Calorimetric Study on Oxygen Addition to Cobalt(II) Complexes with Tris-(2-aminoethyl)amine and 3,7-Diazanonane-1,9-diamine†

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Through spectrophotometric and potentiometric measurements it has been verified that in aerated aqueous solutions of Co^{II} containing tris(2-aminoethyl)amine (tren) as ligand, the doubly bridged μ-peroxo–μ-hydroxo dicobalt ion $[Co_2L_2(O_2)(OH)]^{3+}$ (L = tren) is totally formed at pH >6.5. In aerated aqueous solutions of Co^{II} and 3,7-diazanonane-1,9-diamine (dadn) at pH 6.5 only the singly bridged μ-peroxo dicobalt ion $[Co_2L_2(O_2)]^{4+}$ (L = dadn) is present. This complex at higher pH adds OH^- ions in its axial positions; at pH >10.5 the singly bridged μ-peroxo–dihydroxo dicobalt ion $[Co_2L_2(O_2)(OH)_2]^{2+}$ is totally formed. The singly bridged complex $[Co_2L_2(O_2)]^{4+}$, after several hours, converts irreversibly into the doubly bridged μ-peroxo–μ-hydroxo ion $[Co_2L_2(O_2)(OH)]^{3+}$, while the singly bridged $[Co_2L_2(O_2)(OH)_2]^{2+}$ ion slowly autoxidizes to Co^{III}. By means of calorimetric measurements, usually carried out at constant pH, the enthalpies of formation of $[Co_2L_2(O_2)]^{4+}$ and $[Co_2L_2(O_2)(OH)_2]^{2+}$ (L = dadn) and $[Co_2L_2(O_2)(OH)]^{3+}$ (L = tren) have been obtained. These results are compared with the enthalpies relative to the oxygen addition to $[Co(trien)]^{2+}$ ion (trien = triethylenetetra-amine), and the enthalpy effects, connected with the change from a linear amine (trien) to its branched isomer (tren) and from the sequence 5,5,5 (trien) to the sequence 5,6,5 (dadn) of the chelate rings, are discussed.

In a previous paper[1] we examined the thermodynamic aspects of the addition of molecular oxygen to the Co^{II} complex with triethylenetetra-amine (trien). Here the thermodynamics of binding of molecular oxygen to Co^{II} complexes with the branched isomer tris(2-aminoethyl)amine (tren) and with the linear next homologue 3,7-diazanonane-1,9-diamine (dadn), in aqueous solutions at 25 °C, is examined.

As far as the Co^{II}–tren–O_2 system is concerned, Yang and Grieb[2] observed that, for addition of tren to aerated solutions of Co^{II}, the doubly bridged ion $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$ is formed with a very fast reaction, which is quantitative also at a ligand:Co^{II} ratio only slightly greater than 1:1. The formation of the doubly bridged ion was also observed by McLendon and Martell[3] who, from pH-metric measurements, obtained a value of $\beta_{O_2} = 10^{26.92}$ dm^6 mol^{-2} atm^{-1} for the constant of formation from Co^{II} and free ligand L, where $\beta_{O_2} = [Co_2L_2(O_2)(OH)][H^+]/[Co]^2[L]^2p_{O_2}$ and a value of $\Delta H^\circ = -63 \pm 10$ kcal mol^{-1} from the temperature dependence of log β_{O_2}. Fallab and co-workers,[4–8] through *X*-ray structure determinations, found that the $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$ complex exists only in the form with the tertiary amino groups of the two ligands *cis* with respect to the peroxo bridge. These authors also carried out a detailed kinetic analysis of the H^+-catalyzed reactions of formation and dissociation of $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$, and an analysis of the u.v.–visible spectra of the singly bridged $[X(tren)Co(\mu\text{-}O_2)Co(tren)X]^{4+}$ ion, where X is an additional (neutral) unidentate ligand. For the Co^{II}–dadn–O_2 system, Simon and co-workers[9–11] observed the formation of the singly bridged $[Co_2L_2(O_2)]^{4+}$ ion and gave values for the equilibrium constants for the formation of both $[CoL]^{2+}$ ($K_{CoL} = 3.2 \times 10^{12}$ dm^3 mol^{-1}) and $[Co_2L_2(O_2)]^{4+}$ ($K_{O_2} = 2.5 \times 10^{10}$ dm^6 mol^{-2}) at 20 °C in 0.1 mol dm^{-3} KNO_3, where $K_{O_2} = [Co_2L_2(O_2)]/[CoL]^2[O_2]$. The formation of the singly bridged μ-peroxodicobalt complex from $[Co(dadn)]^{2+}$ has been confirmed by Machida *et al.*,[12] who stated as a general rule that the '5,6,5 chelate ring sequence' could well place the N_4 donors on a plane (*trans* configuration) that leaves only axial sites for the formation of the singly bridging μ-peroxo adduct. Values are also given[12] for the constants of formation at 35 °C and ionic strength $I = 0.2$ mol dm^{-3} for the μ-peroxo ion ($\beta_{O_2} = 1.1 \times 10^{31}$ dm^{12} mol^{-4}) and its $[Co(dadn)]^{2+}$ parent ion ($K_{CoL} = 3.2 \times 10^{13}$ dm^3 mol^{-1}), together with the value of $K_{O_2} = 1.1 \times 10^9$ dm^6 mol^{-2} for the formation of μ-peroxo ion starting from $[CoL]^{2+}$. Clearly, the last value is not consistent with the two previous ones. Moreover, the disagreement between the data of Simon and co-workers[9–11] and Machida *et al.*[12] is very large and certainly not justified by the different conditions of temperature and ionic strength in the case of K_{CoL}. For the addition of O_2 to [CoL] complexes instead, the differences between the two K_{O_2} values reported may be justified by the different temperatures.

We report here the results of an analysis devoted to identifying the species present, at various pH, in solutions of Co^{II} and tren or dadn, both under anaerobic and aerobic conditions, and to determine, through calorimetric measurements, their enthalpies of formation.

