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Thermodynamic and kinetic aspects of the binding reaction of molecular oxygen on Co(II) complexes in aqueous solutions

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Abstract - A short survey is given of the main characteristics of the reaction of uptake of molecular oxygen by biological dioxygen carriers. Co(II) complexes able to bind dioxygen are then examined in order to determine whether the type and features of the peroxocomplexes formed are related to the nature of the ligand and the solvent. The thermodynamic and kinetic data relative to the formation in aqueous solution of peroxocompounds starting from Co(II) complexes with ligands belonging to three families (open-chain, macrocyclic and macropolytopic) of saturated polyamines are also examined in greater detail.

INTRODUCTION

Studies on natural and synthetic systems that bind and release molecular oxygen have a long hystory and various books (ref. 1) and monographic papers (ref. 2) illustrate the growth of insight into this topic. The present state of the art is clearly illustrated in the comprehensive book edited by A.E.Martell and D.T.Sawyer (ref. 3).

Liquid fluorocarbons present an unusually high ability to dissolve molecular oxygen (ref. 4) and their use as artificial blood has been proposed (ref. 5). However, all other systems able to take and release dioxygen include an active site containing one or more atoms of a transition metal, to which the oxygen molecule is bonded.

BIOLOGICAL DIOXYGEN CARRIER SYSTEMS

Biological oxygen carrier systems are composed of metalloproteins containing Fe(II) or Cu(I) atoms in their active site. In the respiratory tetrameric protein, mammalian haemoglobin (ref. 1a-1c), each monomeric subunit contains one atom of Fe(II) bound to four nitrogens of the macrocyclic tetrapyrrol protoporphyrin IX, thus constituting a single "heme" prostetic group. The heme group,in turn, is bound by means of an axial histidine molecule to a polypeptide chain of about 150 amino acid residues, producing an α or β subunit with molecular weight of about 1.6×10^4 daltons. Two α subunits and two β subunits, held together by means of non-covalent interactions, make up the molecule of $\alpha_2\beta_2$ deoxyhaemoglobin. On saturation, this molecule binds one molecule of oxygen for each active site, producing the $\alpha_2\beta_2(O_2)_4$ oxyhaemoglobin molecule, characterized by a ratio $Fe:O_2 = 1:1$, with the O_2 molecule bonded to Fe(II) in an end-on fashion. The monomeric myoglobin is also present in Mammalia; this is structurally very similar to a subunit of haemoglobin, but has a much higher affinity for oxygen.

The other two classes of respiratory metalloproteins, in spite of their names, are not of the heme type. The monomeric myohaemerythrin is in fact a binuclear iron protein (ref. 1d,6a,6b) (molecular weight 1.35×10^4 daltons), utilized by several marine invertebrates, in which one of the two iron atoms of the active site is able to bind one oxygen molecule, so that a ratio $Fe:O_2 = 2:1$ is achieved. The two iron atoms are octahedrally coordinated, each being triply bonded by two bidentate protein carboxylates and by one μ-oxo group, while the other five coordinate sites are occupied by histidines. Haemerythrins are usually formed of eight monomeric units.

Haemocyanins (ref. 1d) are found, for example, in the blood of gastropods and crustaceans solely in hexamer or multihexamer forms of a very high molecular weight (5×10^5 to 10^8 daltons); as their active sites, they contain two copper atoms which bind dioxygen in a binuclear dibridged peroxo form. The remaining coordination sites of copper are bonded with histidines (ref. 7).

The best known and most studied biological oxygen carrier, haemoglobin, binds oxygen very quickly; at half saturation, the oxygen pressure, $(P_{O_2})_{1/2}$, is about 27 Torr (Note a). The affinity of haemoglobin for dioxygen may be changed through heterotropic interactions with protons, inorganic anions such as Cl^- or HPO_4^{--}, or organic phosphate such as 2,3-diphosphoglycerate (DPG), adenosine triphosphate (ATP) or inositol hexaphosphate (IHP). The curves of oxygen binding, without or in the presence of affectors, always show an S-shaped form, however. Each molecule of haemoglobin may enter a very high number of oxygenation-deoxygenation cycles without the irreversible oxidation to Fe(III) of its Fe(II).

These astonishing features, allow living organisms to have a correct supply of oxygen even when environmental conditions change considerably. They are the result of a high degree of organization of the molecule, whose structure has been very carefully investigated by Perutz (ref. 1c,8). In particular, the lack of any irreversible oxidation to Fe(III) is ensured by insertion of Fe(II) into the macrocyclic porphyrinic cavity encapsulated into a hydrophobic pocket formed by the polypeptide chains in the globin. Cooperativity in binding of the dioxygen is due to the different affinity for this molecule on the part of the two quaternary R (relaxed, high ligand affinity) and T (tense, low affinity) states the molecule may assume. Regulation of oxygen affinity is related, e.g., by the preferential allosteric binding of one organic phosphate molecule to the tetrameric deoxyhaemoglobin (ref. 9).

Co(II) DIOXYGEN COMPLEXES

Studies on synthetic dioxygen carrier complexes have certainly been of help in understanding how the thermodynamic properties of biological dioxygen carriers are correlated with their structure. Now the contrary is certainly true. Natural dioxygen carrier systems have been widely used (ref. 10), as models in planning good synthetic dioxygen carrier systems. The latter, of course, do not possess the flexibility of behaviour of haemoglobin, but they succeed in carrying out some limited but nevertheless useful functions for oxygen transport (ref. 10), soft oxygenation reactions (ref. 11), and the uptake and storage of atmospheric oxygen (ref. 12), and as artificial blood (ref. 13).

