons 2LCo^{II}O_2 \qquad (c)$$

In the above scheme L Co^{III}–O–O$^\bullet$ should correspond to the narrow singlet signal at 3300 G; L Co^{II}O$_2$ should correspond to the 8-line signal at 3300 G.

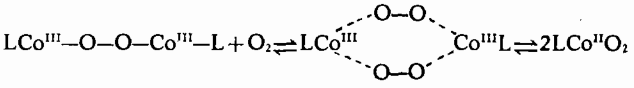
We can justify this scheme on the following considerations. We can intuitively suggest that the first step in the oxygenation process is the formation of an 1:1 O$_2$/Co adduct as indicated in (a). This adduct reacts very rapidly with a still unconverted Co^{II} species according to reaction (b) giving the diamagnetic 1:2 adduct. Accordingly we observe initially the decrease of the signal of the starting Co^{II} chelate together with an increase in the resolution due to magnetic dilution of the system (Figure 1b).

No radical signal due to LCo^{III}–O–O$^\bullet$ is observed in the first oxygenation steps because this species reacts rapidly with the starting Co^{II} chelate which is still the main species present. The narrow singlet signal begins to appear only at the intermediate oxygenation levels, when the 1:2 adduct reaches a maximum of concentration (Figures 1c, 3a). The final 8-line 1:1 adduct begins to build up at oxygenation levels higher than 50%, when reaction (c) is more important on the ground of the concentration of the various species in solution.

We believe on this evidence that the 1:1 O$_2$/Co adduct formation is a general step in the oxygenation processes. The difference in O$_2$/Co ratio in the final products (see Table I) depends on various factors of which the most general could be the solubility of the various species (mainly L Co^{III}–O–O–Co^{III} L) in equilibrium.

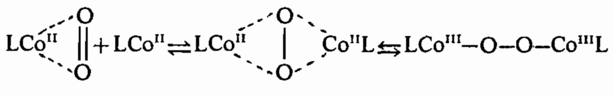
The fact that the observation of the narrow signal seems to be conditioned by the presence of protic agents could be justified by some kind of stabilizing interaction LCo^{III}–O–O$^\bullet$ - - - - HR leading to a cage effect around the radical and to a decrease of electron density on the oxygen. Against this interpretation it could be argued that the narrow signal is due to radicalic species following the oxidation of the solvent or of the ligand. The reported results (see experimental section) rule out such consideration.

The evolution of the 1:2 to the 1:1 final adduct could proceed by interaction of the 1:2 adduct with oxygen through an intermediate tentatively formulated as:



$$LCo^{III}–O–O–Co^{III}–L + O_2 \rightleftharpoons LCo^{III}\begin{matrix} O–O \\ O–O \end{matrix}Co^{III}L \rightleftharpoons 2LCo^{II}O_2$$

The reaction of the 1:1 adduct with Co^{II} accounts for the reversibility of the oxygenation process via decomposition of LCo^{II}O$_2$ to give some LCo^{II} that could react with another LCo^{II}O$_2$ following the path



$$LCo^{II}\begin{matrix} O \\ \| \\ O \end{matrix} + LCo^{II} \rightleftharpoons LCo^{II}\begin{matrix} O \\ | \\ O \end{matrix}Co^{II}L \leftrightarrows LCo^{III}–O–O–Co^{III}L$$

The equilibrium LCo^{III}–O–O–Co^{III}L $\rightleftharpoons$ LCo^{II} + LCo^{III}–O–O$^\bullet$ accounts for the reappearence of the radical form in the reverse reaction (Figure 3a).