Thermodynamic Studies on the Addition of Molecular Oxygen to Cobalt(II) Complexes. Part 1. The Cobalt(II)–Ethylenediamine–Oxygen System in Aqueous Solution at 25 °C

Sergio Cabani,* Norberto Ceccanti, and Giovanni Conti
Institute of Physical Chemistry, University of Pisa, Italy

The equilibrium constant for the formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ (en = ethylenediamine) in 1 mol dm^{-3} KCl aqueous solution, at 25 °C, has been determined using polarographic oxygen analysis, pH metric, and spectrophotometric techniques. The enthalpy of formation of this complex has been obtained by direct calorimetric measurements. The thermodynamic functions for the addition of O_2 to $[Co(en)_2]^{2+}$ in order to form the doubly bridged dicobalt complex $[Co_2(en)_4(O_2)(OH)]^{3+}$ have been calculated. The enthalpy change is very large, but the stability of the binuclear species with respect to $[Co(en)_2]^{2+}$ is strongly reduced by a large entropy effect which cannot be explained in terms of the value of the partial molar entropy of oxygen in 1 mol dm^{-3} KCl solution.

Increasing interest [1,2] has been shown in oxygen-carrier complexes of Co^{II} owing to their ability to mimic natural systems controlling important biological functions and to their use in O_2 storage and in organic syntheses. Thermodynamic data relative to the formation of these systems, particularly enthalpy changes, are nevertheless scarce. To the best of our knowledge, ΔH values are available only for the formation of a few binuclear cobalt(II) oxygenated complexes in water.[1]

As part of a research program on the thermodynamics and kinetics of reversible oxygen addition to cobalt(II) complexes, we consider in this paper the thermodynamics of formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ (en = ethylenediamine) species in aqueous solution. The kinetics of oxygen addition to $[Co(en)_2]^{2+}$ have been carefully studied by Miller *et al.*[3] Zehnder *et al.*[4] considered instead the kinetic aspects of the decomposition, in acidic solution, of isomeric μ-hydroxo-μ-peroxo-bis[bis(ethylenediamine)cobalt] cations. Values of the stability constant for the formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ have been reported by Nakon and Martell [5] and by Powell and Nancollas; [6] they differ, however, by 4.4 log K units. Moreover, when other papers on the Co^{II}–en–O_2 system are examined,[7,8] some doubts arise about the formula of the oxygenated complex. Finally, from direct calorimetric measurements, values of enthalpy changes relative to the formation of an oxygenated complex of Co^{II} with en have been obtained,[6] but the attribution of these to a well defined reaction is uncertain and some approximations are not justified.

In this paper the results of a calorimetric study of oxygen addition in aqueous solutions of Co^{II}–en, over a wide range of en : Co ratios and at various pH values, are reported. New data on the equilibrium formation constant of the oxygenated complex, obtained by different methods, are also reported.

Experimental

Materials.—Ethylenediamine dihydrochloride was prepared from commercial ethylenediamine and crystallized twice from ethanol–water mixtures. A *ca.* 0.5 mol kg^{-1} $Co(NO_3)_2$ stock solution, standardized by gravimetric analysis of $[Co(py)_4(NCS)_2]$ (py = pyridine), was used in all experiments.

Apparatus.—The apparatus used in calorimetric measurements was similar to that described.[9] The cell has been improved and modified in order to permit bubbling of oxygen. Oxygen was pumped into the cell from a reservoir placed in a thermostat bath and then recycled in order to avoid evaporation of the calorimetric solution. In a typical run a known quantity of $Co(NO_3)_2$ stock solution was added to the ligand solution contained in the cell and previously saturated with oxygen, by breaking of a glass bulb. Bubbling of oxygen was maintained during the whole experiment.