The metal ions which form synthetic complexes able to bind dioxygen are: Mn(II) (ref. 14), Ru(III) (ref. 15), V(IV) (ref. 16), Fe(II) (ref. 17), Cu(I) (ref. 18) and Co(II).

The dioxygen complexes of Co(II) have been known since 1938 (ref. 19) and have been investigated (ref. 1e,2c,2h,3,21) in great detail. The ways molecular oxygen binds Co(II) complexes, together with the further evolution that oxygen-adducts may have, are represented in the following scheme:

$$\begin{array}{l} mCo + nL + rO_2 \\ \qquad\searrow \\ \qquad\quad Co_mL_n(O_2)_r \longrightarrow \text{Products of irreversible autooxidation} \\ \qquad\nearrow \\ Co_mL_n + rO_2 \end{array} \qquad (1)$$

L is the main ligand bonded to the Co(II) and X a secondary ligand which may be bonded to Co(II) in an axial position, or in a bridged form connecting two cobalt atoms.

Bearing in mind the nature of the ligand and that of the solvent, all the situations of dioxygen binding at the active sites of biological carrier systems are probably reproduced in the synthetic Co(II) complex carriers.

Mononuclear dioxygen complexes in which the ratio $Co:O_2 = 1:1$ is achieved include:

i) Complexes formed in organic aprotic solvents (e.g. toluene, acetonitrile, DMF, DMSO) generally at low temperatures ($T<273$ K) when dioxygen is added to Co(II) complexes having a ketoimine N_2O_2 set as the main ligand, as occurs in the Schiff bases (ref. 20a-20d), or a thioimine N_2S_2 set as in sacsacen and bensacacen (ref. 21a-21b). A secondary ligand occupying the axial position is usually associated with the main ligand. Monodentate aromatic bases such as pyridines or substituted imidazoles, are used as secondary ligands. Mononuclear dioxygen complexes are alsó formed with N_4 set ligands made up of porphyrins, "picket-fence" porphyrins or porphyrins having pendant groups able to mask the axial position of the cobalt as in "capped-" or "basket-handle-" or "bridged-" or "double-capped" porphyrins (ref. 22a-22g). Some macrocyclic sets of the N_4 type (ref. 23) and cobalt cyclidene complexes (ref. 24a-24c) with an N_4 set, are also able to form 1:1 dioxygen adducts.

ii) Complexes formed in aqueous solution with an N_4 set ligand such as coboglobins (ref. 25a-25d) which differ from the heme metalloproteins in the substitution of Fe(II) with Co(II). It is noteworthy

Note a: Throughout this paper 1 Torr = 133.3224 Pa.

that tetrameric CoHb shows S-shaped oxygen binding curves typical of the cooperative uptake of dioxygen as occurs in natural FeHb. The Co(II) cyclidene complexes, already mentioned, are also able to act as 1:1 dioxygen carriers in aqueous solutions (ref. 10).

As regards the thermodynamic characteristics displayed by mononuclear Co(II) complexes involved in the reaction:

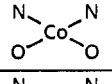
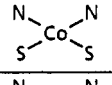
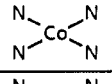
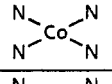
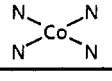
$$CoLB + O_2 = CoLBO_2 \qquad (2)$$

it has been found convenient to express their affinity for oxygen by considering the value of the oxygen pressure at half the position of the binding curve $A°_{O_2} = -\Delta G°_{O_2} = -RT\ln(P_{O_2})_{1/2}$. The $A°_{O_2}$ values depend on the temperature, the nature of the solvent and obviously on the nature of the ligand. In selected sets of ligands, the $(P_{O_2})_{1/2}$ values may be related to effects arising from some controlled structural modifications of the system which accept the dioxygen, such as the introduction of different secondary ligands B (axial effect), or the introduction of a different substituent in the main ligand, and so on. The experimentally determined oxygen pressure in the equilibrated system generally ranges from 1 to 1000 Torr. As a consequence, values of $A°_{O_2}$ ranging from 0 to 11.5 kJ mol^{-1} at 200 K or from 0 to 17.2 kJ mol^{-1} at 300 K (standard state for oxygen = 1 Torr) are determined.

It appears possible, however, to speak of relative affinity for oxygen when the $(P_{O_2})_{1/2}$ values are compared for a set of mononuclear Co(II) complexes studied at the same temperature and in the same solvent, but it is arbitrary to establish a succession of affinities when different temperatures and solvents are considered.

In order to have an idea about the succession of the standard affinities for oxygen on the part of different Co(II) complexes, we might assume as a term of comparison the temperature at which the equilibrium oxygen pressure is $(P_{O_2})_{1/2}$ = 10 Torr. In these conditions, $A°_{O_2}$ = 2.303 RT and the affinities are directly proportional to the temperatures. Of course this criterion cannot be fully accepted owing to the different values the $\Delta H°_{O_2}$ quantities have. However it is perhaps more logical to carry out a comparison between the categories of Co(II) complexes able to bind oxygen according to eq. (2) by considering the enthalpy $\Delta H°_{O_2}$ and the entropy $\Delta S°_{O_2}$ changes associated with the uptake of dioxygen (ref. 26). This comparison is made in Table 1 where mean values of $\Delta H°_{O_2}$ corresponding to a specified set of ligands are given, together with the range of values used for the averaging operation, the number of compounds, the solvent and temperature range. Such an unusual average based on the enthalpy values of oxygen addition to compounds belonging to the same set, may be partly justified by the fact that the enthalpy effect of oxygen binding on the Co(II) inserted into a determined ligand set is largely predominant with respect to enthalpy effects connected, for example, with substitutions, introductions of lateral chains into the frame of the basic structure, axial bonding of one secondary ligand and so on. Finally it should also be noted that the $\Delta H°_{O_2}$ values for systems in Table 1 were often obtained by considering the dependence of K_{O_2} on the temperature, and they are very often subject to large errors.