Experimental

Materials.—Commercial tren and dadn (Strem Chemicals) were purified by precipitation as their tetrahydrochloride salts and their purity checked by elemental analysis. A $Co(NO_3)_2$ stock solution (*ca.* 0.5 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 grade products and were used without further purification.

Apparatus.—The calorimetric apparatus has been described previously.[13] Spectrophotometric measurements were performed by using a Pye Unicam SP8-150 u.v.–visible spectrophotometer; potentiometric measurements were made on a Radiometer PHM 84 pH-meter, equipped with a GK2351-B combined glass electrode. The free oxygen in the solution was measured by means of a Beckman Oxygen Analyser (model 0260) equipped with an oxygen electrode capable of measuring

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† *Non-S.I. units employed:* cal = 4.184 J, atm = 101 325 Pa.

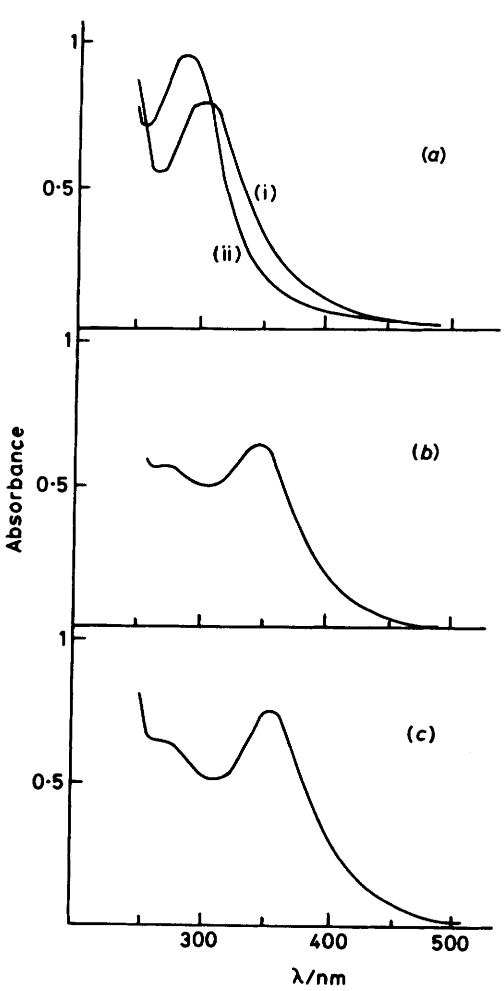

Figure 1. Spectra of oxygenated solutions of Co^{II} and various ligands: (*a*) dadn (3.65×10^{-3} mol dm^{-3}), $Co(NO_3)_2$ (1.50×10^{-3} mol dm^{-3}), pH 6.53 (i), pH 10.58 (ii); (*b*) trien (8.5×10^{-3} mol dm^{-3}), $Co(NO_3)_2$ (2.20×10^{-3} mol dm^{-3}), pH 7.5; (*c*) tren (4.02×10^{-3} mol dm^{-3}), $Co(NO_3)_2$ (1.80×10^{-3} mol dm^{-3}), pH 8.5. Path length 0.1 cm

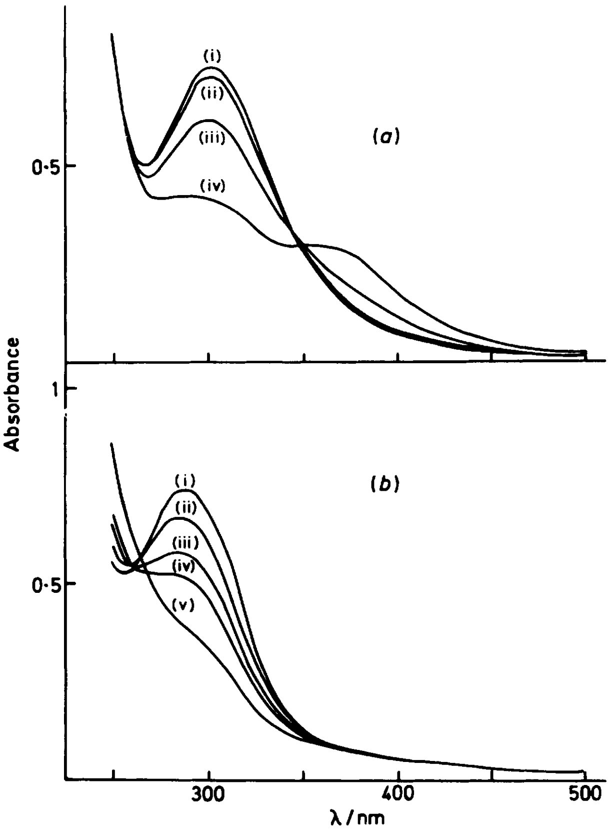

Figure 2. Spectra of oxygenated solutions of dadn and $Co(NO_3)_2$: (*a*) dadn (3.50×10^{-3} mol dm^{-3}), $Co(NO_3)_2$ (1.29×10^{-3} mol dm^{-3}), pH 6.53, after 5 min (i), 15 min (ii), 1 h (iii), and 6 h (iv) from preparation; (*b*) dadn (4.20×10^{-3} mol dm^{-3}), $Co(NO_3)_2$ (1.17×10^{-3} mol dm^{-3}), pH 10.58 after 5 min (i), 1 h (ii), 6 h (iii), 9 h (iv) and 24 h (v) from preparation. Path length 0.1 cm

oxygen concentrations up to a maximium of 199.0 parts per million (for details see ref. 13).

Results

The u.v. spectra of oxygenated solutions of Co^{II}–dadn at pH 6.53 and 10.58, and Co^{II}–tren at pH 8.5 are reported in Figure 1 and compared with the spectrum of oxygenated solutions of Co^{II}–trien at pH 7.5.

