Inorganica Chimica Acta, 103 (1985) 105–110

Five-coordinated Metal Complexes of Bis(2-hydroxy-1-naphthylideneimine-3-propyl)amine and their Reactivity towards Dioxygen.
Part II. EPR Evidence for the Role of the Solvent on the Stability of the $Co(III)O_2^-$ Species*

ARTURO COLLIGIANI**, CALOGERO PINZINO

Istituto di Chimica Fisica dell'Università di Pisa and Istituto di Chimica Quantistica ed Energetica Molecolare, C.N.R., 56100 Pisa, Italy

GIORGIO VALENTINI

Istituto di Chimica Organica Industriale dell'Università di Pisa, 56100 Pisa, Italy

RENZO CINI, PIERO ZANELLO and ARNALDO CINQUANTINI

Dipartimento di Chimica dell'Università di Siena, 53100 Siena, Italy

Received November 5, 1984

Abstract

Dioxygen adducts of bis(2-hydroxy-1-naphthylideneimine-3-propyl)amine cobalt(II) complexes, in which either a hydrogen atom or a methyl group are present on the amino nitrogen atom of the ligand, were obtained and studied by EPR spectroscopy. The study shows an unexpectedly strong effect of the solvent (toluene or dimethylsulfoxide) on the stability of the adducts. The EPR study carried out at room and lower temperatures gave indications that an intramolecular process plays a major role in the decay of the cobalt–oxygen species.

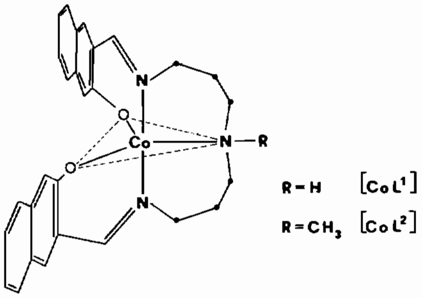
Introduction

An ideal dioxygen carrier can be generally defined as a system which meets the following requirements: ease of reaction with dioxygen to produce a stable derivative (adduct); quantitative release of the bound dioxygen under mild conditions with re-generation of the initial system.

These features obviously imply that a dioxygen carrier can work repeatedly without any loss of its properties.

In this context, transition metal complexes with tetradentate ligands have been extensively studied [1b, 2] due to their interest as dioxygen carriers in biochemistry [3] and as catalysts in organic chemistry [4, 5].

On the contrary, complexes with pentadentate ligands have so far received only minor attention, the examples reported in the literature being concerned with some derivatives of salicylaldehyde with triamines [6–17] and some keto-iminates [18].



The paramagnetic $Co(II)O_2^-$ species generated by addition reaction of bubbled dioxygen to pentadentate Co(II) complexes have been studied by the EPR technique, in order to evaluate the effect of the naphthyl group on the stability of the adduct. The two Co(II) precursors, indicated here as $[CoL^1]$ and $[CoL^2]$, are easily obtainable by condensation of 2-hydroxy-1-naphthaldehyde and bis(3-aminopropyl)amine and *in situ* reaction with cobalt(II) acetate [12]. The two d^7 high-spin unoxygenated precursors [12] did not show any EPR signal under experimental conditions, due to the extremely short relaxation times of the Co(II) species [9, 19].

Purging the oxygenated solution with argon caused the disappearance of the EPR signal, which can be regenerated (but not quantitatively), by subsequent oxygenation of the system, and so on in further cyclic treatments.

---

*A brief summary of this work was presented at the 1st Int. Conf. on Bioinorg. Chem., Florence (Italy), June 13–17, 1983, see ref. 1a.

**Author to whom correspondence should be addressed.

0020-1693/85/$3.30

We have observed that under constant dioxygen pressure, the EPR signal of our complexes showed a progressive decrease with time, due to a partial transformation of the EPR-active species into non-paramagnetic ones. This feature can be regarded as being the major process responsible for the incomplete reversibility of the investigated complexes as dioxygen carriers.