TABLE 1. Enthalpy and entropy changes for the formation of mononuclear Co:O_2 = 1:1 complexes.[a]

Ligand set	Basic Structure	Range of Temperature (°C)	Solvent	N° of compounds	$-\Delta H°_{O_2}$ kJ mol^{-1}	$-\Delta S°_{O_2}$ J K^{-1}mol^{-1}	Ligands	Ref.
N_2O_2		-31 ÷ 16	Toluene	17	69 ± 4	305 ± 8	Salen, acacen, benacen, ...	20a-d
N_2S_2		-51	Toluene	8	52 ± 6	264 ± 25	Sacsacen, Bensacacen	21a-b
N_4		-70 ÷ 30	Toluene	22	41 ± 8	218 ± 8	Porphyrins	22a-g
N_4		25	Water	(4)[b] 3	63 ± 4[c] 56 ± 6	247 ± 20[c] 209 ± 10	Co Hb Co Mb	25a 25b-d
N_4		25	Water	9	69 ± 10	265 ± 6	Cyclidenes	10

[a] Values for dioxygen addition to CoL complexes are averages of those reported by Jones et al. (ref. 2c), except for cyclidene-dioxygen-Co(II) complexes, which are taken from Busch (ref.10). Standard state for the dioxygen: gas at 1 Torr. [b] Number of subunits.[c] Mean value for dioxygen addition to one subunit.

As general characteristics of the thermodynamics of the reaction of dioxygen addition to form mononuclear complexes, it may be observed that the uptake of oxygen is always associated with very large, negative $\Delta H°_{O_2}$ and $\Delta S°_{O_2}$, both noticeably dependent on the ligand set. The $\Delta S°_{O_2}$ values, in addition to the non-specific entropic effect arising from the transfer of one molecule of dioxygen from a free state into a bonded state, are also determined by the different solvation and internal degrees of freedom that the complexes have when the system changes from an anaerobic to an aerobic state.

As far as the peroxocomplexes in which a $Co:O_2 = 2:1$ ratio is achieved are concerned, the dioxygen acts as a bridge between two Co(II) atoms. Sometimes another bridge may be formed, as in the formation of the well-known μ-hydroxo-μ-peroxo-Co(II) complexes. It may be recalled that this structure is also found in natural haemocyanins, but there the double bridge is supported by two copper atoms.

In aqueous solution, the first step of the reaction which produces dinuclear peroxocomplexes is a fast addition of oxygen to form the $CoLO_2$ species. The latter often reacts very quickly with CoL to produce the monobridged peroxo binuclear complex $Co_2L_2O_2$. This is the only peroxo species present in solution when L is a pentadentate ligand (e.g. tetren, terpyridine + 1,10-phen or 2,2'-bpy) or a macrocyclic tetraazotate ligand with a large cavity (e.g. cyclam, [15]aneN$_4$). In other cases, an equilibrium between the monobridged peroxo and the dibridged olate peroxo $Co_2L_2O_2OH$ species may be established, and is often totally shifted towards the dibridged form. It is also possible that one or two hydroxy groups may occupy the axial positions, producing monobridged dinuclear hydroxocomplexes $Co_2L_2O_2(OH)_m$ (m = 1,2).

The reactions of formation of these mono- and dibridged peroxo species:

$$2CoL + O_2 = Co_2L_2O_2 \quad (3)$$

$$2CoL + O_2 + H_2O = Co_2L_2O_2OH + H^+ \quad (4)$$

show that $(P_{O_2})_{1/2}$ needed to obtain half the amount of the peroxo compounds now depends directly on the concentration of the complex (eq. 5a) and/or that of the hydrogen ion (eq. 5b):

$$(P_{O_2})_{1/2} = 1/K_{O_2} C°_{CoL} \quad (5a)$$

$$(P_{O_2})^{OH}_{1/2} = (H^+)/K_{O_2,OH} C°_{CoL} \quad (5b)$$

where

$$K_{O_2} = (Co_2L_2O_2)/(CoL)^2 P_{O_2} \quad (6a)$$

$$K_{O_2,OH} = (Co_2L_2O_2OH)(H^+)/(CoL)^2 P_{O_2} \quad (6b)$$

The formation of monobridged peroxo complexes in aqueous solution is related to the competitive reactions of Co(II) and H^+ for the ligand, and for this reason it is only possible for pH values which depend on the affinities the ligands show towards the proton. As far as the formation of the dibridged peroxo complexes is concerned, dependence on the pH is now twofold: indirect, as for monobridged complexes, and direct, since the proton concentration is present in the expression of the equilibrium constant (eq. 6b).

To compare oxygen affinity of the monobridged and the dibridged complexes these observations must be taken into account . For this purpose, the suggestion was made some time ago (ref. 26) that consideration should be given to an η_{O_2} function defined as:

$$\log \eta_{O_2} = \log K_{O_2,OH} + pH_{1/2} \quad (7)$$

where $pH_{1/2}$ is the pH at which half of the μ-peroxo-μ-hydroxo dibridged complex is formed. The η_{O_2} quantity has the same dimensions as the K_{O_2} quantity and comparisons become possible between the dioxygen affinity of the monobridged and dibridged complexes is concerned. For the compounds studied so far, the $\log K_{O_2}$ values range from ~4 to ~15, while $\log \eta_{O_2}$ values go from ~3 to ~12 (ref. 26). No evident effect of increase in affinity for oxygen of olates with respect to monobridged compounds emerges.

