Dioxygen Addition to Cobalt(II) Complexes with a Binucleating Macrocyclic Ligand

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The behaviour of $Co(NO_3)_2$ and 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane aqueous solutions towards molecular dioxygen has been examined over a large range of ratios *R* between the ligand and cobalt(II) concentrations and in the presence of different types of anions at high concentrations. Both binuclear, $Co_2L(O_2)(OH)$, and mononuclear, $Co(H_mL)(O_2)$, peroxo complexes are formed depending on the value of *R*. The formation of the binuclear species is rapid, while that of the mononuclear complexes is slow. Phosphate anions (Y) enter into the bi- and mono-nuclear peroxo complexes, giving $Co_2L(O_2)Y$ and $CoL(O_2)Y$ species. The kinetics of dioxygen uptake under various experimental conditions has been studied and reaction schemes are proposed.

Much attention has been devoted for some time to the reaction of dioxygen addition to mononuclear cobalt(II) complexes with simple [1] or overstructured [2] ligands, both in order to understand some aspects of the behaviour shown by haemoproteins in the processes of dioxygen uptake and release, and to obtain synthetic systems which might be used for the separation of dioxygen from air, for the activation of dioxygen or as artificial blood. Only in the last decade attention has been turned also to dioxygen adducts of binuclear cobalt(II) complexes with binucleating macrocyclic ligands. In addition to this interest in the formation of peroxo complexes from these Co_2L species, they could be good models of non-haem biological dioxygen carriers such as haemerythrins [3] and haemocyanins.[4] It is known that these latter natural dioxygen carriers contain two metal ions for each subunit. However, their structure as well as the mechanism of uptake and the release of dioxygen are far less well known than for the haemoproteins myoglobin and haemoglobin.

After a first study concerning the formation of peroxo and superoxo complexes of a dicobalt cofacial diporphyrin,[5] attention was turned to the dioxygen adducts of dicobalt complexes with binucleating macrocyclic ligands such as 7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]-pentatriacontane,[6] 7,19-dioxa-1,4,10,13,16,22-hexaazacyclotetracosane [7] and hexaaza tetra(Schiff bases).[8] In all cases, dibridged μ-peroxo-μ-hydroxo complexes are formed which differ noticeably from each other in their affinity for dioxygen, as well as in their resistance to irreversible autoxidation. In the case of 7,19-dioxa-1,4,10,13,16,22-hexaazacyclotetracosane moreover, in the presence of appropriate species Y (*e.g.* bidentate anions such as oxalate [9] and mesoxalate [10] or organic molecules such as catechol [11] or 4,5-dihydroxybenzene-1,3-disulfonic acid [12] triply bridged μ-peroxo-μ-hydroxy-μ-Y complexes are formed which are very interesting because they give hospitality in the same cavity to the dioxygen and to the reductant, which may react with each other.[13] In the above-mentioned studies only 24-membered macrocyclic ligands were taken into consideration and only the ratio Co:L = 2:1 was chosen. Martell [12] has in effect proposed to consider also 30-membered macrocyclic ligands such as dipyridyl[30]ane-N_6O_4, -N_{10} and -$N_4S_2O_4$. To the best of our knowledge, however, no paper on this topic has been published until now.

In this article, the formation of dioxygen adducts of the cobalt(II) complex with the 30-membered macrocyclic saturated polyamine 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane {abbreviated as [30]aneN_{10}} is reported. Studies on this system have already been carried out under anaerobic conditions and the formation of mono- and bi-nuclear species has been demonstrated.[14,15] It has also been found that, in the presence of phosphate anions, these cobalt(II) complexes can bind the anions forming cascade-like complexes.[15] Here the dioxygen uptake by this system is studied both in non-buffered and in borate- and in phosphate-buffered aqueous solutions at various pH values and over a large range of the ratio $R = c^\circ_L : c^\circ_{Co}$, where c°_L and c°_{Co} are the stoichiometric molar concentrations of [30]aneN_{10} (L) and cobalt, respectively. The study was carried out by considering: (*a*) the proton balances in non-buffered media; (*b*) binding curves for dioxygen; (*c*) UV spectra, recorded at various times, of solutions differing in the type of anions added, pH, the values of *R* and the method of preparation.

Experimental

Materials.—The salt [30]aneN_{10}·10HCl was prepared in accordance with ref. 16. A $Co(NO_3)_2$ stock solution (0.507 mol dm^{-3}) standardized by gravimetric analysis of $[Co(py)_4(NCS)_2]$ (py = pyridine) was used in all experiments. All the other chemicals were reagent products used without further purification.

Apparatus and Procedures.—Free dioxygen was determined by using a Beckman oxygen analyser (model 0260) equipped with an oxygen electrode capable of measuring oxygen concentrations up to a maximum of 199.0 ppm. The electrode was calibrated in air-saturated and in oxygen-saturated KCl (1 mol dm^{-3}) aqueous solutions.[17] The cell was designed to contain the oxygen sensor, a glass electrode for pH measurements and two openings for introducing the reagents by means of microsyringes or microburettes. It was filled, leaving no vapour space, with aqueous solutions of [30]aneN_{10} equilibrated with air or with gaseous oxygen at 1 atm (101 325 Pa) and adjusted to the selected pH value. A known amount of $Co(NO_3)_2$ stock solution was added and the concentration of free dioxygen measured at various times. In the case of non-buffered solutions of the ligand, the pH was kept constant at its starting value by adding measured amounts of a concentrated aqueous solution of NaOH. A Radiometer PHM84 pH meter

Table 1 Proton balances associated with the formation of cobalt(II) complexes with [30]aneN$_{10}$ under aerobic conditions at different R and pH values

Experiment*	pH	R_1	R	R_2
1	8.11	5.87	0.50	2.59
2	11.03	9.15	0.60	1.00
3	9.00	7.11	0.57	2.36
4	7.80	5.40	0.73	2.91
5	7.93	6.00	0.92	2.85
6	8.58	6.16	1.06	2.56
7	7.70	5.08	1.06	3.13
8	7.84	5.84	1.09	3.05
9	7.50	5.10	1.50	2.98
10	8.12	6.01	5.20	2.98

* Experiments 5, 6 and 8 were carried out in 0.1 mol dm^{-3} KNO$_3$, the others in 0.1 mol dm^{-3} NaClO$_4$ aqueous solutions at 25 °C. The following procedure was used. (*i*) Known quantities of NaOH stock solution were added to oxygenated aqueous solutions of the ligand (L = [30]aneN$_{10}$·10HCl) in order to realize the pH values reported in the second column. The values of the ratio R_1 between the moles of NaOH added and the moles m_L of ligand are given in the third column. (*ii*) Known quantities of Co(NO$_3$)$_2$ stock solution were added in order to achieve the R ($m_L : m_{Co}$) values reported in the fourth column. (*iii*) The pH was brought to its initial value by adding measured quantities of NaOH stock solution. The values of the ratio R_2 between the moles of NaOH added and the moles of cobalt are listed in the fifth column. The adjustment and the measurements of pH were made by taking into account the kinetics of the dioxygen binding reaction.