Measurements of absorbed oxygen were made in separate experiments with a Beckman model 0260 Oxygen Analyzer. The cell used, without vapour space, was also fitted with a glass electrode for pH determination. The oxygen sensor was calibrated in air-saturated and in oxygen-saturated KCl (1 mol dm^{-3}) solutions. The solubility of oxygen in this medium was calculated taking into account the ion specific salting-out constants for O_2 reported by Schumpe *et al.*[10] The equilibrium constant for the uptake of oxygen was determined by adding from a microburette successive amounts of $Co(NO_3)_2$ stock solution to oxygenated solutions of the ligand and measuring both the pH and the oxygen content after each addition. Usually about 30 min were needed for the pH to assume a constant value. The $c_{en}^0 : c_{Co}^0$ ratio was varied from 3 to 30 : 1, the pH from 6.7 to 7.4, and c_{Co}^0 from 7×10^{-4} to 25×10^{-4} mol dm^{-3} (c^0 = initial concentration). Spectrophotometric measurements were performed by using a Pye Unicam SP8-150 UV/VIS spectrophotometer.

Results and Discussion

Equilibrium Constants.—The uptake of O_2 by Co^{II}–en complexes shows features dependent on pH, $c_{en}^0 : c_{Co}^0$ ratio (R), and on the order of addition of reagents. In the presence of excess of ligand and for concentrations of Co^{II} ranging from 10^{-2} to 10^{-4} mol dm^{-3} the reaction occurs in the pH range 5.5—7.5 and is very rapid. A decrease of pH is involved, but contrary to the rapid oxygen uptake it occurs over some minutes. The oxygenated solutions are stable for some days and exhibit two bands with absorption maxima at 357 and 275 nm. The first band is well resolved and, at pH > 8, where the complex formation is complete, has an absorption coefficient ε = 5 800 dm^3 mol^{-1} cm^{-1}; the second, having ε = 5 800 dm^3 mol^{-1} cm^{-1} at high R values, becomes an inflection when R is reduced. At low values of R (*ca.* 2) the spectra show the above features only for pH > 9.5 and several hours after cobalt(II) addition, and the absorption coefficient at 357 nm also falls to *ca.* 4 300 dm^3 mol^{-1} cm^{-1}.

When a solution of $[Co_2(en)_4(O_2)(OH)]^{3+}$ is prepared, the value of the absorption coefficient at 357 nm is 5 800 dm^3 mol^{-1} cm^{-1} as observed when a cobalt(II) salt is added to an oxygenated aqueous KCl (1 mol dm^{-3}) solution containing a large excess of en.[11] When the solutions are prepared by adding cobalt(II) salt to aqueous KCl (1 mol dm^{-3}) containing en at R = 2 and pH < 9.5, the uptake of oxygen is rapid

Table 1. Species believed to be present in aqueous oxygenated solutions of Co^{II} and ethylenediamine (en)

Species	pH range	R [a]	Experimental evidence	Stability constant (25 °C)	Ref.
(A) $[Co_2(en)_4(O_2)]^{4+}$	9.4—10.9	3	Kinetics, absorption spectra	—	3
	9	excess of en	Polarographic, spectrophotometric	—	*b*
(B) $[Co_2(en)_4(O_2)(OH)]^{3+}$	8—11	2	Proton balance	—	*c*
	5.5—10.5	2	Potentiometric titration, oxygen absorption	$10^{24.9}$ dm^{12} mol^{-4} atm^{-1}	5
		2	Absorption spectra, elemental analysis	—	13
	7.1—7.6	14—32	Polarographic oxygen analysis, proton balance	$10^{10.84}$ dm^3 mol^{-1} [d]	6
	—	—	Crystal isolation, kinetics [e]	—	4
	—	—	Chemical behaviour, kinetics [e]	—	*f*
	9—10	6	Preparation, *X*-ray structure, absorption spectra, kinetics [e]	—	11
(C) $[Co_2(en)_5(O_2)]^{4+}$	5.5—10.0	2.5, 3	Potentiometric titration, absorption and n.m.r. spectra	$10^{37.1}$ dm^{18} mol^{-6} atm^{-1}	8
(D) $[Co_2(en)_6(O_2)]^{4+}$	—	2—5	Absorption spectra, elemental analysis, O_2 uptake	—	*g*
(A) $\rightleftharpoons$ (B) + H^+	—	2	Rapid oxygen uptake, slow pH change towards equilibrium	—	5
(C) $\rightleftharpoons$ (B) + Hen^+	Highly alkaline	2, 2.5	Oxygen uptake, elemental analysis of both solids, absorption spectra	At $R = 2.5$ and pH = 8.2: 70% (C) and 30% (B)	7