The interpretation of the u.v. spectra of Co^{II} peroxo complexes, given by Sasaki *et al.*,[14] Lever and Gray,[15] Fallab and Zehnder,[8] and Barraclough *et al.*,[16] allows us to establish the formation of the doubly bridged μ-peroxo–μ-hydroxo species for both Co^{II}–tren–O_2 and Co^{II}–trien–O_2 systems, whereas, in the case of the Co–dadn–O_2 system, singly bridged μ-peroxo species $[Co_2L_2(O_2)]^{4+}$ and $[Co_2L_2(O_2)(OH)_2]^{2+}$ are formed, at pH 6.53 and pH 10.58 respectively. The presence of OH^- ions in the above complexes is confirmed by the amount of NaOH necessary to maintain constant pH when oxygen is bubbled into anaerobic solutions of Co^{II} and tren (mole ratio of NaOH to Co, $m_{NaOH}/m_{Co} = 0.5$), at pH $\geqslant 6.5$, and into anaerobic solutions of Co^{II} and dadn at pH > 10.5 ($m_{NaOH}/m_{Co} \simeq 1$). Finally, our polarographic measurements of the absorbed oxygen indicate the complete formation of the oxygenated complexes, at pH $\geqslant 6.5$ and a ligand:cobalt ratio of 1:1, for both tren and dadn. The spectra in Figure 1 (*b*) and (*c*), recorded after many hours, show no change. On the contrary, the spectra of oxygenated Co^{II} solutions containing dadn clearly exhibit evolution with time (Figure 2).

In Figure 2 we report the spectra of solutions of Co^{II} saturated with O_2 (1 atm), and containing an excess of dadn, recorded immediately after preparation at pH 6.53 and 10.58 respectively, together with the spectra recorded after several hours. It is evident that, at pH 6.53 the initial singly bridged μ-peroxo ion, $\lambda_{max.}$ 300 nm (ε 10 500 dm^3 mol^{-1} cm^{-1}), converts into a doubly bridged μ-peroxo–μ-hydroxo ion, $\lambda_{max.}$ 370 and 290 nm (ε 4 600 and 5 200 dm^3 mol^{-1} cm^{-1}). This statement, justified by the interpretation of the spectra (see refs. 8, 14—16), it is also supported by the fact that the pH decreases slowly during the reaction, and NaOH (mol ratio NaOH:Co of 0.5:1) has to be added in order to re-establish the initial pH after the reaction is completed. The spectra at pH 10.58, recorded at various times, show only a slow oxidation to the Co^{III} complexes. However, the formation of the doubly bridged μ-peroxo–μ-hydroxo ion is so slow that it does not affect the calorimetric determination of the enthalpy of formation of the singly bridged μ-peroxo ion. Analogously, the irreversible oxidation to Co^{III} does not affect calorimetric measurements; this reaction is slow for the peroxo complexes with dadn and very slow for those with tren.[3]

Table 1. Calorimetric data for the system Co–tren–O_2 at 25 °C in aqueous KNO_3 solution (0.1 mol dm^{-3})

Atmosphere	Experiment	$10^4 m_L$/ mol	$10^4 m_{Co}$/ mol	pH	$10^4 m_{NaOH}$^{a}/ mol	$q_{obs.}$^{b}/ J	$-\Delta H_Y^{X\,c}$/ kJ mol^{-1}	X	Y^d
N_2	A	20.80	3.950	12.48	—	22.22	56.23	Co	$[CoL(OH)]^+$
		12.85	4.450	12.75	—	25.61	57.53	Co	$[CoL(OH)]^+$
O_2	B	12.37	3.952	12.35	—	52.22	264.26	Co	$[Co_2L_2(O_2)(OH)]^{3+}$
		9.66	2.964	12.58	—	38.74	261.42	Co	$[Co_2L_2(O_2)(OH)]^{3+}$
O_2	C	31.98	4.450	6.75	2.25	39.41	177.15	$[CoL]^{2+}$	$[Co_2L_2(O_2)(OH)]^{3+}$
		43.00	5.480	6.80	2.94	50.42	184.01	$[CoL]^{2+}$	$[Co_2L_2(O_2)(OH)]^{3+}$
O_2	D	12.64	2.964	11.89	—	23.35	157.53	$[CoL(OH)]^+$	$[Co_2L_2(O_2)(OH)]^{3+}$
		13.55	4.940	12.36	—	39.50	159.91	$[CoL(OH)]^+$	$[Co_2L_2(O_2)(OH)]^{3+}$

[a] Moles of NaOH added to maintain constant pH during the reaction. [b] Heat evolved in the reaction, corrected only for the dilution of the stock solutions of $Co(NO_3)_2$ or of NaOH. [c] $\Delta H_Y^X = -jq_{obs.}/m_{Co}$: $j = 1$ (experiment A), $j = 2$ (experiments B—D). [d] $[Co_2L_2(O_2)(OH)]^{3+}$ represents the doubly bridged μ-hydroxo–μ-peroxo ion for L = tren.

Table 2. Enthalpies of reaction for the system Co–tren–O_2 at 25 °C in aqueous KNO_3 solution (0.1 mol dm^{-3})

Reaction	No. of experiments	pH	m_{NaOH}/m_{Co}^{a}	$-\Delta H$/kJ mol^{-1}
(I) $Co^{2+} + L + OH^- \longrightarrow [CoL(OH)]^+$	6	>12	—	56.9 ± 1.7^b
(II) $2Co^{2+} + 2L + OH^- + O_2(aq) \longrightarrow [Co_2L_2(O_2)(OH)]^{3+}$	4	>12	—	251.0 ± 2.5
(III) $2[CoL]^{2+} + OH^- + O_2(aq) \longrightarrow [Co_2L_2(O_2)(OH)]^{3+}$	6	6.7—6.8	0.5	167.8 ± 3.3
(IV) $2[CoL(OH)]^+ + O_2(aq) \longrightarrow [Co_2L_2(O_2)(OH)]^{3+} + OH^-$	7	>12	—	146.0 ± 2.9
(V) $Co^{2+} + L \longrightarrow [CoL]^{2+}$	—	—	—	41.8 ± 2.9^c

[a] Ratio of moles of NaOH to moles of cobalt added to maintain constant pH. [b] Using the equations (II) and (IV) gives $\Delta H_{CoL(OH)} = -52.7 \pm 2.9$ kJ mol^{-1}. [c] Obtained by combining equations (II) and (III): *cf.* $\Delta H_{CoL} = -44.4 \pm 0.6$ kJ mol^{-1} (P. Paoletti, M. Ciampolini, and M. Sacconi, *J. Chem. Soc.*, 1963, 3589).