The relative contributions of the enthalpic and entropic terms to the stability of the peroxocomplexes in aqueous solution can be determined from the data in Table 2, where the enthalpy changes for dioxygen addition are all calorimetric measurements. The entropy changes correspond to the transfer of one mole of dioxygen from the ideal 1 mol dm^{-3} aqueous concentration into ideal 1 mol dm^{-3} aqueous solution of the dioxygen adduct.

TABLE 2. Thermodynamic functions of formation of some CoL and $Co_2L_2O_2(OH)_m$ (m = 0,1,2) complexes in aqueous solution at 298 K. Standard state for the dioxygen: O_2 (aq) ideal 1 mol dm^{-3} aqueous solution. (ΔX in kJ mol^{-1}).[a]

	Co,L ΔX CoL			CoL,O_2(aq) [a] ΔX $Co_2L_2O_2$			CoL,O_2(aq),OH [b] ΔX $Co_2L_2O_2OH$			CoL,O_2(aq),OH [a] ΔX $Co_2L_2O_2(OH)_2$			Ref.
	-ΔG	-ΔH	TΔS	-ΔG	-ΔH	TΔS	-ΔG	-ΔH	TΔS	-ΔG	-ΔH	TΔS	
$(en)_2$	(60.9)[c]	58.4[c]	(2.5)[c]				107.0	172.8	-65.8				27
tren	72.5	44.6	27.9				105.6	167.8	-62.3				28
trien	62.5	44.8	17.7				114.1	167.8	-53.7				29
2,3,2-tet	70.2	49.0	21.2	61.0	125.9	-64.9					158.2		28
3,2,3-tet	63.0	50.4	12.6				98.2				158.2		d
tetren [e]	76.6	59.6	17.0	91.2	178.9	-87.7							30
[12]aneN$_4$	78.8	48.0	30.8					159.0					31
[14]aneN$_4$	81.6			47.4	86.1	-38.7				131	132.0	~0	32
[15]aneN$_4$		62.2		29.7						110	112.3	~0	33
4-IMDIEN [e]	79.0	55.3	23.7	72.0	138.1	-66.1							34
4-IMDPT [e]	64.9	38.5	26.4	53.5	84.1	-30.6							34
PYDIEN [e]	84.1	64.5	19.6	64.8	136.5	-71.7							34
PYDPT [e]	65.5	54.8	10.7	44.0	82.5	-38.5							34
EPYDEN [e]	79.9	50.7	29.2	84.1	143.2	-59.1							34
PYEN	71.4						87.7						35

[a] Monobridged structures. [b] Dibridged structures. [c] Refers to the reaction Co + 2en ⇄ Co(en)$_2$; ΔG and TΔS bracketed because not comparable with the other data. [d] Unpublished results. [e] The axial position is occupied by one nitrogen of the pentadentate ligand.

TABLE 3. Spectrophotometric features of peroxocomplexes of Co(II) formed with saturated polyamines in aqueous solutions at 298 K. (Extinction coefficients expressed in dm^3 mol^{-1} cm^{-1}).

	$Co_2L_2O_2$ monobridged-μ- peroxo-complex	$Co_2L_2O_2OH$ dibridged-μ-peroxo-μ-hydroxo-complex	$Co_2L_2O_2(OH)_2$ monobridged-μ-peroxo-bishydroxo-complex
[12]aneN$_4$		λ_{max} = 364nm; ε = 6700 pH > 8.5	
[14]aneN$_4$	λ_{max} = 300nm; ε = 9000 *pH = 6*		λ_{max} = 280nm; ε = 12300 *pH > 11*
[15]aneN$_4$	[a] λ_{max} = 310nm (sh) pH = 6-8		λ_{max} = 280nm; ε = 13000 pH > 10.5
2,2,2-tet		[b] λ_{max} = 355nm; ε = 6950 λ_{max} = 275nm (sh); ε = 6000 pH > 6	
2,3,2-tet	[c] λ_{max} = 300nm; ε = 10500 pH = 6.6	[d] λ_{max} = 370nm; ε = 4600 λ_{max} = 290nm; ε = 5200 pH = 6.6	[c] λ_{max} = 285nm; ε = 12700 pH > 10.5
3,2,3-tet		[e] λ_{max} = 375nm; ε = 5800 λ_{max} = 300nm; ε = 6000 pH = 7.8 - 8	[f] λ_{max} = 305nm; ε = 13500 pH = 7.8 - 8 --- [g] λ_{max} = 285nm; ε = 11400 pH > 10.5
tren		[c] λ_{max} = 365nm; ε = 7000 λ_{max} = 275nm (sh); ε = 6000 pH > 6.4	
tetren			[h] λ_{max} = 308nm; ε = 14000 pH > 6
en		[i] λ_{max} = 357nm; ε = 5800 λ_{max} = 275nm (sh); ε = 5800 pH 6 ÷ 8; $C°_{en}/C°_{Co}$ > 6	[m] λ_{max} = 310nm; pH > 9.0; $C°_{en}/C°_{Co}$ = 2 t = 48h

[a] Formation is not complete at P_{O_2} = 1 atm. [b] Stable. [c] Spectrum observed immediately after bubbling O_2. [d] Spectrum (stable) observed after one day. [e] Spectrum (stable) observed after 30 min. [f] Monobridged monohydroxo-μ-peroxo-dicobalt (II); spectrum observed immediately after bubbling O_2. [g] Monobridged dihydroxo-μ-peroxo-dicobalt (II): spectrum observed immediately after bubbling O_2. [h] Stable. It is not an hydroxo complex, the axial position is occupied by a nitrogen of the ligand. [i] Spectrum observed after a few minutes at high ratios $C°_{en}/C°_{Co}$. Stable. [m] The band at λ_{max} = 357 nm is formed quickly; it disappears in ~48 hours.