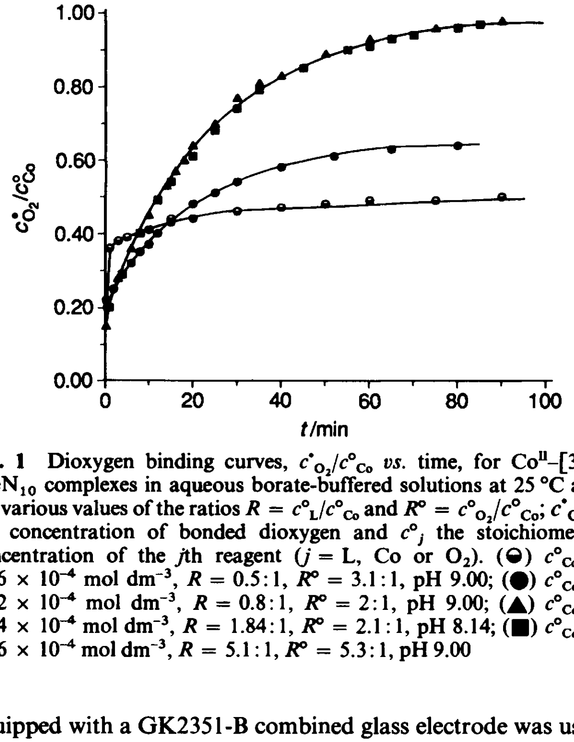

Fig. 1 Dioxygen binding curves, $c^\bullet_{O_2}/c^\circ_{Co}$ *vs.* time, for Co^{II}–[30]-aneN$_{10}$ complexes in aqueous borate-buffered solutions at 25 °C and for various values of the ratios $R = c^\circ_L/c^\circ_{Co}$ and $R^\circ = c^\circ_{O_2}/c^\circ_{Co}$; $c^\bullet_{O_2}$ is the concentration of bonded dioxygen and c°_j the stoichiometric concentration of the *j*th reagent (j = L, Co or O$_2$). (⊖) c°_{Co} = 2.96 × 10^{-4} mol dm^{-3}, R = 0.5:1, R° = 3.1:1, pH 9.00; (●) c°_{Co} = 4.12 × 10^{-4} mol dm^{-3}, R = 0.8:1, R° = 2:1, pH 9.00; (▲) c°_{Co} = 4.24 × 10^{-4} mol dm^{-3}, R = 1.84:1, R° = 2.1:1, pH 8.14; (■) c°_{Co} = 1.66 × 10^{-4} mol dm^{-3}, R = 5.1:1, R° = 5.3:1, pH 9.00

equipped with a GK2351-B combined glass electrode was used for the pH measurements.

Spectrophotometric measurements were carried out with a Perkin Elmer Lambda 6 UV/VIS spectrophotometer equipped with a rapid-mixing apparatus (Applied Photophysic model RX1000). Two procedures were used to collect the spectra and to analyse their evolution with time, namely: (*a*) known amounts of buffered oxygenated aqueous solutions of ligand were mixed with known amounts of oxygenated aqueous solutions of Co(NO$_3$)$_2$ by means of the rapid-mixing apparatus and spectra were recorded at various times in the range R = 0.5–5:1; (*b*) buffered oxygenated solutions at R = 0.5 were prepared and their spectra recorded within a few minutes of preparation; further amounts of the ligand were then added so as to produce high values of R. The spectra of these latter solutions were recorded over a large range of times.

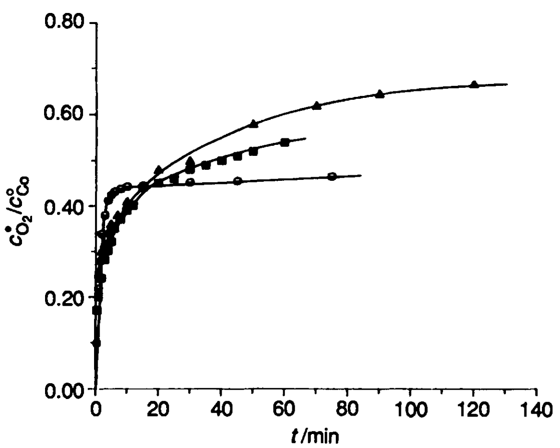

Fig. 2 Dioxygen binding curves, $c^\bullet_{O_2}/c^\circ_{Co}$ *vs.* time, at 25 °C for Co^{II}–[30]aneN$_{10}$ complexes in phosphate-buffered aqueous solutions at pH 8 and for various values of the ratios R and R°. (⊖) c°_{Co} = 12.1 × 10^{-4} mol dm^{-3}, R = 0.56:1, R° = 0.63:1, (■) c°_{Co} = 4.24 × 10^{-4} mol dm^{-3}, R = 1.49:1, R° = 2.33:1, (▲) c°_{Co} = 3.22 × 10^{-4} mol dm^{-3}, R = 5.72:1, R° = 2.77:1

Results

Proton Balances and Dioxygen Binding.—Table 1 summarizes the results of experiments carried out by measuring the amount of NaOH necessary to keep the pH constant when an aerated stock solution of Co(NO$_3$)$_2$ is added to 0.1 mol dm^{-3} KNO$_3$ or 0.1 mol dm^{-3} NaClO$_4$ aerated aqueous solutions of the ligand. These results, combined with those of dioxygen uptake, enable the following conclusions to be drawn.

(*a*) At low R values, where binuclear [Co$_2$L]$^{4+}$ (pH < 9) or [Co$_2$L(OH)]$^{3+}$ (pH > 11) species prevail under anaerobic conditions,[14] binuclear [Co$_2$L(O$_2$)(OH)] peroxo complexes are always formed in the presence of dioxygen. In effect, at R = 0.5, the ratio between cobalt and bonded dioxygen proves to be Co:O$_2$ = 2:1, furthermore, in the range pH 8–9 (experiments 1 and 3 of Table 1), the values of the ratio R_2 between the moles of NaOH added to keep the pH fixed at the initial value and moles of cobalt added (experiment 1) agree with the prevailing reaction (1). At pH 11 (see experiment 2 of Table 1), on the other hand, the value of R_2 suggests that reaction (2) is operating.

$$2Co^{2+} + H_4L^{4+} + O_2 + 5OH^- \longrightarrow [Co_2L(O_2)(OH)]^{3+} + 4H_2O \quad (1)$$

$$2Co^{2+} + HL^{+} + O_2 + 2OH^- \longrightarrow [Co_2L(O_2)(OH)]^{3+} + H_2O \quad (2)$$

(*b*) At R > 1:1, in the range pH 7.5–8.1, mononuclear complexes such as [Co(HL)]$^{3+}$ and [Co(H$_2$L)]$^{4+}$ prevail under anaerobic conditions.[15] These latter bind the dioxygen by forming mononuclear [Co(HL)(O$_2$)]$^{3+}$ and [Co(H$_2$L)(O$_2$)]$^{4+}$ complexes respectively, in accordance with the reactions (3)

$$Co^{2+} + H_nL^{n+} + O_2 + 3OH^- \longrightarrow [Co(H_mL)(O_2)]^{(n-1)+} + 3H_2O \quad (3)$$

($m = n - 3$). This assumption agrees both with the measurement of dioxygen uptake, which give, at R > 1:1, a ratio Co:O$_2$ = 1:1, and with the proton balances, which give R_2 = 3:1 in all the experiments carried out at R > 1:1 (experiments 8–10 of Table 1).