The calorimetric measurements were performed in such a way that we have obtained a complete picture of the enthalpy changes connected with the formation of complexes, under both anaerobic and aerobic conditions, and over a wide pH range. Some calorimetric measurements, however, have been carried out in pH ranges where only one complex ion was present, or highly prevalent. Under such conditions the only difficulty is to obtain a reliable correction for the proton distribution which follows from: (*i*) the addition of $Co(NO_3)_2$ to solutions of the ligand under nitrogen or under oxygen; (*ii*) the bubbling of oxygen into solutions where $[CoL]^{2+}$ was present. The difference in the values reported previously for the equilibrium constants of proton addition to polyazotate ligands are generally so pronounced as to produce, depending on the selected β_{H_iL}, serious (and sometimes enormous) differences in the calculated β_{H_iL} values of ΔH (i = number of protons, β_{H_iL} = overall protonation constant), in particular when pH is not kept constant during the reaction. Therefore, in order to evaluate the distribution of the protonated species before and after the complexation or oxygenation reaction, it is preferable to have an homogeneous set of new data, even if not of high precision, rather than to use the β_{H_iL} values reported in the literature and to combine data of different accuracy.

Furthermore it is advisable to obtain conditions which allow verification, by direct experiment, of the thermodynamic state of the solutions with respect to the concentration of the species which participate in the reaction and of all others which are involved in coupled reactions. In order to attain reliable results we found it advisable to operate at constant pH and with an excess of ligand. This may be achieved by adding to the reactant [$Co(NO_3)_2$ or O_2] an amount of NaOH solution such that the pH is constant during each experiment. It is thus possible to avoid any correction due to the distribution, on the ligand in excess, of protons released in the formation of Co^{II} complexes and, moreover, to evaluate directly the total amount of protons involved in the reaction. This may assist in (*i*) identifying the stoicheiometry of the reaction, (*ii*) establishing the degree of protonation of the ligand used in the experiment at the pH at which the reaction occurs, and (*iii*) calculating the correction term for deprotonation of the ligand involved in the complexation. For this last purpose the enthalpies of protonation ΔH_{H_iL} have to be known. Experimental data of the evolved heat of reaction were reduced to equations of the forms (1) or (2).

$$aCo^{2+} + aL + bO_2(aq) + cOH^- \longrightarrow [Co_aL_a(O_2)_b(OH)_c]^{(2a-c)+} \quad (1)$$

$$2[CoL]^{2+} + O_2(aq) + dOH^- \longrightarrow [Co_2L_2(O_2)(OH)_d]^{(4-d)+} \quad (2)$$

The study of the system Co–tren–O_2 was particularly simple. In fact, at pH >6.5 and in aerated solutions of Co^{II} and tren, only the doubly bridged μ-peroxo–μ-hydroxo dicobalt ion $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$ is formed. The formation of this species, starting from $[CoL]^{2+}$, was studied at pH ≃ 6.6; starting from Co^{2+} or $[CoL(OH)]^+$, at pH > 12. In this way no correction for deprotonation of the ligand was necessary.

As an example, we report some data in Table 1. The mean values of the reaction enthalpies, calculated considering all the experiments, are summarized in Table 2. The internal consistency among ΔH values is acceptable as may be ascertained by comparing, for the same reaction, the value obtained from direct measurements, or that calculated using ΔH values derived from different sets of experiments (see footnote to Table 2).

As far as the Co–dadn–O_2 system is concerned, the situation is more complicated, as shown by Figure 3. Here we plot, *versus* pH, the Bjerrum function of protonation, $\bar{n}_H = \Sigma i\beta_{H_iL}[H^+]^i/(1 + \Sigma\beta_{H_iL}[H^+]^i)$, calculated by the β_{H_iL} values from ref. 17, together with the experimental $\bar{n}_H$(exp.) values defined as $\bar{n}_H$(exp.) = m_{NaOH}/m_{Co} [m_{NaOH} = moles of NaOH added to maintain constant pH, and m_{Co} = total moles of $Co(NO_3)_2$ in the solution]. It is evident that, under N_2, the formation of

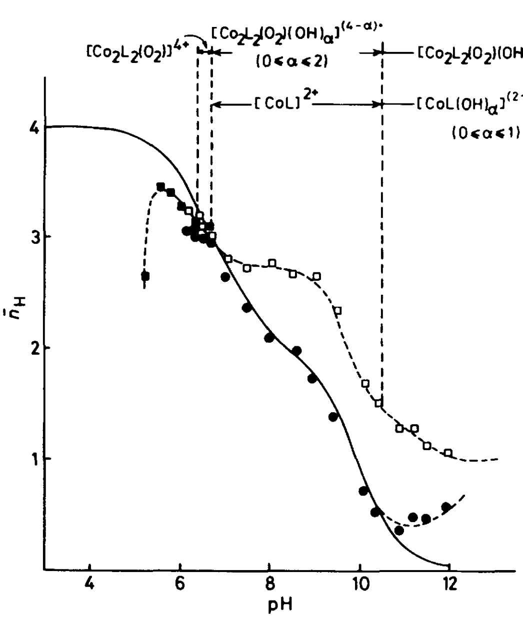

Figure 3. Bjerrum's function $\bar{n}_H$ *vs.* pH for dadn in KNO_3 (0.1 mol dm^{-3}), at 25 °C: (——) calculated using β_{H_iL} values from ref. 7. The points have been calculated from the ratio m_{NaOH}/m_{Co}: (●) Co^{2+} added to ligand solution under N_2; (■) Co^{2+} added to ligand solution under O_2; (□) O_2 added into solutions containing preformed $[CoL]^{2+}$. The complexes present at various pH under anaerobic and aerobic atmospheres are indicated