In Part I of this paper [12] the use of the electrochemical approach did not allow to completely clarify this last feature. Because for other Co(II) complexes it was demonstrated that the solvent could play an important role for the dioxygen uptake reaction [20], we decided to investigate whether the solvent was also involved in the decay process of the oxygenated species. This feature is particularly interesting in that for these pentadentate complexes, contrary to tetradentate derivatives, the solvent cannot be coordinated *'trans'* to the dioxygen molecule so that the effect of the reaction medium should, in principle, play a minor role.

Experimental

EPR spectra were obtained at X-band using a Varian E-112 Century Line spectrometer. The H_0 magnetic field was modulated at 100 KHz and standardized against an external reference of DPPH. Spectra at low temperatures were recorded by means of a Varian variable-temperature control apparatus.

Ultrapure dioxygen (Matheson, UHP 99.998%) was fed through a capillary tube directly into the sample tube put inside the microwave cavity. The bubbling of the gas was carefully controlled and maintained at 2–5 ml/min in order to prevent solvent evaporation. The same procedure was followed for the bubbling of the inert gas which purged away the dioxygen from solution, and consequently from the $Co(III)O_2^-$ species. Ultrapure argon (Matheson, UHP 99.999%) or alternatively commercial nitrogen containing O_2 as contaminant (500 ppm) was used. The concentrations of toluene (Tol) and dimethylsulfoxide (Dmso) solutions were around 10^{-4} mol dm^{-3}. Both solvents were carefully purified, dried [21] and degassed (Ar gas) before dissolution of the complexes.

Results

Figure 1 shows two typical EPR spectra of Tol solutions of $[CoL^1]$ and $[CoL^2]$ after dioxygen bubbling at room temperature. The signal of $[CoL^1]$-oxygenated species clearly consists of the eight-line pattern characteristic of a nuclear spin $I = 7/2$, whilst the signal of the $[CoL^2]$-oxygenated species is less resolved, due to the possible exchange between isomeric forms. The g_{iso} values (2.037 and 2.022) are very close to those reported in the literature for other pentadentate complexes with ligands quite different from the naphtalene ring [18]. The EPR signal was absent for freshly prepared [CoL] ($L = L^1, L^2$) solutions before the dioxygen bubbling, both for Tol and Dmso solutions.

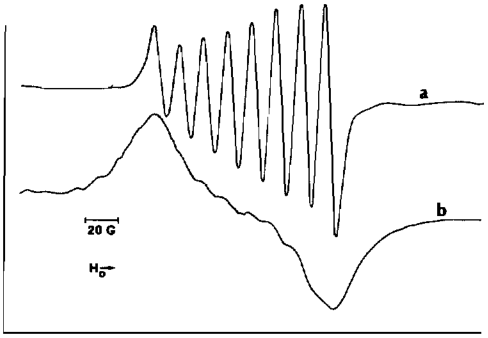


Fig. 1. Isotropic solution EPR spectra of the [CoL] oxygen adducts in toluene at room temperature. (a) $[CoL^1]O_2$; (b) $[CoL^2]O_2$.

During the dioxygen bubbling the intensity of the EPR signal reached the maximum within few minutes, due to the formation of the $Co(III)O_2^-$ species.

For Tol and Dmso solutions of [CoL], saturated with dioxygen and allowed to stand under O_2, the intensity of the maximized EPR signals decreased with time according to exponential laws (see Fig. 2) consistent with first order kinetics. Table I reports the values of decay constants. No solid matter was found in EPR tubes at the end of the run, excluding the fact that the observed phenomena might depend on the separation of solid products.

TABLE I. Values of Decay Constants for $[CoL^1]$ and $[CoL^2]$ Dioxygen Adducts in Tol and Dmso Solutions at Room Temperature.

Oxygen adduct	Decay constant[a] (min)
$[CoL^1]O_2$–Tol	247.5 ± 9.8
$[CoL^2]O_2$–Tol	145.6± 3.4
$[CoL^1]O_2$–Dmso	90.6 ± 2.0
$[CoL^2]O_2$–Dmso	204.5 ± 6.8

[a] Defined as the time in which the intensity of the EPR signal reduces of 1/e factor.