Figs. 1 and 2 reproduce, as examples, some curves for dioxygen binding at different values of R and different pH values

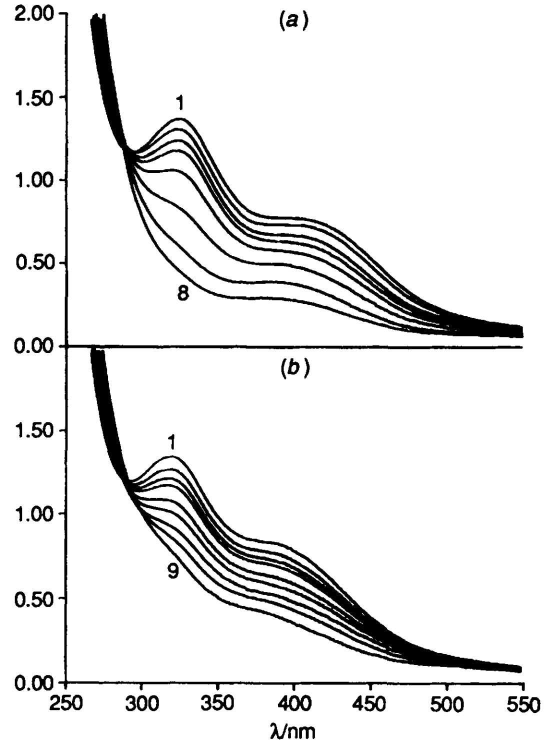

Fig. 3 Spectral evolution with time of oxygenated aqueous solutions of Co^{II}–[30]aneN$_{10}$ at 25 °C and p_{O_2} = 101 kPa. (*a*) Phosphate buffer at pH 8.0, c°_{Co} = 4.12 × 10^{-4} mol dm^{-3}, R = 0.5:1, R° = 3:1. Spectra 1–3 recorded after 1, 27, 87 min, 4–8 after 3, 7, 21, 47 and73 h. (*b*) Borate buffer at pH 9.0: c°_{Co} = 4.12 × 10^{-4} mol dm^{-3}, R = 0.5:1, R° = 3:1. Spectra 1–7 recorded after 2, 4, 6, 8, 14, 20 and 40 min, 8 and 9 after 2 and 20 h

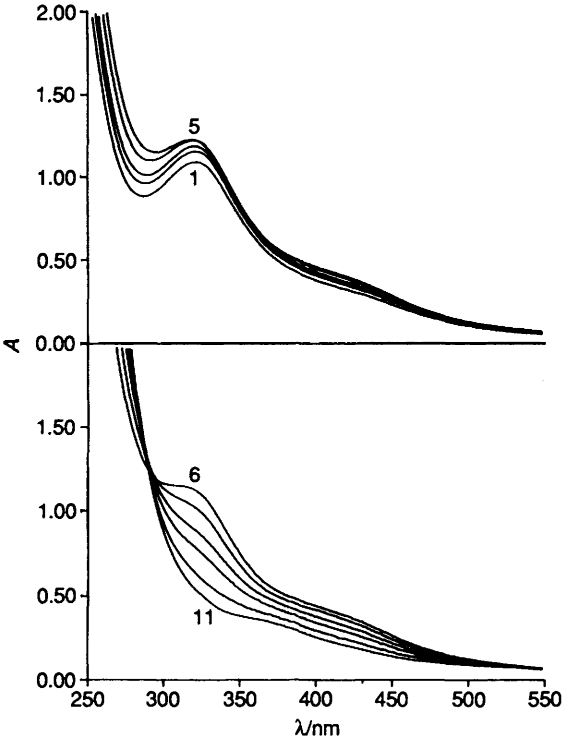

Fig. 4 Spectral evolution with time of oxygenated aqueous solutions of Co^{II}–[30]aneN$_{10}$ at 25 °C and p_{O_2} = 101 kPa. Phosphate buffer at pH 8.0, c°_{Co} = 4.12 × 10^{-4} mol dm^{-3}, R = 3:1, R° = 3:1. Spectra 1–5 recorded after 2, 4, 6, 12 and 20 min, 6–11 after 1, 2, 5, 10, 23 and 47 h

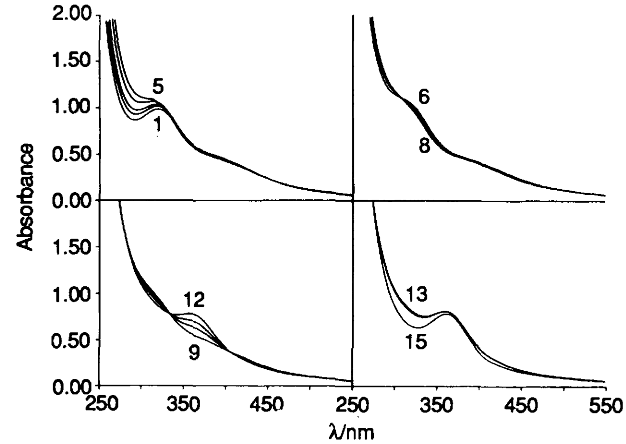

Fig. 5 Spectral evolution with time of oxygenated aqueous solutions of Co^{II}–[30]aneN$_{10}$ at 25 °C and p_{O_2} = 101 kPa. Borate buffer at pH 9.0, c°_{Co} = 4.12 × 10^{-4} mol dm^{-3}, R = 3:1, R° = 3:1. Spectra 1–5 recorded after 2, 4, 6, 12 and 21 min, 6–8 after 31, 52, 78 min, 9–12 after 2, 4, 6 and 13 h, and 13–15 after 20, 24 and 73 h

achieved by use of borate or phosphate buffers, respectively. In borate-buffered solutions at R = 0.5:1 the uptake of dioxygen is fast and the binding curves converge towards the ratio $c'_{O_2}:c^{\circ}_{Co}$ = 0.5:1, where c'_{O_2} is the concentration of bonded dioxygen and c°_{Co} is the concentration of cobalt. For R = 0.5–1:1, together with the first fast uptake of dioxygen, a second relatively slow dioxygen addition occurs which makes the $c'_{O_2}:c^{\circ}_{Co}$ ratios converge at values larger than 0.5:1. At R > 1:1 a unique process for dioxygen uptake is observed, and the corresponding curve converges at $c'_{O_2}:c^{\circ}_{Co}$ values near to 1:1. It may be deduced that, in borate aqueous solutions, at R = 0.5:1, mainly binuclear peroxo complexes are formed, while at R > 1:1 the addition of dioxygen produces mononuclear superoxo species analogously to what is found for non-buffered KNO_3 or $NaClO_4$ aqueous solutions.