$[CoL]^{2+}$ is quantitative from pH 7.6 to 10.5. At pH <7.6 the formation of $[CoL]^{2+}$ is incomplete; at pH >10.5 the species $[CoL(OH)]^+$ begins to form and its formation is complete at pH 12.5. Under O_2 the formation of $[Co_2L_2(O_2)]^{4+}$ is complete only at pH 6.5 (see also Figure 4). In the range from pH 6.5 to 10.5, together with the singly bridged μ-peroxo ion there are also species with one or two hydroxo groups bonded to Co^{II} in axial positions. At pH >10.5 both the $[CoL]^{2+}$ and the $[CoL(OH)]^+$ species concur to form the singly bridged dihydroxo–μ-peroxo ion $[Co_2L_2(O_2)(OH)_2]^{2+}$.

Using this information as a starting point for planning and interpreting the calorimetric experiments, we obtained results which completely confirm this picture. This may be seen in Figure 4 in which curves of $\Delta H_{obs.}$ *versus* pH are plotted, where $\Delta H_{obs.} = -2q_{obs.}/m_{Co}$ ($q_{obs.}$ = heat evolved).

When O_2 is bubbled into solutions containing Co^{II} and ligand, the values of $\Delta H_{obs.} = -2q_{obs.}/m_{Co}$, obtained at different pH, allow us to identify three different situations. At pH <6.5 the reaction is as in equation (3) where $\bar{n}_{CoL}$ is the degree of

$$(2\bar{n}_{CoL})[CoL]^{2+} + 2(1 - \bar{n}_{CoL})Co + 2(1 - \bar{n}_{CoL})H_{\bar{n}_H}L + O_2 + 2\bar{n}_H(1 - \bar{n}_{CoL})OH^- \longrightarrow [Co_2L_2(O_2)]^{4+} + \bar{n}_H(1 - \bar{n}_{CoL})H_2O \quad (3)$$

formation of $[CoL]^{2+}$ and $\bar{n}_H$ is the degree of protonation of the ligand.

The values $\Delta H_{obs.}$ are related to reaction (3) by equation (4)

$$\Delta H_{obs.} = \Delta H_{Co_2L_2O_2}{}^{CoL} + 2(1 - \bar{n}_{CoL})\Delta H_{CoL} + 2\bar{n}_H(1 - \bar{n}_{CoL})[\Delta H_w - (\Delta\bar{H}_{HL})_{\bar{n}_H}] \quad (4)$$

where ΔH_w is the heat of formation of water from its ions ($\Delta H_w = -56.57$ kJ mol^{-1}) and $(\Delta\bar{H}_{HL})_{\bar{n}_H}$ is the mean enthalpy protonation function of the ligand: $(\Delta\bar{H}_{HL})_{\bar{n}_H} = \Sigma\beta_{H_iL}[H^+]^i\Delta H_{H_iL}/\Sigma i\beta_{H_iL}[H^+]^i$. For the calculation of $(\Delta\bar{H}_{LH})_{\bar{n}_H}$ we used the values of β_{H_iL} and ΔH_{H_iL} given in ref. 17.

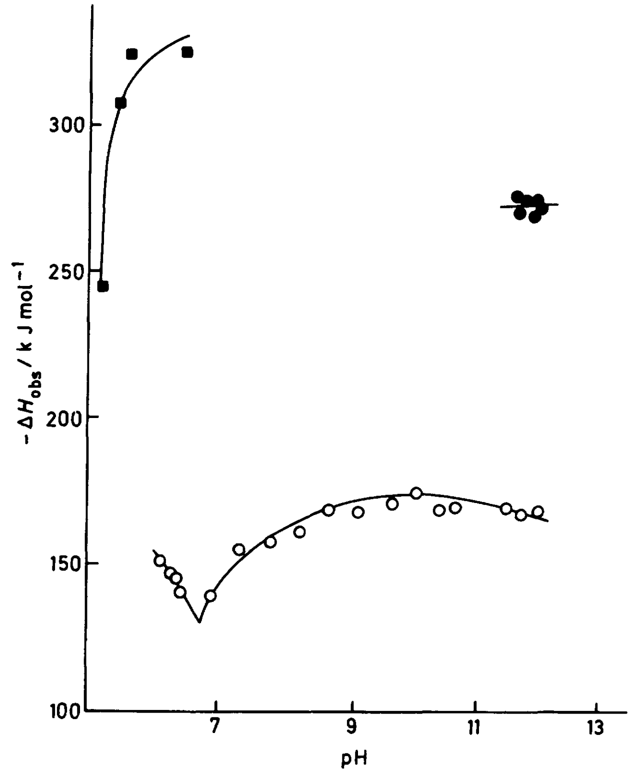

Figure 4. Enthalpy changes $-\Delta H_{obs.} = 2q_{obs.}/m_{Co}$ for the addition of Co^{II} to oxygenated solutions of dadn (■, ●) or bubbling O_2 into anaerobic solutions of Co^{II} and dadn (○). $q_{obs.}$ Is the heat evolved after correction for the following: heat of dilution of $Co(NO_3)_2$ stock solution (●); heat of dilution of NaOH stock solution (○); heat of dilution of $Co(NO_3)_2$ stock solution and heat of dilution of NaOH stock solution (■)