The values reported here were obtained through a non-linear best-fitting of the experimental points reported in Fig. 2. The intensity changes with time of the EPR signals were monitored for each line of spectra of type a in Fig. 1. The decay constant values measured for each line are substantially the same for every spectrum, and values reported in Table I represent an average of the measurements.

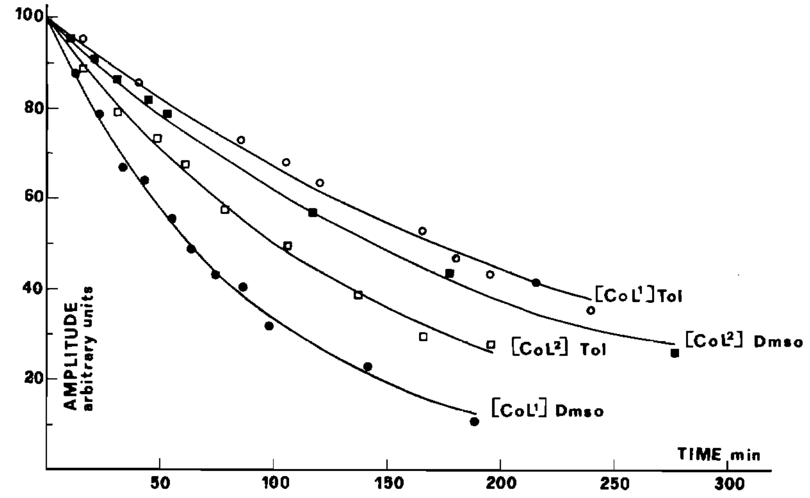


Fig. 2. Time-decay amplitude of the EPR spectra of $[CoL^1]O_2$ and $[CoL^2]O_2$ in toluene and dimethylsulfoxide at room temperature. Continuous lines are the best-fitting curves obtained by a non-linear exponential treatment of the experimental points.

For spectra of type b (Fig. 1) the changes of intensity with time were monitored by following the decrease of the peak-to-peak amplitudes of the two more pronounced features at low and high values of H_0.

Figure 3 shows EPR spectra recorded at decreasing temperatures for the oxygen adducts of $[CoL^1]$ in Tol. The hyperfine structure, still visible at −20 °C (spectrum a), progressively decreases on decreasing temperature; at −80 °C (spectrum d) the signal is so broad that it cannot be revealed at lower temperatures.

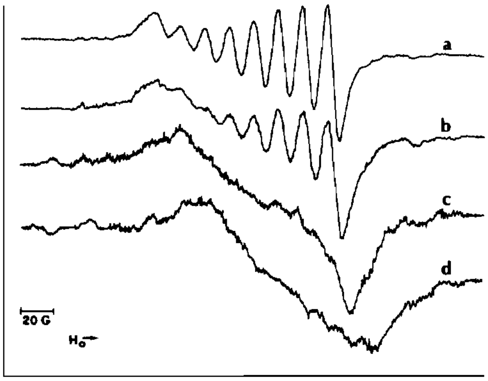


Fig. 3. Isotropic toluene solution EPR spectra of $[CoL^1]O_2$ at decreasing temperature. (a) −20 °C, (b) −40 °C, (c) −60 °C, (d) −80 °C.

Figure 4 shows EPR spectra for the oxygen adduct of $[CoL^2]$ in Tol, recorded under the same experimental conditions. In this case the hyperfine structure is practically absent in the spectrum recorded at room temperature, and increases progressively on decreasing temperature down to −60 °C (spectrum c). On further lowering the temperature below −60 °C (spectrum d), the hyperfine structure disappears again. EPR spectra recorded at around the temperature of liquid nitrogen gave frozen-glass type signals, analogous to other spectra already reported in the literature [9, 18] (n.b. the freezing point of Tol is −95 °C).