Large differences are now found in the entropy changes for the uptake of dioxygen whereas in the formation of mononuclear peroxocomplexes they span a rather narrow range despite dramatic changes in the type of ligand and solvent. As far as the enthalpy changes are concerned, dioxygen produces a very large effect which is usually more than twice that produced when its addition gives mononuclear species.

Connections between molecular structures of the peroxo complexes and their thermodynamic properties *(a) saturated open-chain polyamines; (b) saturated macrocyclic polyamines; (c) polytopic saturated polyamines.*

As far as open-chain and macrocyclic polyamines are concerned, the types of peroxocomplexes which are formed in KNO_3 0.1 mol dm^{-3} aqueous solution at 298 K and at various pH's, are summarized in Table 3 together with their U.V. spectral characteristics.

For open-chain ligands the initial fast reaction of oxygen uptake yielding $CoLO_2$ species is followed by an even faster reaction giving rise to monobridged peroxocomplexes $Co_2L_2O_2$. At pH = 6.5 - 8.0, these produce dibridged μ-peroxo-μ-hydroxo complexes $Co_2L_2O_2OH$ which are stable for a long time. Their formation is very rapid for ligands in which all the nitrogens are connected with ethylenic chains, independently of whether they are disposed in separate units (en), linear chains (2,2,2-tet) or branched chains (tren). When propylenic chains replace ethylenic chains, formation is slower: the half time for the formation of the dibridged species $Co_2L_2O_2OH$ (L = 2,3,2-tet) starting from its corresponding peroxo monobridged complex $Co_2L_2O_2$ is $\tau \simeq 150$ minutes at pH ≃ 7. When the ligand is 3,2,3-tet, the monobridged hydroxo-peroxo complex is immediately formed when oxygen is bubbled in solutions at pH ≃ 8: the latter converts into its isomeric dibridged species with a half time of $\tau \simeq 4$ minutes.

Together with an increase in kinetic inertness in the formation from their monobridged peroxo parent, dibridged olate complexes containing six-membered chelate rings also show a decreased thermodynamic stability with respect to those with only five-membered chelate rings. Thus, while the latter do not give monobridged hydroxo species even at very high pH's, complexes with one or more six-membered chelate rings at pH > 10 produce monobridged dihydroxo $Co_2L_2O_2(OH)_2$ species. These are unfortunately not stable with respect to degradative oxidation.

When the ligand is a saturated macrocyclic tetraazotate compound, only monobridged peroxocomplexes are formed at pH = 6 ÷ 8, and monobridged hydroxo complexes at pH > 10. The latter quickly give products of irreversible oxidation. When only ethylenic chains connect the nitrogens of the macrocycle (cyclen), the dioxygen is bound in a dibridged μ-peroxo-μ-hydroxo complex as in the open-chain ligands.

The thermodynamic features of oxygen uptake are summarized in Table 2 where, together with the thermodynamic data $\Delta X(CoL,O_2 \rightarrow Co_2L_2O_2)$ for oxygen uptake (X = G,H,S) according to reaction scheme 1, the formation of CoL complexes in anaerobic atmosphere is also considered. The ΔH and ΔS data for the formation of Co(II)-cyclam are lacking because the rate of formation of CoL is slow, and calorimetric measurements of ΔH_{CoL} have not been carried out.

The most important points emerging from table 2 are:

i) The CoL complexes with macrocyclic ligands are more stable than those with open-chain ligands. Stability increases in all cases when ethylenic chains are replaced by propylenic chains: compare the value of K (Co,L → CoL) for 2,3,2-tet with that for 2,2,2-tet and the value for [14]aneN$_4$ with that for [12]aneN$_4$.

ii) The affinity for dioxygen is higher in the monobridged peroxocomplexes involving open-chain ligands than in those with macrocyclic ligands: compare the value of K ($CoL,O_2 \rightarrow Co_2L_2O_2$) of 2,3,2-tet with those of [14]aneN$_4$ and [15]aneN$_4$.

iii) The peroxocomplexes of macrocyclic ligands, with or without OH^- groups bonded in the axial position to Co(II), undergo a significant decrease in stability when the number of propylenic chains increases: compare K ($CoL,O_2 \rightarrow Co_2L_2O_2$) and K ($CoL,O_2,OH \rightarrow Co_2L_2O_2(OH)_2$) values of [14]aneN$_4$ and [15]aneN$_4$.

iv) The enthalpy changes for oxygen binding are in any case very large, sometimes more than twice that corresponding to the uptake of oxygen by CoMb (ΔH_{O_2} = -55.7 kJ mol^{-1} in water (ref. 25)). The considerations made for stability, i.e. for the free energy, may be repeated for the enthalpy. In other words, the entropic terms do not play an important role in determining the behaviour of peroxocomplexes when they are formed by adding dioxygen to Co(II) complexes with polyazotate saturated open-chain ligands. For the latter, the entropy changes connected with the passage of oxygen from the free state to the bonded state are always negative and noticeably larger in magnitude than the $TS°_{O_2}$ = 32.48 kJ mol^{-1} value associated with one mole of oxygen in ideal 1 mol dm^{-3} aqueous solution at 298 K: see $T\Delta S°_{O_2}$ values for the formation of the $Co_2L_2O_2$ species by the addition of one mole of O_2(aq) (standard state: ideal 1mol dm^{-3} aqueous solution) to two moles of Co(II)-2,3,2 tet ($T\Delta S°_{O_2}$ = -64.9 kJ mol^{-1}) or to two moles of Co(II)tetren ($T\Delta S°_{O_2}$ = -87.6 kJ mol^{-1}).