In the range 6.5 < pH < 10.5 the process is as in equation (5), with $0 \leqslant \alpha \leqslant 2$; in this case, this leads to equation (6)

$$2[CoL]^{2+} + O_2 + \alpha OH^- \longrightarrow [Co_2L_2(O_2)(OH)_\alpha]^{(4-\alpha)+} \quad (5)$$

$$\Delta H_{obs.} = \Delta H_{Co_2L_2O_2}{}^{CoL} + \frac{\alpha}{2}[\Delta H_{Co_2L_2O_2(OH)_2}{}^{CoL} - \Delta H_{Co_2L_2O_2}{}^{CoL}] \quad (6)$$

(charges are omitted from the subscripts and superscripts). Finally, at pH >10.5, the reaction is as in equation (7), with $2 \geqslant \alpha \geqslant 0$, leading to equation (8).

$$\alpha[CoL]^{2+} + (2 - \alpha)[CoL(OH)]^+ + O_2 + \alpha OH^- \longrightarrow [Co_2L_2(O_2)(OH)_2]^{2+} \quad (7)$$

$$\Delta H_{obs.} = \Delta H_{Co_2L_2O_2(OH)_2}{}^{CoL} + \frac{(2 - \alpha)}{2} \cdot [\Delta H_{Co_2L_2O_2(OH)_2}{}^{CoL(OH)} - \Delta H_{Co_2L_2O_2(OH)_2}{}^{CoL}] \quad (8)$$

When Co^{II} ions are added to dadn solutions, under O_2, the process (9) occurs, with $0 \leqslant \alpha \leqslant 2$. The results from Figure 4,

$$2Co^{2+} + 2H_{\bar{n}_H}L + O_2 + (2\bar{n}_H + \alpha)OH^- \longrightarrow [Co_2L_2(O_2)(OH)_\alpha]^{(4-\alpha)+} + (2\bar{n}_H)H_2O \quad (9)$$

Table 3. Calorimetric data for the system Co–dadn–O_2 at 25 °C in aqueous KNO_3 solution (0.1 mol dm^{-3})

Atmo-sphere	Experi-ment	$10^4 m_L$/ mol	$10^4 m_{Co}$/ mol	pH	$10^4 m_{NaOH}$[a]/ mol	$\bar{n}_H$[b]	η[c]	$q_{obs.}$[d]/ J	q_I[e]/ J	q_{II}[f]/ J	$-\Delta H_Y^X$[g]/ kJ mol^{-1}	X	Y
N_2	A	18.86	2.964	6.19	9.12	(3.41)	0.919	24.92	11.39	—	49.66	Co	$[CoL]^{2+}$
		9.73	2.964	6.40	8.95	(3.26)	0.947	24.10	10.62	—	48.03	Co	$[CoL]^{2+}$
		10.42	2.964	6.52	8.90	(3.17)	0.969	23.81	10.51	—	46.32	Co	$[CoL]^{2+}$
N_2	B	12.25	3.952	8.55	7.75	1.96	1.961	28.12	7.94	—	51.04	Co	$[CoL]^{2+}$
		12.02	4.446	9.00	7.80	1.75	1.754	30.67	7.91	—	51.21	Co	$[CoL]^{2+}$
O_2	C	7.43	3.532	5.80	12.06	(3.66)	0.93	57.40	15.40	—	254.97	Co	$[Co_2L_2(O_2)]^{4+}$
		7.44	3.458	6.43	10.81	(3.23)	0.96	54.73	13.05	—	251.37	Co	$[Co_2L_2(O_2)]^{4+}$
O_2	D	9.24	4.470	12.38	—	—	—	60.92	—	—	272.59	Co	$[Co_2L_2(O_2)(OH)_2]^{2+}$
		10.58	4.742	12.52	—	—	—	64.27	—	—	271.04	Co	$[Co_2L_2(O_2)(OH)_2]^{2+}$
O_2	E	18.86	2.964	6.19	0.48	(3.41)	0.081	22.43	1.004	1.213	136.36	$[CoL]^{2+}$	$[Co_2L_2(O_2)]^{4+}$
		9.73	2.964	6.40	0.35	(3.26)	0.053	21.88	0.594	0.787	138.32	$[CoL]^{2+}$	$[Co_2L_2(O_2)]^{4+}$
		10.42	2.964	6.52	0.28	(3.17)	0.031	21.09	0.335	0.460	136.94	$[CoL]^{2+}$	$[Co_2L_2(O_2)]^{4+}$

[a] Moles of NaOH added to maintain constant pH during the reaction. [b] Bjerrum's function calculated as $\bar{n}_H = m_{NaOH}/m_{Co}$ or as $\bar{n}_H = \Sigma i\beta_{H_iL}[H^+]^i/\Sigma\beta_{H_iL}[H^+]^i$ (values in parentheses), β_{H_iL} values were taken from ref. 17. [c] The parameter η allows the state of the solution in different situations to be characterized: $\eta = m_{NaOH}/m_{Co}$, may be identified with $\bar{n}_H$ when the cobalt is present only as $[CoL]^{2+}$ or $[Co_2L_2(O_2)(OH)_2]^{2+}$ (experiments B and D respectively); $\eta = m_{NaOH}/m_{Co}$, $\bar{n}_H^{calc.}$ may be identified with the degree of formation, $\bar{n}_{Co_2L_2O_2}$, of $[Co_2L_2(O_2)]^{2+}$ [the $\bar{n}_H^{calc.}$ value is obtained by using the β_{H_iL} values of ref. 17 (experiment C)]; $\eta = m_{NaOH}/m_{Co}$, $\bar{n}_H^{calc.}$ may be identified as the degree of formation, $\bar{n}_{CoL}$, of $[CoL]^{2+}$ (experiment A); $(1 - \eta)$ is the cobalt fraction which reacts with $H_{\bar{n}_H}L$ when O_2 is bubbled into the solution (experiment E). [d] Heat evolved in the reaction, corrected only for the dilution of the stock solutions of $Co(NO_3)_2$ and NaOH. [e] Heat corresponding to the process involving the release and the neutralization of the protons bonded in the amount of $H_{\bar{n}_H}L$ which reacts with the cobalt. [f] Heat corresponding to the formation of $[CoL]^{2+}$ with O_2 as reagent and when the formation of $[CoL]^{2+}$ under N_2 was incomplete. [g] Enthalpy changes in the formation of species Y starting from species X. $\Delta H_Y^X = -j(q_{obs.} - q_I - q_{II})/m_{Co}\chi$, where $\chi = \bar{n}_{CoL} = m_{NaOH}/m_{Co}\bar{n}_H^{calc.}$ and $j = 1$ (experiment A); $\chi = 1$ and $j = 1$ (experiment B); $\chi = \bar{n}_{Co_2L_2O_2} = m_{NaOH}/m_{Co}\bar{n}_H^{calc.}$ and $j = 2$ (experiment C); $\chi = 1, j = 2$ (experiments C and E).