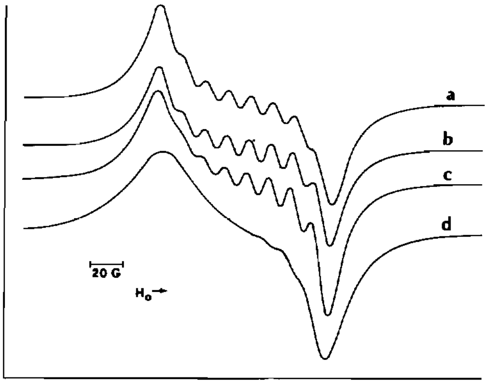


Fig. 4. Isotropic toluene solution EPR spectra of $[CoL^2]O_2$ at decreasing temperature. (a) −20 °C, (b) −40 °C, (c) −60 °C, (d) −80 °C.

Discussion

EPR spectra reported in Fig. 1 do not give a quantitative evaluation of the percentage of the [CoL] complex which has been transformed into the $[CoL^1]O_2$ and $[CoL^2]O_2$ adducts. However, electrochemical measurements whose results have been reported in Part I [12] have shown that in Dmso solution about 65% of the $[CoL^1]$ is transformed into $[CoL^1]O_2$, whereas about 100% of

$[CoL^2]O_2$ is present after 30 min of dioxygen bubbling.

We assume that Tol solutions also behave in the same manner, because we have observed that the rate of dioxygen uptake, and consequently the time necessary for the maximization of the EPR signal, do not differ substantially for Tol or Dmso solutions. This also suggests that the rate of adducts formation depends mainly on the time necessary for equilibration of the dioxygen concentration in solution. This is apparently in contrast with some recent studies [20] which demonstrate that the solvent may exert an important influence also on the kinetic of the oxygen uptake.

However, this EPR study being mainly devoted to a better understanding of the mechanism through which the decay of oxygenated adducts takes place, the starting amount of adducts was not of particular interest.

Figure 2 and Table I allow us to evaluate immediately how the oxygen adducts under study exhibit good properties as oxygen carriers at room temperature, having decay times that are almost one order of magnitude longer than those of the already-reported keto-iminate pentadentate adducts [18]. For the latter, in which a variety of substituents can be present on the propylamine chains, it is possible to calculate decay constants of the order of 10 min at 0 °C. Measurements were not performed at room temperature because the decay process was too rapid.

For the adducts studied by us there is a substantial qualitative agreement between EPR data and those data discussed in Part I. The presence of only 65% of $[CoL^2]O_2$ after a 30 min dioxygen bubbling can be reasonably explained by taking into account that during the oxygenation process, the progressively formed oxygenated species decay with a decay constant of 90.6 min. Accordingly, $[CoL^1]O_2$ can be determined almost quantitatively due to its higher decay constant (204.1 min).

Data reported in the same Table also indicate that the solvent exerts a strong influence on the decay process, so that the relative stability of the two adducts is reversed in two different solvents. $[CoL^2]O_2$ exhibits a decay constant of 145.6 min and $[CoL^1]O_2$ of 247.5 min in Tol solutions. These findings suggest that attention must be paid when discussing dioxygen adducts as effective dioxygen carriers, because the behaviour of the oxygenated species may be different in different solvents, as far as reversibility is concerned.

Data reported in Table I show that the $[CoL^1]O_2$ adduct is the more reversible one in Tol solution, whereas $[CoL^2]O_2$ adduct is the more effective dioxygen carrier in Dmso solution. In Tol solutions both adducts showed decay times much longer when the temperature was lowered to 0 °C. However, we have not performed quantitative measurements.

Because the two types of solvents used in our experiments strongly differ as regards polarity, electronic affinity and other chemical and physical properties, long decay times can be mainly attributed to the molecular structure of our complexes.

In particular we can identify in the naphthalene ring, fused in the molecule of the complex, the main chemical reason of the higher stability of these systems in comparison with other systems in which aromatic rings are bound as substituents to the propylamine chains. Also the analogous adduct obtained with salicylaldehyde as ligand seems to be characterized by very long decay times, although quantitative data have not been reported [2, 22].

On the other hand it is very easy to assume that the presence of a benzene or naphthalene ring fused in the molecule may affect strongly the electronic distribution in the complex, so that the reactivity of the bound dioxygen is influenced.