Also in aqueous Na_2HPO_4–NaH_2PO_4 buffered solutions, at 0.05 mol dm^{-3} total salt concentration, a rapid dioxygen uptake is followed by a second slow step of dioxygen binding (Fig. 2). The first reaction is favoured at low R values. Under these conditions, the ratio $c'_{O_2}:c^{\circ}_{Co}$ converges towards 0.5:1. At high R values this ratio converges towards values higher than 0.5:1.

A comparison of the dioxygen binding curves for borate- and phosphate-buffered solutions at similar R (= $c^{\circ}_{L}:c^{\circ}_{Co}$) and R° (= $c^{\circ}_{O_2}:c^{\circ}_{Co}$) values shows that, in the presence of phosphate anions, the formation of the bi- and mono-nuclear peroxo complexes is slowed. Remembering that the results of pH-metric studies of formation of Co^{II}–[30]aneN$_{10}$ complexes under anaerobic conditions and in the presence of phosphate anions are consistent with the formation of complexes of a cascade-type,[15] it is reasonable to suppose that $Co_2L(O_2)Y$ and $CoL(O_2)Y$ (Y = phosphate anion) species* are formed in phosphate-buffered solutions at low and at high R values, respectively. This hypothesis is strengthened by the UV spectra which differ remarkably from those corresponding to non-buffered or borate-buffered solutions (Figs. 3–5).

The kinetic analysis of the formation of binuclear species $[Co_2L(O_2)(OH)]$ (in borate solutions) or $Co_2L(O_2)Y$ (in phosphate solutions) and of the mononuclear species $Co(H_mL)(O_2)$ (in borate) or $CoL(O_2)Y$ (in phosphate) was carried out on the basis of a simplified hypothesis suggested by the clear difference in the time required for the uptake of dioxygen leading to the formation of bi- or mono-nuclear species and by the characteristics of the evolution with time of the UV spectra of solutions prepared in two steps, first at R = 0.5:1 and then brought to R > 1:1 by the addition of the

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* The charges have been omitted owing to the difficulty in obtaining a reliable proton balance in buffered solutions.

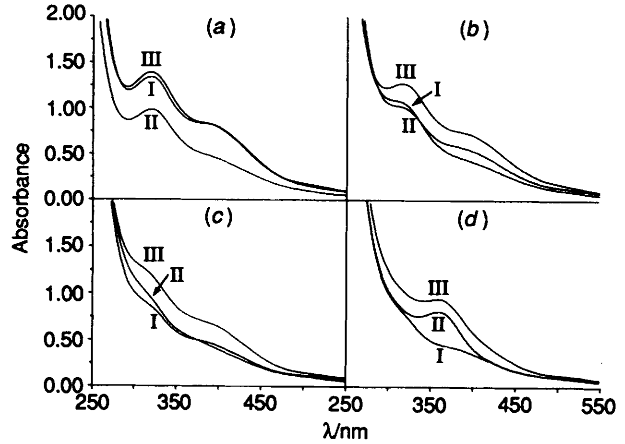


Fig. 6 Spectra of Co^{II}–[30]aneN_{10}–O_2 systems in borate-buffered solutions, (pH 9 and 25 °C) at various times t from preparation: (*a*) 2, (*b*) 20, (*c*) 140 min, (*d*) 21 h. Curves: I, $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 0.5{:}1$, $R° = 3{:}1$; II, $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 3{:}1$, $R° = 3{:}1$; III, prepared in two steps; in the first step $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 0.5{:}1$, $R° = 3{:}1$; 2 min after preparation the ligand was added in order to achieve $R = 4{:}1$ and spectra were recorded at the times t indicated

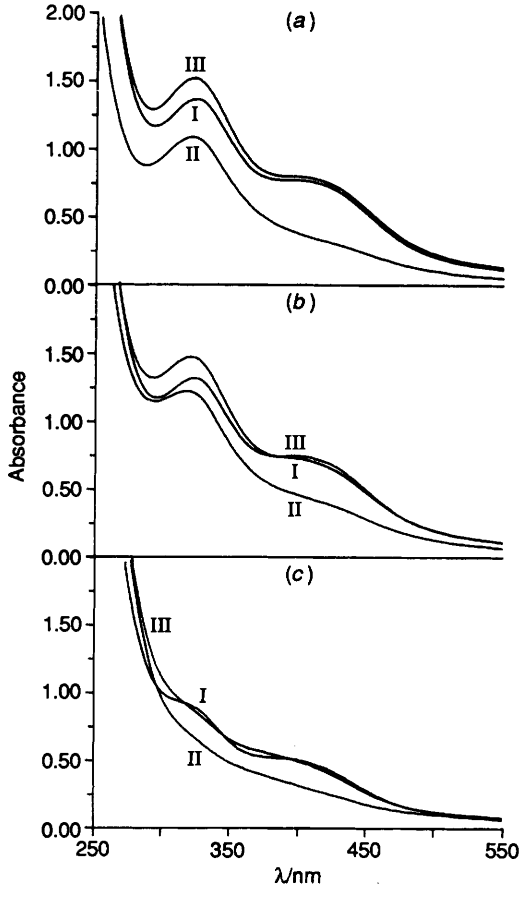


Fig. 7 Spectra of Co^{II}–[30]aneN_{10}–O_2 systems in phosphate-buffered solutions (pH 8 and 25 °C) at various times t from preparation: (*a*) 1, (*b*) 20 min, (*c*) 15 h. Curves: I, $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 0.5{:}1$, $R° = 3;1$; II, $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 3{:}1$, $R° = 3{:}1$; III, prepared in two steps, in the first step $c°_{Co} = 4.12 \times 10^{-4}$ mol dm^{-3}, $R = 0.5{:}1$, $R° = 3{:}1$, 2 min after preparation the ligand was added to the solution in order to achieve the ratio $R = 2{:}1$ and the spectra were recorded at the times indicated

ligand (see Figs. 6 and 7). In order to analyse the dioxygen binding curves, the following procedure was adopted.

(*i*) The two reactions of dioxygen uptake leading to the formation of bi- and mono-nuclear peroxo complexes were assumed to be independent of each other. For both the reactions, carried out at constant pH, a second-order rate law with respect to the $Co^{II}L$ complex and the dioxygen was assumed to be valid. Under this hypothesis, the formation of binuclear peroxo complexes [*i.e.* $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$] may be described by equation (4) where c_{O_2} is the concentration

$$dc_{O_2}/dt = -k_1(c_{O_2} - c^*{}_{O_2})c_{O_2} \qquad (4)$$

of free dioxygen at time t and $c^*{}_{O_2}$ the concentration of free dioxygen when the formation of the binuclear complexes is complete. Therefore $(c_{O_2} - c^*{}_{O_2})$ represents the total concentration of binuclear deoxygenated Co_2L or $Co_2L(Y)$ complexes at time t.

In the case of the formation of mononuclear complexes [*i.e.* $Co(H_mL)(O_2)$ or $CoL(O_2)Y$] the rate law is (5) where $c°_{O_2}$ is the

$$dc_{O_2}/dt = -k_2(c°_{Co} - 2c°_{O_2} + c^*{}_{O_2} + c_{O_2})c_{O_2} \qquad (5)$$

concentration of free dioxygen at time $t = 0$ and $c°_{Co}$ the total stoichiometric concentration of cobalt. Therefore $(c°_{Co} - 2c°_{O_2} + c^*{}_{O_2} + c_{O_2})$ is the concentration of mononuclear complexes [$Co(H_mL)$ or $CoL(Y)$] at time t.