Table 4. Enthalpies of reaction for the system Co–dadn–O_2 at 25 °C in aqueous KNO_3 solution (0.1 mol dm^{-3})

	Reaction	No. of experiments	pH	$-\Delta H$/kJ mol^{-1}
(I)	$Co^{2+} + L \longrightarrow [CoL]^{2+}$	15	6.2—10.5	50.2 ± 3.8[a]
(II)	$2Co^{2+} + 2L + O_2(aq) \longrightarrow [Co_2L_2(O_2)]^{4+}$	6	5.2—6.7	240.6 ± 4.2
(III)	$2Co^{2+} + 2L + 2OH^- + O_2(aq) \longrightarrow [Co_2L_2(O_2)(OH)_2]^{2+}$	6	12.2—12.6	260.2 ± 2.5
(IV)	$2[CoL]^{2+} + O_2(aq) \longrightarrow [Co_2L_2(O_2)]^{4+}$	6	6.2—6.5	125.5 ± 2.1[b]
(V)	$2[CoL]^{2+} + 2OH^- + O_2(aq) \longrightarrow [Co_2L_2(O_2)(OH)_2]^{2+}$	—	7—10.5	161.1 ± 3.2[c]

[a] This experimental value of ΔH_{CoL} agrees very well with that (−49.6 kJ mol^{-1}) obtained by combining reactions III and V, but not with the value (−57.6 kJ mol^{-1}) obtained from reactions II and IV. The disagreement may be explained in part by the difficulty of obtaining good values for the species $[Co_2L_2(O_2)]^{4+}$ which exists only in a very narrow pH range. [b] This value is the mean of the value (−126.4 ± 2.1 kJ mol^{-1}) obtained from six experiments in the pH range 6.2—6.5 and that (−124.7 ± 2.0 kJ mol^{-1}) which is the intercept of a straight line [equation (6) in the text] plotted from data collected in the range $7 < pH < 10.5$. [c] This value is the sum of the intercept (−124.7 kJ mol^{-1}) and the slope (−36.4 kJ mol^{-1}) of the straight line [equation (6) in the text], plotted from eight data points collected in the range $7 < pH < 10.5$.

and the potentiometric data in Figure 3, show that the complete formation of $[Co_2L_2(O_2)]^{4+}$ occurs only at pH 6.5. At higher pH, OH^- ions enter the peroxo complex and $\alpha = 2$ at pH > 10.5. At pH $\geqslant 6.5$, $\Delta H_{obs.}$ has to be written as in equation (10).

$$\Delta H_{obs.} = \Delta H_{Co_2L_2O_2(OH)_\alpha} + 2\bar{n}_H[\Delta H_w - (\Delta H_{LH})_{\bar{n}_H}] \quad (10)$$

In Table 3 we report some experimental data for the system Co–dadn–O_2, while the results obtained are summarized in Table 4. In this case also the internal consistency is acceptable.

Discussion

We agree substantially with previous results[2–12] concerning the type of μ-peroxo ions derived from Co^{II} complexes with trien, dadn, and tren. However, in our opinion, the rule[12] relating the formation of a singly or doubly bridged μ-peroxo compound to the fact that the parent complex $[CoL]^{2+}$ has a planar (*trans*) or a non-planar (*cis*) conformation is not quite correct. Indeed, in the case of dadn the thermodynamic stability of the doubly bridged μ-peroxo–μ-hydroxo ion is larger than that of the corresponding singly bridged μ-peroxo ion, so that, at pH 6.5, the formation of the latter ion is observed only for kinetic reasons. The existence of the singly bridged ion is, however, favoured at higher pH values, when OH^- ions enter in axial positions.

The thermodynamic data for the formation of μ-peroxo ions, and of their parent ions, for the ligands here considered, are summarized in Table 5. Concerning the free energy function, we note the large disagreement in the literature among different workers. This may be related in part to the purity of the ligand, and in part to the experimental method, usually limited to pH-metric titrations. Such a method cannot give totally reliable results, mainly because of the uncertainty in the values of the equilibrium constants for the proton addition on the ligand, and also when the titration procedure is used only at a few values of the ratio L:Co. Of course, using more than one method, in order to measure other concentration terms (besides H^+), *e.g.* the concentration of free O_2 (O_2 sensor electrode) and of bonded O_2 (spectrophotometry), could improve the situation. However, the high values of equilibrium constants, K_{O_2} prevent good values of ΔG_{O_2} being obtained. The situation is different for ΔH_{O_2}, whose determination is favoured by the high stability of the μ-peroxo compounds.