We can now re-examine our results in the light of some of the commonly proposed mechanisms for the decay of the oxygenated species [23].

First of all, the possibility that the decay of the adducts implies the loss of the coordinated O_2 followed by regeneration of the starting, EPR inactive [CoL] complex can be ruled out because no EPR signal can be obtained by bubbling dioxygen into a solution of a completely decayed system. Moreover, the small amount of adduct which is formed when commercial nitrogen is bubbled into a solution of [CoL], due to O_2 impurity, decays with the same decay constant as the adduct formed by oxygen bubbling, the same occurring when air is used as oxygenating agent. We therefore argue that decay is not controlled by the concentration of dioxygen in solution.

The possibility of the reaction of an adduct molecule with a [CoL] species to give a diamagnetic, peroxo-bridged dimeric complex can also be discarded, although such a mechanism has been already invoked to explain the decay of other dioxygen adducts [23]. We have observed that the measured decay constants are completely reproducible for runs carried out with different [CoL] concentrations, this ruling out the possibility that an intermolecular process involving the $[CoL]O_2$ species is operative.

We suggest that our results substantiate the hypothesis that the dioxygen initially coordinated to the cobalt complex can be utilized in an intramolecular process by which the coordinated ligand or the metal itself are irreversibly oxidized giving EPR inactive final products, according to an already-proposed mechanism [24].

The strong influence of the solvent on the decay process seems to suggest that the solvent is also involved in the oxidation mechanism. Its role might be accomplished either by simple steric hindrance for the intramolecular migration of the dioxygen, or by a direct influence of its polarity and electronegativity on the electronic distribution on ligand.

The changes observed in our EPR spectra upon decreasing the temperature (Figs. 3 and 4) were the same as observed in ref. [18], where they were related to the possible existence of an interconversion mechanism between *'cis'* and *'trans'* isomeric forms with respect to the amino nitrogen atom of the propylamine chain in the equatorial plane. If interconversion rates are much lower or comparable to the EPR time scale, a relative sharpening or broadening of the spectrum must be expected.

The temperature-dependence of the EPR signals of our complexes was analogous to that observed for keto-iminato cobalt systems with quite different ligands [18]. If the interconversion hypothesis is correct, our results imply that the nature of substituents on the side-chains of the ligand play a very slight role (if any) even when they are very bulky ligands, as naphthalene fused rings. The only substituent which seems to be important is the one present on the amino-nitrogen atom in the equatorial plane. Analogously to the previously cited complexes [18], the dioxygen adduct of [CoL^2], having a methyl group on the amino nitrogen atom, at room temperature shows an unresolved EPR signal whose resolution increases upon decreasing temperature (Fig. 4, spectra a, b and c). The [CoL^1] adduct, in which the methyl group is substituted by a proton, shows opposite behaviour being the resolution of the EPR spectrum lower upon decreasing temperature (Fig. 3, spectra a, b, c and d).

It seems unlikely that such different interconversion rates should be attributed simply to the different steric hindrance of the methyl group with respect to protons. In ref. [18], dioxygen adducts having a phenyl substituent on the amino nitrogen atom did not give any EPR signal at room temperature and only a broad unresolved signal at −63 °C.

The main effect of the substituent of the amino nitrogen atom might be exerted on the delocalization of the unpaired electron of the $Co-O_2$ system on the other orbitals used by the cobalt in the complex, this affecting in turn the g_{iso} value. This value is related to the value of the spin–orbit splitting, to the splitting of the $2p_g$ orbitals of the dioxygen, and consequently to the value of the electronic relaxation times [25].

A marked difference of the relaxation times can result in EPR spectra characterized by quite different shapes and intensities, depending on the nature of the substituent and temperature. From our data and from data reported for keto-iminato complexes [18] on average the g_{iso} value for adducts containing the proton on the amino nitrogen ($g_{iso} \simeq 2.35$) is higher than for those having a methyl group in the same position ($g_{iso} \simeq 2.25$). Unfortunately, for systems containing the phenyl group, the g_{iso} values have not been reported.