For Co(II) complexes with macrocyclic ligands, the entropy changes related to the formation of the peroxocomplexes are negative, but much smaller than those found for the formation of the corresponding peroxocompounds with open-chain polyazotate amines.

v) Introduction of OH^- strengthens the energy of the systems (compare ΔH ($CoL,O_2 \rightarrow Co_2L_2O_2$) values with ΔH ($CoL,O_2,OH \rightarrow Co_2L_2O_2(OH)_2$) values) particularly when dibridged structures are formed (see the case of cyclen and the open-chain amines)

vi) Strengthening due to the formation of a double bridge results in an increased resistance to the irreversible oxidation to the Co(III).

It would appear to be significant that in the case of macrocyclic compounds, the change from Co(II)-[12]aneN$_4$ to Co(II)-[15]aneN$_4$ represents an evolution towards "good" oxygen carriers. This is reflected in a large decrease (in absolute terms) in the enthalpies of oxygen addition: ΔH ($CoL,O_2,OH \rightarrow Co_2L_2O_2OH$) (L = cyclen) < ΔH ($CoL,O_2,OH \rightarrow Co_2L_2O_2(OH)_2$) (L = cyclam) < ΔH ($CoL,O_2,OH \rightarrow Co_2L_2O_2(OH)_2$) (L = [15]aneN$_4$) and a large decrease in the equilibrium constants for oxygen binding K ($CoL,O_2 \rightarrow Co_2L_2O_2$) (L = cyclam) < K ($CoL,O_2 \rightarrow Co_2L_2O_2$) (L = [15]aneN$_4$).
The CoL complex with [15]aneN$_4$ shows the following interesting features: as the first step in the process of oxygen addition to Co[15]aneN$_4$, a mononuclear $CoLO_2$ complex is formed which immediately evolves to the dinuclear $Co_2L_2O_2$ complex. The latter is a better model for natural oxygen carriers with respect to the dinuclear $Co_2L_2O_2(OH)$ complexes usually formed with the open-chain ligand. The dinuclear $Co_2L_2O_2$ complex (L = [15]aneN$_4$) may be involved in cycles of uptake-release of oxygen simply by alternating the bubbling of gaseous oxygen and nitrogen. Unfortunately, a severe degradation of the system takes place, due to the irreversible oxidation to Co(III). We think it might also be useful to consider the [16]aneN$_4$ ligand and prepare macrocyclic ligands with crowded lateral chains which could prevent irreversible oxidation and also enhance the uptake and release of oxygen. In effect, this has already been performed with success by Busch (ref. 10 & 24), with the preparation of similar macrocyclic compounds: cyclidenes.

Co(II) complexes with open-chain ligands, on the other hand, do not seem to be good systems for the exchange of oxygen, though they protect the oxygen bonded by the formation of dibridged μ-hydroxo-μ-peroxo compunds. The larger the number of five-membered chelate rings, the more effective this protection is.

As regards the uptake of oxygen by Co(II) complexes with ligands that can lodge more than one atom of Co(II), the formation of peroxo monobridged and hydroxo-peroxo dibridged dicobalt complexes, starting from dicobalt complexes with bistren and bisdien (ref. 36 & 37), has been reported by Motekaitis et al. Other dioxygen dinuclear complexes of Co(II) with macropolycyclic ligands, in which the peroxobridged or the μ-hydroxo-μ-peroxo dibridged structures are formed, have recently been described (ref. 11). Our preliminary results (ref. 38) concerning the reaction of dioxygen addition upon complexes of Co(II) with the macropolytopic saturated ligand decaazacyclotriacontane, [30]aneN$_{10}$ will now be described.

Unlike the Co(II) complexes with saturated open-chain and saturated macrocyclic polyamines considered above, which bind dioxygen in a few seconds, the uptake of dioxygen by the dinuclear Co_2[30]aneN$_{10}$ complex requires a time many orders of magnitude longer. Moreover, the trends of the dioxygen binding curves show that mononuclear ($Co:O_2 = 1:1$) or dinuclear ($Co:O_2 = 2:1$) dioxygen complexes can be obtained depending on the nature of the anions present in solution and the value of the ratio $R = C°_L/C°_{Co}$ between the stoichiometric concentration of the ligand and that of the cobalt. The form and the evolution with time of the U.V./Vis. spectra of oxygenated solutions agree with these results (Fig. 1).