Table 5. Thermodynamic data for the formation of $[CoL]^{2+}$ and $[CoL(OH)]^{+}$ (L = tren, trien, or dadn) and their peroxo derivatives, T = 25 °C, aqueous KNO_3 (0.1 mol dm^{-3})

Reaction	L	log K	$-\Delta H$/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
$Co^{2+} + L \longrightarrow [CoL]^{2+}$	tren	12.69[a]	44.56[b]	92.0
	trien	10.95[c]	44.56[c]	58.6[c]
	dadn	(13.5)[d] 12.3[f]	48.95[e]	71.1
$Co^{2+} + L + OH^- \longrightarrow [CoL(OH)]^+$	tren		56.90[e]	
	trien		44.7[g]	
	dadn		53.14[e]	
$2Co^{2+} + 2L + O_2(aq) \longrightarrow [Co_2L_2(O_2)]^{4+}$	dadn	(31.0)[d] 33.7[h]	240.6[e]	−155
$2[CoL]^{2+} + O_2(aq) \longrightarrow [Co_2L_2(O_2)]^{4+}$	dadn	(9.0)[d] 10.7[i]	125.9[e]	−218
$2Co^{2+} + 2L + O_2(aq) + OH^- \longrightarrow [Co_2L_2(O_2)(OH)]^{3+}$[k]	tren	43.8[j]	251.0[e]	−12.6
	trien	41.9[l]	256.9[m]	−58.6[c]
	dadn		(248.5)[n]	
$2[CoL]^{2+} + O_2(aq) + OH^- \longrightarrow [Co_2L_2(O_2)(OH)]^{3+}$[k]	tren	18.5[j]	167.8[e]	−209
	trien	20.0[l]	167.8[m]	−180[c]
	dadn		(149.8)[n]	
$2Co^{2+} + 2L + O_2(aq) + 2OH^- \longrightarrow [Co_2L_2(O_2)(OH)_2]^{2+}$	dadn		258.6[e]	
$2[CoL]^{2+} + O_2(aq) + 2OH^- \longrightarrow [Co_2L_2(O_2)(OH)_2]^{2+}$	dadn		158.2[e]	

[a] From ref. 3. [b] From P. Paoletti, M. Ciampolini, and M. Sacconi, *J. Chem. Soc.*, 1963, 3589. [c] From L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115. [d] From ref. 12; T = 35 °C, KNO_3, I = 0.2 mol dm^{-3} (these values are given in parentheses because of the internal incompatibility among the data reported). [e] This work. [f] From ref. 9; T = 20 °C, I = 0.1 mol dm^{-3}. A value of log K_{CoL} = 12.5 is also reported in ref. 10. [g] Unpublished data. [h] From ref. 9; T = 20 °C, KNO_3, I = 0.1 mol dm^{-3}. [i] From ref. 9; T = 20 °C, KNO_3, I = 0.1 mol dm^{-3}. A value of log K_{O_2} = 10.4 is also reported in ref. 10. [j] From ref. 3: the values reported have been modified taking into account the different units $\{[O_2]$ or $p_{O_2}\}$ and the different ways of writing the reaction of formation of the μ-peroxo–μ-hydroxo complex. [k] $[Co_2L_2(O_2)(OH)]^{3+}$ represents the doubly bridged μ-hydroxo–μ-peroxo ion for L = tren and trien and, occasionally in this table, also the singly bridged μ-peroxo–hydroxo ion for L = dadn. [l] Value obtained by adding the value of the ionic product of water to the value reported in ref. 1. [m] Value obtained by adding the heat of formation of water to the value reported in ref. 1. [n] This value has been estimated as the mean of the enthalpies of formation of the corresponding singly bridged μ-peroxo and singly bridged μ-peroxo–dihydroxo ions.

In Table 5 we report ΔH° values for the formation of $[CoL]^{2+}$ and the peroxo derivatives, starting from Co^{II} and free ligand L, and the enthalpies of oxygen addition to $[CoL]^{2+}$ ions. Together with $[Co(tren)]^{2+}$ and $[Co(dadn)]^{2+}$, we include also the $[Co(trien)]^{2+}$ ion, previously studied.[1] It can be observed that, starting from Co^{II} and free ligand L, ΔH_{CoL} has practically the same values for L = trien and tren, despite noticeably different structural features of the two isomers. The enthalpy of binding of dadn to Co^{II} is larger in magnitude, due to the favoured co-ordination with the metal presented by the alternating 5,6,5-membered chelate sequence compared with the 5,5,5 chelate.[17,18] Curiously, however, the situation is reversed when an OH^- group is introduced in an axial position: the $[CoL(OH)]^+$ complex, with L = tren, is now more stabilized (from an enthalpic point of view) compared with the analogous complexes having L = dadn and trien.

As far as the oxygen addition is concerned, no difference is found between the two isomers tren and trien; the doubly bridged μ-peroxo–μ-hydroxo ions are in effect formed with the same enthalpy change no matter whether Co^{II} or $[CoL]^{2+}$ is the starting material. These changes in enthalpy are larger than those found in the formation of the singly bridged μ-peroxo ion, and also those estimated for the ion $[(dadn)Co(\mu\text{-}O_2)(\mu\text{-}OH)\text{-}Co(dadn)]^{3+}$. The same ΔH values are found only when the singly bridged dihydroxo–μ-peroxo ion of dadn is compared with the doubly bridged μ-peroxo–μ-hydroxo ions of tren and trien, and the Co^{2+} ion is the starting material. When the starting materials are the $[CoL]^{2+}$ ions, the enthalpic stability is still higher for the doubly bridged μ-peroxo–μ-hydroxo complexes (L = tren or trien) with respect to the singly bridged dihydroxo ion (L = dadn). It seems therefore that the doubly bridged structures are always favoured, from an enthalpic point of view, compared with the singly bridged structures; for enthalpic reasons again, the $[Co(dadn)]^{2+}$ complexes produce the doubly bridged μ-peroxo–μ-hydroxo dicobalt ion, although the singly bridged μ-peroxo complex, with or without hydroxo groups, is initially formed. When hydroxo groups are present in both the axial positions, it is not possible to detect the formation of the dibridged ion, because, in alkaline media, irreversible oxidation to Co^{III} is largely favoured.

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