[a] $R = c_{en}^0 : c_{C}^0$. [b] A. Bettelheim, M. Faraggi, I. Hodara, and J. Manassen, *J. Chem. Soc., Faraday Trans. 1*, 1977, 150. [c] M. S. Michailidis and B. Martin, *J. Am. Chem. Soc.*, 1969, **91**, 4683. [d] Referred to reaction (5). [e] Kinetics of dissociation in acidic solution of isomeric forms of (B). [f] P. Brüstlein-Banks and S. Fallab, *Helv. Chim. Acta*, 1977, **60**, 1601. [g] P. Bijl and G. de Vries, *J. Chem. Soc., Dalton Trans.*, 1972, 303.

and the band at 357 nm slowly decreases and finally disappears after about 48 h. A band at 310 nm is present which is not found in the solutions of higher R values.

The complexity of the oxygenated Co–en aqueous solutions justifies, to some extent, the various proposals about the possible species and equilibria present. Table 1 summarizes the experiments performed previously and the reasonings advanced in order to account for the supposed species and equilibria. We outline below the reasons for proposing the formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ in solution at pH > 8 and $R > 2$.

Fallab *et al.*[11] examined the structure of solid $[Co_2(en)_4(O_2)(OH)][ClO_4]_3 \cdot H_2O$ by *X*-ray analysis, and observed that aqueous solutions of this complex showed the same spectrum as the complex obtained by adding Co^{II} to the solutions containing an excess of en ($R > 6$). In some of our experiments the spectra, pH, and O_2 concentration were followed for solutions of the above μ-peroxo-μ-hydroxo-compound as prepared according to the literature method.[7,11] The results of Fallab *et al.* were perfectly reproduced either in KCl (1 mol dm^{-3}) solution, or in solutions containing a large excess of en in KCl (1 mol dm^{-3}) and adjusted to pH = 9.44.

Spectra of solutions prepared from the solid binuclear complex had the same features and the same absorption coefficient as those obtained by bubbling O_2 gas into solutions at pH = 9 containing Co^{II} and en at $R > 9.0$. Solutions obtained by adding $[Co_2(en)_4(O_2)(OH)][ClO_4]_3 \cdot H_2O$ crystals to KCl (1 mol dm^{-3}) aqueous solutions containing en showed, after a period of 30 min, negligible change in absorption spectra, pH, and free-oxygen content. On the contrary, neutral solutions of the same complex in KCl (1 mol dm^{-3}) but without excess of ligand showed a sensitive decrease of both absorption coefficient and H^+ concentration, namely to $\varepsilon = 5\,200$ dm^3 mol^{-1} cm^{-1} and pH = 9.2. A small increase in free-oxygen content was also observed.

Calorimetric experiments confirmed the above results: a rapid attainment of equilibrium at pH > 8 and high R values; but a slow process, not considered in the kinetic scheme of Miller *et al.*,[3] at $R < 4$. Although this called for a more detailed kinetic study on the Co^{II}–en–O_2 system, we consider here experimental conditions only where the μ-peroxo-μ-hydroxo-complex is rapidly formed, possibly through a previous μ-peroxo-monobridged species.