Approximate values of k_1 and k_2 were thereafter calculated in accordance with equations (6) and (7).

$$\ln \frac{c_{O_2}}{c_{O_2} - c^*{}_{O_2}} = k_1 c^*{}_{O_2} t + x_1 \qquad (6)$$

$$\ln \frac{c_{O_2}}{c°_{Co} - 2c°_{O_2} + c^*{}_{O_2} + c_{O_2}} = k_2(2c°_{O_2} - c°_{Co} - c^*{}_{O_2})t \times x_2 \qquad (7)$$

(*ii*) The values of k_1, k_2 and $c^*{}_{O_2}$ [equations (6) and (7)] were then refined by using the criterion of best fitting to describe the dioxygen binding curves. The total amount $c^{\bullet}{}_{O_2}$ of bonded dioxygen in the Co^{II}–[30]aneN_{10} complexes has been calculated as the sum of dioxygen consumed in both reactions on the basis of equations (8)–(10). The agreement between the

$$c^{\bullet}{}_{O_2} = c°_{O_2} + c^*{}_{O_2} - c^*{}_{O_2}\frac{e^{\alpha}}{e^{\alpha} - 1} - \left(2c°_{O_2} - c°_{Co} - c^*{}_{O_2}\right)\frac{e^{\alpha'}}{e^{\alpha'} - 1} \qquad (8)$$

$$\alpha = k_1 c^*{}_{O_2} t + \ln [c°_{O_2}/(c°_{O_2} - c^*{}_{O_2})] \qquad (9)$$

$$\alpha' = k_2(2c°_{O_2} - c°_{Co} - c^*{}_{O_2})t + \ln \frac{c^*{}_{O_2}}{c°_{Co} - 2(c°_{O_2} - c^*{}_{O_2})} \qquad (10)$$

experimental and the 'best' calculated $c^{\bullet}{}_{O_2}$ data was satisfactory for any R value. This justifies both the validity of the hypothesis made about the types of the peroxo complexes and the approximation of neglecting the interaction of the two reactions of dioxygen uptake. Tables 2 and 3 summarize the kinetic data obtained for all the experiments, and give some information about the distribution of the species.

From the data of Table 2 it may be deduced that, in borate-buffered solutions, the formation of peroxo complexes by oxygen addition to Co_2L species is much faster than that of peroxo complexes corresponding to $Co(H_mL)$ protonated species; the k_2 values show a slightly increasing trend when the pH increases from 8.14 to 9.00 and to 9.97. At pH 9.00 and 25 °C, a mean value of $k_2 = 54 \pm 5$ dm^3 mol^{-1} min^{-1} is calculated for dioxygen addition in the presence of $B(OH)_4^-$ species. From the same table it can also be deduced that the rate of the first reaction of dioxygen addition, which occurs at $R < 1{:}1$, is probably close to the rate of dioxygen diffusion at

Table 2 Kinetic parameters for the binding reactions of dioxygen with Co^{II}–[30]aneN_{10} complexes in borate-buffered aqueous solutions (0.05 mol dm^{-3} sodium tetraborate) at 25 °C

$10^4c^\circ_{Co}$/mol dm^{-3}	c°_L/c°_{Co}	$10^4c^\circ_{O_2}$/mol dm^{-3}	pH	t^{*a}/min	$10^{-3}\,k_1{}^b/dm^3\,mol^{-1}\,min^{-1}$	$k_2{}^c/dm^3\,mol^{-1}\,min^{-1}$	$\alpha_1{}^d$
3.640	0.40	7.63	9.00	0.5	(8)	12	62
2.945	0.50	7.72	9.00	1	(5)	22	104
3.184	0.51	8.78	8.14	3	(2)	15	75
5.377	0.61	7.63	9.00	1	(8)	19	28
4.124	0.80	8.19	9.00	1.5	(4)	49	30
5.710	1.15	2.28	9.00	1	(30)	37	19
6.790	1.20	9.16	8.14	≈0.2	(4)	51	11
2.480	1.50	6.94	9.00	≈0.1	(7)	69	6
4.137	1.57	9.46	9.00	1	(7)	61	24
4.240	1.58	8.97	9.97	0		66	0
4.240	1.84	8.81	8.14	≈0.2		73	5
1.820	2.90	8.34	9.00	0		59	0
1.655	5.10	8.75	9.00	0		52	0
2.068	5.25	8.25	9.00	≈0.2		69	11

[a] The time at which the formation of $Co_2L(O_2)(OH)$ was assumed to be complete. [b] Refers to the formation of $Co_2L(O_2)(OH)$ complexes. The rapidity of this reaction makes it impossible to consider the reported values as true kinetic constants (see text). [c] Kinetic constant for the formation of $Co(H_mL)(O_2)$. [d] The percentage of the dioxygen which may be bonded as $Co_2L(O_2)(OH)$, evaluated as $(c^\circ_{O_2} - c^*_{O_2})/c^\circ_j$ is the reagent in deficiency (j = L or Co) and $c^*_{O_2}$ is the concentration of free dioxygen at the time t^*.

Table 3 Kinetic parameters for the binding reactions of dioxygen with Co^{II}–[30]aneN_{10} complexes in aqueous $Na_2HPO_4 + NaH_2PO_4$ buffered solutions (0.05 mol dm^{-3} total phosphate ions) at pH 8

T/°C	$10^4c^\circ_{Co}$/mol dm^{-3}	c°_L/c°_{Co}	$10^4c^\circ_{O_2}$/mol dm^{-3}	t^{*a}/min	$k_1{}^b/dm^3\,mol^{-1}\,min^{-1}$	$k_2{}^c/dm^3\,mol^{-1}\,min^{-1}$	$\alpha_1{}^d$
25	12.10	0.560	7.625	8	2600	15	78
	12.73	0.585	2.281	4	2235	*e*	94
	10.80	0.600	7.281	10	1914	36	70
	6.36	1.010	2.281	12	2056	*e*	
	6.36	1.071	9.719	2	1811		23
	2.12	1.470	2.281	12	1095	29	24
	4.24	1.490	9.875	5	666	22	32
	3.22	5.720	8.906	2.5	1907	29	30
36	6.36	0.96	7.094	10	1137	7	34
	3.82	1.29	7.125	3	2150	16	20

[a] The time at which the formation of $Co_2L(O_2)Y$ was assumed to be complete. [b] Kinetic constant for the formation of $Co_2L(O_2)Y$. [c] Kinetic constant for the formation of $CoL(O_2)Y$. [d] The percentage of the dioxygen bonded as $Co_2L(O_2)Y$ at t^*. It was evaluated for R° $(= c^\circ_{O_2} : c^\circ_{Co}) > 1:1$, as $(c^\circ_{O_2} - c^*_{O_2})/c^\circ_j$ where j is the reagent in deficiency (j = L or Co) and $c^*_{O_2}$ is the concentration of free dioxygen at time t^*. [e] Dioxygen all bonded on $Co_2L(O_2)Y$ species.