When the ratio $C°_L/C°_{Co}$ is equal to R = 0.5 in aqueous solutions buffered at pH 8 ÷ 9 with 0.05 mol dm^{-3} borate, or at pH 7.8 ÷ 8.5 with KH_2PO_4-Na_2HPO_4 buffer at 0.05 mol dm^{-3} overall phosphate concentration, the uptake of dioxygen occurs in a few minutes and the amount of bonded dioxygen corresponds to the ratio $Co:O_2 = 2:1$. The spectra, both in phosphate and in borate buffered solutions, at $t \rightarrow 0$ present two maxima at about the same wavelengths and of about the same absorbance: λ_{max} = 325 nm and λ_{max} = 410 nm in phosphate and λ_{max} = 320 nm and λ_{max} = 400 nm in borate. Their evolution is also similar. An isosbestic point at λ = 290 nm is developed after many hours in both cases. As a reasonable scheme of reaction, formation of a dinuclear peroxo complex, followed by irreversible autooxidation, occurs at R = 0.5 independently of the nature of the anions present in solution.

For large values of R (R > 1) in borate buffered solution, but also in water and in 0.1 mol dm^{-3} KNO_3, the uptake of dioxygen occurs in two steps. The first rapid step of a few minutes, is overlapped by a second step lasting about 60-80 minutes. The total amount of the bonded dioxygen is now in the ratio $Co:O_2 = 1:1$. The spectra show an increase in the absorption of the bands at λ_{max} = 320 nm and at λ_{max} = 400 nm in the early ten minutes (Fig. 2a). The maximum at λ = 320 nm then disappears after about 1 hour. The subsequent evolution of the spectra, in the range of time 1-20

hours, is such as to produce the formation of four isosbestic points at λ = 290 nm, λ = 335 nm, λ = 405 nm and λ = 500 nm (Fig. 2b). At long times the spectra, in the range of wavelengths 270-550 nm, show only one band with maximum at λ = 360 nm. The binding curves and spectra suggest that rapid formation of a dinuclear dioxygen species is followed by that of a mononuclear dioxygen species which suffers subsequent rearrangements before degrading into autoxidation products.

In phosphate buffered solutions, at R>1, the uptake of dioxygen becomes relatively slow. At P_{O_2} = 1 atm and pH = 8, about 20 minutes are necessary for the dioxygen binding curve attain a constant value, which still corresponds to a ratio $Co:O_2 = 2:1$. The spectra are similar to those collected at R = 0.5. The maxima are now attained after about 20 minutes (Fig. 2c). The subsequent development of the isosbestic point is also slowed down (Fig. 2d).

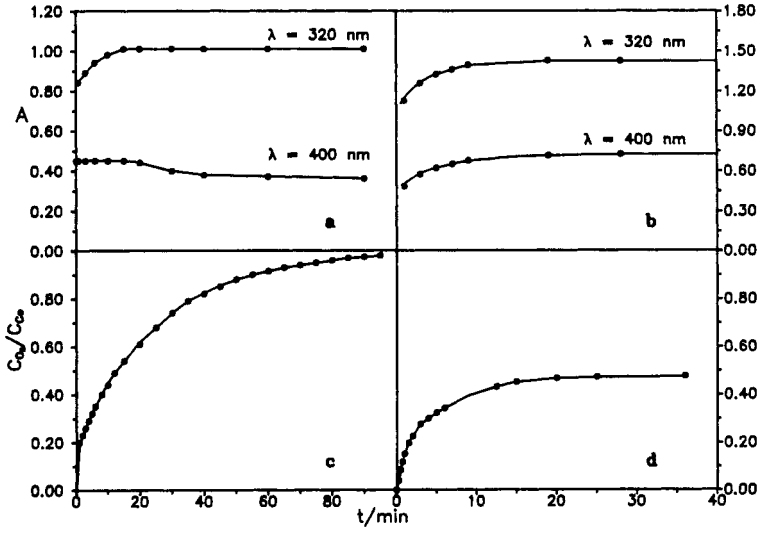


Fig.1. Evolution with time of the absorbance at λ = 320 nm and λ = 400 nm of oxygenated aqueous solutions of [30]aneN$_{10}$ and Co(NO$_3$)$_2$ at 298 K (P_{O_2} = 101 kPa): (a) $C°_{Co}$ = 4.47x10^{-4} mol dm^{-3}, $C°_L$ = 4.56x10^{-4} mol dm^{-3}, borate buffer at pH = 9.0; (b) $C°_{Co}$ = 4.91x10^{-4} mol dm^{-3}, $C°_L$ = 4.66x10^{-4} mol dm^{-3}, phosphate buffer at pH = 8.0.
Evolution with time of the ratio between dioxygen bonded (C_{O_2}) and stoichiometric cobalt concentration ($C°_{Co}$) for aqueous solutions of [30]aneN$_{10}$ and Co(NO$_3$)$_2$ at 298 K: (c) $C°_{Co}$ = 4.24x10^{-4} mol dm^{-3}, $C°_L$ = 7.80x10^{-4} mol dm^{-3}, $C°_{O_2}$ = 8.80 x10^{-4} mol dm^{-3}, borate buffer at pH = 8.2; (d) $C°_{Co}$ = 6.36x10^{-4} mol dm^{-3}, $C°_L$ = 6.81x10^{-4} mol dm^{-3}, $C°_{O_2}$ = 9.72 x10^{-4} mol dm^{-3}, phosphate buffer at pH = 8.0.