The different solvents used in our experiments do not seem to affect the shape of the EPR signals at room temperature. Upon decreasing the temperature care must be paid on the interpretation of the EPR behaviour because other physical factors may be considered. For example, both spectra d of Figs. 3 and 4, recorded at −80 °C, show a broadened shape which might depend on the increased viscosity of the solvent.

Conclusions

Our results suggest that the nature of the pentadentate ligand may exert a very strong effect in Co(II) system when used as oxygen carriers, especially on the stability of the system towards autooxidation of the ligand.

Special attention must be paid, however, to the reversibility of a dioxygen adduct, because of the sometimes unexpected role that the solvent may play in the related processes.

References

1 (a) R. Cini, P. Zanello, A. Cinquantini, A. Colligiani, and G. Valentini, *Inorg. Chim. Acta, 79,* 203 (1983); (b) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev., 79,* 139 (1979).

2 R. H. Niswander and L. T. Taylor, *J. Am. Chem. Soc., 99,* 5935 (1977).

3 J. E. Lyons, in 'Fundamental Research in Homogeneous Catalysis', Plenum, New York, 1977.

4 G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976).

5 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev., 39,* 295 (1981).

6 B. H. Hoffman, T. Szymanski and F. Basolo, *J. Am. Chem. Soc., 97,* 673 (1975).

7 R. H. Niswander and L. T. Taylor, *Inorg. Chem., 15,* 2360 (1976).

8 B. S. Tovrog, D. J. Kitco and R. S. Drago, *J. Am. Chem. Soc., 98,* 5144 (1976).

9 R. H. Niswander and L. T. Taylor, *J. Magn. Reson., 26,* 491 (1977).

10 P. Zanello, R. Cini, A. Cinquantini and P. L. Orioli, *J. Chem. Soc., Dalton Trans.,* 2159 (1983).

11 P. Zanello, R. Cini and A. Cinquantini, *Inorg. Chim. Acta, 74,* 89 (1983).

12 P. Zanello, R. Cini, A. Cinquantini, A. Colligiani, C. Pinzino and G. Valentini, *Inorg. Chim. Acta, 88,* 105 (1984).

13 R. S. Drago and B. B. Corden, *Acc. Chem. Res., 13,* 353 (1980).

14 R. S. Drago, J. P. Cannady and K. A. Leslie, *J. Am. Chem. Soc., 102,* 6014 (1980).

15 R. S. Drago, J. Gaul, A. Zombeck and D. K. Straub, *J. Am. Chem. Soc., 102,* 1033 (1980).

16 A. Zombeck, R. S. Drago, B. B. Corden and J. H. Gaul, *J. Am. Chem. Soc., 103,* 7580 (1981).

17 P. E. Doan and R. S. Drago, *J. Am. Chem. Soc., 104,* 4524 (1982).

18 M. D. Braydich, J. J. Fortman and S. C. Cummings, *Inorg. Chem., 22,* 484 (1983).

19 (a) A. Abragam and B. Bleaney, in 'Electron Paramagnetic Resonance of transition Ions', Clarendon, Oxford,

1970; (b) R. Orbach and H. J. Stapleton, in S. Geschwind (ed.), 'Electron Paramagnetic Resonance', Plenum, New York, 1972, p. 121.
20 D. P. Rillema, C. M. Wicker and R. D. Morgan, *J. Phys. Chem.*, *87*, 5151 (1983).
21 D. D. Perrin, W. L. F. Almarego and D. R. Perrin, 'Purification of Laboratory Chemicals, 2nd edn.', Pergamon, 1983, p. 229.
22 R. H. Niswander and L. T. Taylor, *Inorg. Chim. Acta*, *18*, L7 (1976).
23 E. Kimura, M. Kodama, R. Machida and K. Ishizu, *Inorg. Chem.*, *21*, 595 (1982).
24 E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, *6*, 2043 (1967).
25 B. M. Hoffman, D. L. Diemente and F. Basolo, *J. Am. Chem. Soc.*, *92*, 61 (1970).