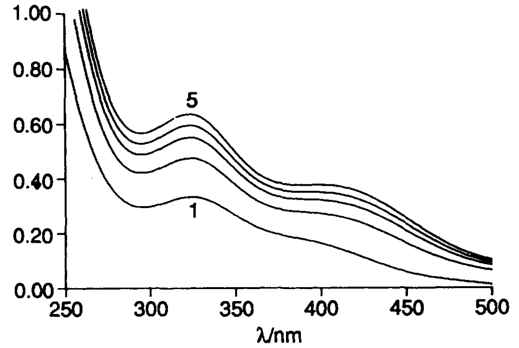


Fig. 8 Spectra recorded at various times for the Co^{II}–[30]aneN_{10}–O_2 system in phosphate-buffered solutions at pH 8, $c^\circ_{Co} = 2 \times 10^{-4}$ mol dm^{-3}, $R = 0.55:1$, $R^\circ = 1.2:1$. Spectra 1–5 were recorded 1, 2, 3, 4 and 6 min after the preparation of the solution

the membrane of the sensor. Despite the fact that under these conditions the kinetic analysis of the formation of $Co(H_mL)(O_2)$ species from dioxygen binding curves is very difficult, the k_2 values obtained from experiments at R ranging from 0.5 to 1 : 1 show a satisfactory agreement with those obtained at $R > 1:1$, when the formation of the $Co(H_mL)(O_2)$ species is the only reaction of dioxygen uptake occurring. This supports the proposed reaction scheme.

As far as the dioxygen uptake in the presence of phosphate ions is concerned, the mean values at 25 °C and pH 8.00 calculated for the formation of binuclear $Co_2L(O_2)Y$ and mononuclear $CoL(O_2)Y$ are $k_1 = 2060 \pm 150$ and $k_2 = 21 \pm 4\,dm^3\,mol^{-1}\,min^{-1}$ respectively (see Table 3).

Spectrophotometric Measurements.—Fig. 3 shows the spectral evolution of buffered aqueous solutions of the Co^{II}–[30]aneN_{10}–O_2 system at $R = 0.5:1$, Figs. 4 and 5 those for solutions at $R = 3:1$ buffered with phosphate and borate, respectively. At $R = 0.5:1$ no substantial difference is found between the spectra in the two media, except for their evolution with time. At high R values, on the contrary, the pattern exhibited in phosphate (Fig. 4) is very different from that shown in borate (Fig. 5). No substantial difference in the shape and in the rate of evolution of the spectra is found when $B(OH)_4^-$ anions are replaced by NO_3^- or ClO_4^- anions. At very long times, independently of the buffer and the ratio R, all the spectra show only one band in the range 250–550 nm, with a maximum at 500 nm of very low absorption coefficient.

At $R = 0.5:1$ the spectra always show two bands, the first with a well developed maximum at λ = 320 nm ($\varepsilon_{320} = A_{320}/c^\circ_{Co} = 3300\,dm^3\,mol^{-1}\,cm^{-1}$) in borate and at 325 nm ($\varepsilon_{325} = 3300\,dm^3\,mol^{-1}\,cm^{-1}$) in phosphate-buffered solutions. The second band presents a flat maximum at λ = 395 nm ($\varepsilon_{395} = 1900\,dm^3\,mol^{-1}\,cm^{-1}$) in borate and 400 nm ($\varepsilon_{400} = 1900\,dm^3\,mol^{-1}\,cm^{-1}$) in phosphate. The intensity of both bands decreases with time and an isosbestic point at λ = 290 nm is observed. The rate of decrease is faster in borate than in phosphate. In effect, in the phosphate medium, in particular at low dioxygen concentrations, in the first few minutes after the preparation of the solution the absorbance increases (see Fig. 8). By monitoring the absorbance change with time at $\lambda = 325$ nm a curve $A_{325} = f(t)$ is obtained, which is consistent with second-order kinetics. The value of the rate constant 25 °C is $k_1 = 2500$ dm^3 mol^{-1} min^{-1}, in good agreement with the value obtained by analysing the dioxygen binding curves in phosphate (see Table 2).

For $R > 1:1$ the analysis of the spectra in *borate-buffered solutions*, but also in 0.1 mol dm^{-3} KNO_3 or 0.1 mol dm^{-3} $NaClO_4$ aqueous solutions, reveals four successive situations. In the first 20 min two bands are present: one with a maximum at $\lambda = 320$ nm, the intensity of which increases slowly with time and becomes an inflection; the second, with a flat maximum at $\lambda = 390$ nm, does not show any significant changes in intensity in this range of time. Between 20 and 60 min, *i.e.* when the second step of dioxygen binding is observed (see Fig. 1), an isosbestic point is developed at $\lambda = 290$ nm but the absorption at $\lambda = 320$ nm remains practically unchanged. In the interval 60–160 min three isosbestic points are formed at $\lambda = 300$, 338 and 405 nm. Many hours after the preparation of the sample, a band with maximum at $\lambda = 360$ nm begins to be noticeable, together with two isosbestic points at $\lambda = 340$ and 390 nm.

A fifth situation is observed for times longer than 15–20 h, where the spectra show finally a single band with a pronounced maximum at $\lambda = 360$ nm, which reaches a limiting $A_{360}/c°_{Co}$ value of 2500 ± 100 dm^3 mol^{-1} cm^{-1} independently of the value of R.

An analysis of the time evolution of spectra corresponding to solutions at various R values shows that the curves $\varepsilon_{320} = f(t)$ present a maximum. The value of this maximum at $R = 0.5:1$ is $\varepsilon = 6600$ ($\varepsilon_{320} = A_{320}/c°_j$; $j = c°_L$ for $R < 1:1$ and $j = c°_{Co}$ for $R > 1$) but on increasing R it decreases to a constant value of $\varepsilon_{320} = 2600$ dm^3 mol^{-1} cm^{-1} for $R > 1.2:1$. The time needed to reach the maximum depends both on R and on the cobalt and dioxygen concentrations. In general, at $R = 0.5:1$, about 1–3 min are necessary, but at $R > 1.2:1$ the time required is about 5–20 min. The decrease in ε from 6600 (at $R = 0.5:1$) to 2600 dm^3 mol^{-1} cm^{-1} (for $R > 1.2:1$) is explained by the fact that at $R = 0.5:1$ binuclear $Co_2L(O_2)(OH)$ species are formed the molar absorption coefficient of which is about twice that of mononuclear $Co(H_mL)(O_2)$, which is formed at high R values. This behaviour is similar to that found in studies of the interaction of oxygen with Co^{II}–bis(histidine).[18] The UV spectrum of oxygenated solutions of Co^{II}–bis(histidine) shows two ligand-to-metal charge-transfer (l.m.c.t.) bands at 324 and 380 nm; the molar absorption coefficient of the binuclear µ-peroxo-bis(histidine) complex formed at high cobalt concentrations, at 324 nm, is $\varepsilon = 6573 \pm 99$ dm^3 mol^{-1} cm^{-1}, approximately twice that of the mononuclear complex with one l.m.c.t. transition. This was deduced from the fact that the absorbance of the oxygenated complex of Co^{II}–bis(histidine) is constant over the range of cobalt concentrations where mono- and bi-nuclear species are coexistent.