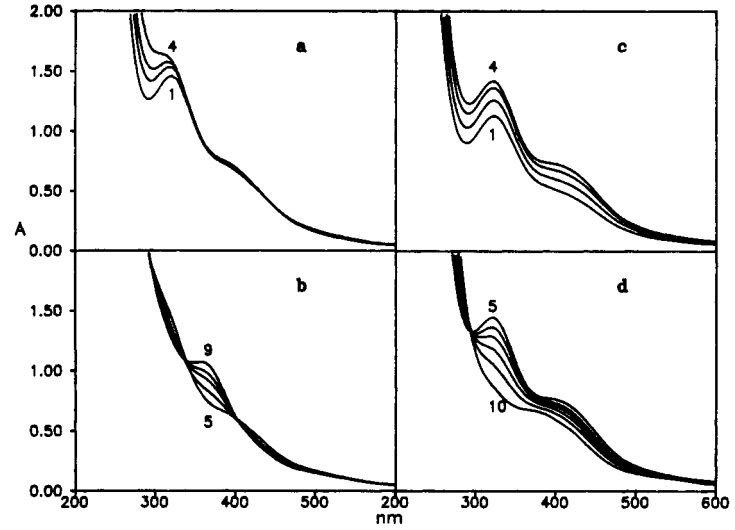


Fig.2. Spectral evolution of oxygenated aqueous solutions of [30]aneN$_{10}$ and Co(NO$_3$)$_2$ at 298 K (P_{O_2} = 101 kPa): (a) and (b): borate buffer at pH = 9.0, $C°_{Co}$ = 5.17x10^{-4} mol dm^{-3}, $C°_L$ = 7.90x10^{-4} mol dm^{-3}. From 1 to 4 spectra recorded after 1, 3, 6 and 14 minutes; from 5 to 9 spectra recorded after 1, 3, 5, 7 and 23 hours. (c) and (d): phosphate buffer at pH = 8.0, $C°_{Co}$ = 4.91x10^{-4} mol dm^{-3}, $C°_L$ = 4.67x10^{-4} mol dm^{-3}. From 1 to 4 spectra recorded after 1, 3, 7 and 19 minutes; from 5 to 10 spectra recorded after 1, 2, 3, 4, 5 and 22 hours.

A valid interpretation of the behaviour of the Co(II) complexes with this macropolytopic ligand cannot be given, but it is certainly interesting that with large macrocyclic ligands able to lodge two cobalt atoms and an anion it is possible to govern the formation of particular types of dioxygen complexes with an appropriate use of two variables, namely the nature of the anion and the value of the ratio ligand/cobalt.

These few examples illustrate the critical way in which the binding of the dioxygen on Co(II) complexes is related to the structure of the ligand. Particular results are: (i) in the series of the open-chain polyamines, an increase in the number of ethylenic chains connecting the nitrogens is matched by increased stability of the dibridged μ-hydroxo- μ-peroxo species, that are much more resistent to irreversible oxidation processes than the monobridged dinuclear species; (ii) in the series of macrocyclic tetramines, except [12]aneN$_4$, monobridged dinuclear complexes are formed. An increase in ring size is matched by reduced affinity for the dioxygen and better reversibility in uptake and release; (iii) the uptake of dioxygen by Co$_2$[30]aneN$_{10}$X is governed by the anion coordination and the value of the ratio R between ligand and cobalt concentrations. Phosphate ions lead, at least in the first few hours, to the formation of binuclear species for any value of R. When other anions are present, the value of R is crucial for the quantity of dioxygen absorbed. For R = 0.5, uptake occurs according to the ratio Co:O$_2$ = 2:1; for R > 1, according to Co:O$_2$ = 1:1. The rate of uptake and the subsequent reactions depend on R. Large values of R slow down the reactions.

The possibility of producing mononuclear and binuclear dioxygen complexes according to the nature of the anion and the value of R is an interesting aspect of dioxygen binding to Co(II) complexes with large polyazamacrocyclic ligands and deserves further investigation.

GLOSSARY

ACACEN	1,12-dihydroxy-4,9-dimethyl-3,10-di-X-5,8-diaza-2,4,8,10-dodecatetraene
[12]aneN$_4$ (cyclen)	1,4,7,10-tetrazacyclododecane
[14]aneN$_4$ (cyclam)	1,4,8,11-tetrazacyclotetradecane
[15]aneN$_4$	1,4,8,12-tetrazacyclopentadecane
[16]aneN$_4$	1,5,9,13-tetrazacyclohexadecane
[30]aneN$_{10}$	1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane
BENACEN	1,10-dihydroxy-3,8-dimethyl-1,10-bis(3-X-phenyl)-4,7-diaza-1,3,7,9-decatetraene
BENSACEN	1,10-dimercapta-3,8-dimethyl-1,10-bis(3-X-phenyl)-4,7-diaza-1,3,7,9-decatetraene
BISDIEN	1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane
BISTREN	1,4,10,13,16,22,27,33-octaaza-7,19,30-trioxabicyclo[11.11.11]pentatriacontane
CoHb	cobalt haemoglobin
CoMy	cobalt myoglobin
DMF	N,N-dimethylformamide
DMSO	dimethyl sulphoxide
EN	ethylenediamine
EPYDEN	2,6-bis[5-(1,4-diazahexyl)]pyridine
4-IMDIEN	1,9-bis(4-imidazolyl)-2,5,8-triazanonane
4-IMDPT	1,11-bis(4-imidazolyl)-2,6,10-triazaundecane
PYDIEN	1,9-bis(2-pyridyl)-2,5,8-triazanonane
PYDPT	1,11-bis(2-pyridyl)-2,6,10-triazaundecane
PYEN	1,6-bis(2-pyridyl)-2,5-diazahexane
SACSACEN	2,11-dimercapta-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene
SALEN	1,6-bis-(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
2,2,2-tet	1,4,7,10-tetraazadecane
2,3,2-tet	1,4,8,11-tetraazaundecane
3,2,3-tet	1,5,8,12-tetraazadodecane
TETREN	tetraethylenepentaamine
TREN	tris(2-aminoethyl)amine

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