In the time evolution of the spectra in phosphate at $R > 1:1$, three general situations may be detected. In the first 20 min approximately, *i.e.* together with the first step of dioxygen uptake (see Fig. 2), two bands are developed: the first with a maximum at $\lambda = 325$ nm and a second one with a plateau at $\lambda = 400$ nm. Between 20 and 60 min the spectra do not show any noticeable changes. At very long times a remarkable decrease in absorption is observed, but no evident change in the spectral shape. An isosbestic point is developed at 290 nm. The shape of the spectra in phosphate at high R values is not different from that at $R = 0.5:1$, while some differences are noticed in the intensity. In particular, $\varepsilon_{325} = A_{325}/c°_j$ reaches its maximum in about 1 min at $R = 0.5:1$ and $R° > 2:1$. At higher R values and $R° > 2:1$, the function $\varepsilon_{325} = f(t)$ needs from 15 to 40 min to reach its maximum value. When the concentration of dioxygen is similar to that of cobalt, the maximum values are reached in very long times ranging from 25 min at $R = 0.6:1$ to 250 min at $R = 5:1$. The considerations above about the molar absorption coefficient of the binuclear peroxo complexes which is about twice that of the mononuclear complexes hold also here for Co^{II}–[30]aneN$_{10}$–O_2 complexes involving phosphate anions.

The effects of the addition of the ligand to solutions containing preformed $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$ peroxo complexes may be appreciated from the spectra reproduced in Figs. 6 and 7 respectively. The curves III show the spectral evolution with time of oxygenated aqueous borate- (Fig. 6) or phosphate-buffered (Fig. 7) solutions of Co^{II}–30[ane]N$_{10}$ complexes prepared in two steps. In the first step a solution at $R = 0.5:1$ is prepared and after 2 min a further amount of the ligand is added in order to achieve a high R value. The spectra of this latter solution are recorded immediately and after various time intervals. For comparison, Figs. 6 and 7 also show the spectra of solutions prepared in the usual manner in a single step for which the ratios between the ligand and Co^{II} are $R = 0.5$ (curves I) and 3:1 (curves II), respectively.

It may be appreciated that in borate-buffered solutions at short times [see Fig. 6(*a*)], the effect of the addition of the ligand to preformed $Co_2L(O_2)(OH)$ complexes produces only a slight increase in the absorption at $\lambda = 320$ nm (compare spectra I and III). Subsequently, spectra I and III differ more and more, while III and II ($R = 3:1$) become similar. After many hours [Fig. 6(*d*)] the spectra at $R = 0.5:1$ practically do not show any band in the range 250–550 nm, while those at high R values present a band with a maximum at $\lambda = 360$ nm, independently of the way the solutions were prepared.

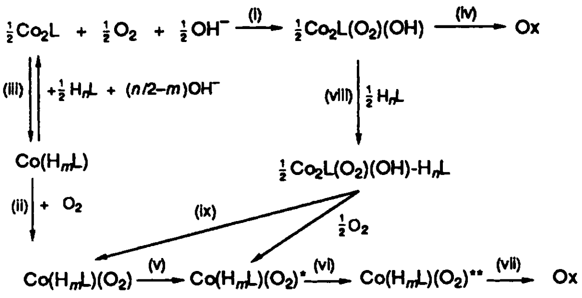
In phosphate-buffered solutions (Fig. 7) an increase in the absorption is observed as the first effect of the further addition of ligand to solutions at $R = 0.5:1$. The subsequent decrease in absorption is slowed for solutions prepared in two steps, which only after a long time show spectra similar to those exhibited by the solutions at high R prepared in a single step, shortly after their preparation.

These experiments suggest that the ligand in excess acts slowly on the preformed $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$ complexes, producing peroxo complexes which are similar to those formed in solutions in which mononuclear $Co(H_mL)$ or $CoL(Y)$ species prevail before the dioxygen addition reaction. The overlapping of degradative oxidation of bi- and mononuclear peroxo complexes prevents the analysis of the kinetics of transformation of the binuclear $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$ complexes into their corresponding mononuclear $Co(H_mL)(O_2)$ or $CoL(O_2)Y$ species as an effect of the free-ligand addition to the preformed binuclear peroxo complexes. The trend with time of curves I–III indicates, however, that the degradative oxidation of the binuclear peroxo complexes is prevented by the addition of further amounts of ligand. Therefore it must be excluded that the binuclear peroxo complexes may act as an oxidant on the ligand in excess. Probably, the added ligand forms with the binuclear peroxo complexes intermediate $Co_2L(O_2)(OH)$–H_nL or $Co_2L(O_2)Y$–H_nL species from which $Co(H_mL)(O_2)$ mononuclear peroxo complexes are generated by a slow process involving the migration of one atom of cobalt and the further addition of one molecule of dioxygen.

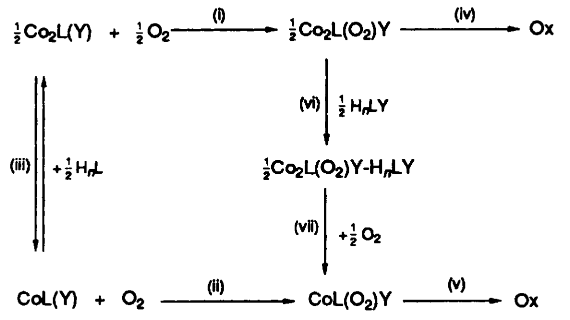
This picture is supported by the dioxygen binding curves corresponding to experiments carried out in two steps. It is very clear that, when the ligand is added to solutions containing preformed $Co_2L(O_2)(OH)$ species, the further uptake of dioxygen occurs over a period much longer (some 10 h) than the time (about 1 h) necessary to achieve the ratio $Co:O_2 = 1:1$ ratio when dioxygen is bonded to Co^{II}–[30]aneN$_{10}$ complexes in borate solutions prepared directly at high R values.

Discussion

Measurements of proton balances and bonded dioxygen,



Scheme 1



Scheme 2

together with the analysis of UV spectra, have shown that many different dioxygen adducts may be formed by the addition of molecular dioxygen to Co^{II}–[30]aneN$_{10}$ complexes. The rate of formation and the structure of these adducts, as well as their kinetic stability towards irreversible processes of oxidation of the cobalt(II) centres, depend on the values of the ratio *R* of the ligand to the cobalt concentration and on the presence of phosphate anions. In particular, the following conclusions can be drawn.

(*a*) At low *R* values (0.5:1), binuclear peroxo complexes, $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$ (Y = phosphate anion), are formed by rapid dioxygen addition to Co_2L and $Co_2L(Y)$ species already characterized by studies carried out under anaerobic conditions.[14,15] The phosphate anions decrease the rate of dioxygen addition compared with other anions, and in phosphate-buffered solutions at a low dioxygen concentration some minutes may be required to achieve the plateau in the curves $c'_{O_2} = f(t)$.

The above-mentioned binuclear peroxo complexes are not stable, and slowly produced complexes of Co^{III} of unidentified structure; however, it is noteworthy that, as a result of the addition of the ligand to solutions containing preformed $Co_2L(O_2)(OH)$ or $Co_2L(O_2)Y$ complexes, these latter are protected against the irreversible process of autoxidation to Co^{III}. Perhaps $Co_2L(O_2)(OH)$–H_nL or $Co_2L(O_2)Y$–H_nL associated species are formed as intermediates between the binuclear peroxo complexes and the excess of ligand. By a very slow reaction, involving the migration of one cobalt atom from the binuclear peroxo complex and the addition of one dioxygen molecule, these associated species could produce mononuclear dioxygen adducts. These latter are also formed in a much shorter time by bubbling dioxygen through solutions at high *R* values or by adding cobalt(II) salts to aqueous oxygenated solutions of [30]aneN$_{10}$ containing a large excess of the ligand.

(*b*) At high *R* values (> 1:1) the uptake of dioxygen produces mononuclear $Co(H_mL)(O_2)$ complexes. About 1 h is required before the ratio Co:O$_2$ = 1:1 is achieved. In the presence of phosphate anions, mononuclear $CoL(O_2)Y$ complexes are still formed, where the dioxygen adduct contains phosphate anions directly bonded to the complex, as has been found under anaerobic conditions where $Co(H_4L)(PO_4)$ and $Co(H_2L)(PO_4)$ species prevail in the range pH 7–10 at high *R* values.[15] The rate of dioxygen binding to these latter species is slower with respect to that to $Co(H_mL)$ species and some hours are required to achieve a plateau in the $c'_{O_2} = f(t)$ curves. This plateau is, on the other hand, less well characterized compared with that achieved in the absence of phosphate anions. The phosphate on one hand decreases the rate of uptake of molecular dioxygen and on the other hand increases the rate of degradative oxidation to cobalt(III) complexes.

The $Co(H_mL)(O_2)$ species are subject to a relatively slow rearrangement which requires about 3 h. After about 5 h a maximum at 360 nm appears, which increases in intensity and reaches its limiting value in about 70 h. The complex, monitored by the band at 360 nm, is very stable, but evolves very slowly towards Co^{III}–[30]aneN$_{10}$ complexes; many months are required for this maximum to become an inflection. By contrast, the $CoL(O_2)Y$ species does not seem to be involved in any molecular rearrangement and, as already observed, directly suffers degradative irreversible oxidation to Co^{III} in a relatively slow reaction which requires some days.

In the absence of phosphate ions it is reasonable to draw up, for aqueous solutions of Co^{II}–[30]aneN$_{10}$ in the range pH 8–10, the reactions in Scheme 1. In phosphate-buffered solutions Scheme 2 is proposed. Nine reactions are contemplated in Scheme 1. Reaction (iii) is an equilibrium involving Co^{II}–[30]aneN$_{10}$ complexes for which there is no information about the rate. At *R* = 0.5:1 the Co_2L species undoubtedly prevail while at high *R* values $Co(H_mL)$ complexes are the main species in solution. No interference between the reactions of dioxygen uptake can therefore occur when *R* = 0.5 [only reaction (i)] or >1:1 [only reaction (ii)]. Also at intermediate *R* values, the interference between the two reactions of dioxygen uptake is negligible. Actually, reaction (i) is faster (k_1 >4000 dm^3 mol^{-1} min^{-1}) than (ii) (k_2 = 54 dm^3 mol^{-1} min^{-1}), but when $Co_2L(O_2)(OH)$ is formed the ratio $R = (c^{\circ}_{L} - c_{Co_2L(O_2)(OH)})/(c^{\circ}_{Co} - 2c_{Co_2L(O_2)(OH)})$ assumes a high value. The equilibrium concentration of Co_2L becomes very small and reaction (ii) becomes the most important way to produce peroxo complexes, even when equilibrium (iii) is rapidly achieved. This is justified by the kinetic analysis of the dioxygen binding curves when both the bi- and the mono-nuclear peroxo complexes are formed. In this case, two well distinguished steps of dioxygen uptake are recognizable and the values of the ratio $c'_{O_2}:c^{\circ}_{Co}$ range from 0.5:1, depending on *R*.

As far as the structure of $Co_2L(O_2)(OH)$ species is concerned it is difficult at the moment to give any answer, owing to the lack of information. It is however to be noted that the distance Co ··· Co is 4.4 Å in monobridged $Co_2L_2(O_2)$ complexes and 3.3 Å in the dibridged $Co_2L_2(O_2)(OH)$ complexes.[1a] For $[Ni_2([30]aneN_{10})(H_2O)_2]^{4+}$ and $[Cu_2([30]aneN_{10})HCl_2]^{3+}$ complexes the Ni ··· Ni and Cu ··· Cu distances are 6.54 and 7.26 Å, respectively.[16,19] If one assumes that also in the $[Co_2([30]aneN_{10})]$ complex the Co ··· Co distance is longer than 6 Å, the formation of complexes in which the dioxygen binds to a single Co in an end-on fashion while the hydroxy ion is bonded to the other Co should be reasonable. Such a structure could be stabilized by the formation of a hydrogen bond between the hydroxy group and the oxygen atom of O$_2$ not bonded to the metal.

When only one atom of cobalt is lodged in the 30-membered cavity of [30]aneN$_{10}$ it seems that the mononuclear oxygenated $Co(H_mL)(O_2)$ species formed is organized in a cryptate structure which protects the cobalt atom from access of the solvent. As a consequence the rate of the irreversible oxidation of Co^{II} to Co^{III} is slowed considerably. Such a situation does not occur when phosphate anions are bonded to the Co^{II}–[30]aneN$_{10}$ complex since the ligand is also engaged in the binding of these anions.

In conclusion, cobalt(II) complexes with the 30-membered macrocyclic ligand interact with molecular dioxygen in a flexible way which is interesting for various reasons. (*i*) Mononuclear species with dioxygen bonded in an end-on fashion may be formed in aqueous solutions at room temperature; this is rather unusual for cobalt(II) complexes with saturated polyazotate ligands. (*ii*) The binuclear peroxo species formed at low *R* values, incorporating two metallic centres in the same cavity, have a structure similar to that shown by binuclear natural dioxygen carriers. The latter host a single active bimetallic site within a single macromolecule. This does not occur with the usual synthetic dicobalt mono- or di-bridged peroxo complexes where two metallic centres are incorporated in two different molecules of the ligand. (*iii*) A protective action against the irreversible oxidation of the binuclear peroxo species may be exercised by the ligand when this is added in excess to solutions containing preformed $Co_2L_2(O_2)(OH)$ species. (*iv*) A protective action against the irreversible oxidation of mononuclear peroxo species is achieved by molecular reorganization after the dioxygen uptake. (*v*) An interaction of the Co^{II}–[30]aneN_{10} complexes with phosphate ions is recognizable, and the effects produced on the stability of the peroxo species may be evaluated.

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