In order to study the formation reaction of the oxygenated complex, three procedures have been followed: (*i*) simultaneous determination of H^+ and free-oxygen concentration; (*ii*) measurement of $[H^+]$ and spectrophotometric determination of oxygenated adduct in solutions saturated with air or with pure oxygen at 1 atm (101 325 Pa); (*iii*) simultaneous determination of all the above concentration parameters. All experiments were performed at 25 °C in KCl (1 mol dm^{-3}) aqueous solutions containing known amounts of en, Co^{II}, and HCl.

For calculating the equilibrium constant (1) corresponding to reaction (2), relationships (3) and (4) for the free-ligand

$$K = [Co_2(en)_4(O_2)(OH)^{3+}][H^+]/[Co^{2+}]^2[en]^4[O_2] \quad (1)$$

$$2\,Co^{2+} + 4\,en + O_2(aq) + H_2O \rightleftharpoons [Co_2(en)_4(O_2)(OH)]^{3+} + H^+ \quad (2)$$

Table 2. Calorimetric data for the formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ in KCl (1 mol dm^{-3}) aqueous solution at 25 °C

10^4 Amount/mol					Heat/J				
en·2HCl	Co^{2+}	NaOH	$R = c_{en}^0 : c_{Co}^0$	pH [a]	$q_{obs.}$	$q_{dil.}$ [b]	$q_{prot.}$ [c]	q_r [d]	$-\Delta H$ (O_2 adduct) [e]/kJ mol^{-1}
57.62	7.070	42.17	8.1	6.88	91.80	2.07	6.32	83.41	236.00
45.51	4.954	32.00	9.2	7.02	67.53	1.46	4.24	61.83	249.62
57.55	6.423	41.12	9.0	7.02	82.72	1.91	5.63	75.18	234.10
57.29	2.600	31.29	22.0	7.22	37.40	1.88	4.28	31.24	240.31
117.60	2.600	62.20	45.2	7.35	35.73	1.88	4.25	29.60	227.69
57.62	3.435	41.17	16.8	7.45	47.78	1.01	3.14	43.63	254.03
57.55	3.436	41.12	16.7	7.45	44.68	1.01	2.91	40.76	237.25
154.14	4.981	106.69	30.9	7.58	69.37	1.46	3.75	64.16	257.62
57.55	1.494	41.12	38.5	7.67	19.41	0.44	1.23	17.74	237.48
57.62	1.095	41.17	52.6	7.71	15.77	0.29	1.13	14.35	262.10
112.21	3.737	98.00	30.0	7.96	51.04	1.10	3.26	46.68	249.83
149.86	4.922	132.01	30.4	7.99	67.11	1.45	4.89	60.77	246.93
74.26	2.544	66.00	29.2	8.00	34.98	0.75	2.21	32.02	251.73
24.75	1.189		20.8	7.31	14.49	0.43	1.07	12.99	218.50 [f]
24.75	0.947		26.1	7.37	11.62	0.35	0.95	10.32	217.95 [f]
24.75	0.894		27.7	7.39	11.03	0.33	0.92	9.78	218.79 [f]
24.75	0.831		29.8	7.40	10.41	0.30	0.89	9.22	221.90 [f]
24.75	0.772		32.1	7.42	9.50	0.28	0.86	8.36	216.58 [f]

[a] Values for the solution after reaction. pH refers to the molar concentration of H^+ ions. [b] Heat of dilution of Co^{2+} stock solution. [c] $q_{prot.} = -\Sigma\Delta m + \Delta H$, where Δm (i = 1 or 2) are the changes in the number of moles of $H_i en^{i+}$ species involved in the reaction and ΔH are the heats of formation of these species. [d] $q_r = q_{obs.} - q_{dil.} - q_{prot.}$. [e] $\Delta H = -q_r/m_{ox}$ where m_{ox} is the number of moles of oxygenated species, equal in all cases to one half of the number of moles of cobalt; the values refer to the reaction $2Co^{2+} + 4en + O_2\ (gas) + H_2O \rightleftharpoons [Co_2(en)_4(O_2)(OH)]^{3+} + H^+$ and include the heat of solution of oxygen in KCl (1 mol dm^{-3}) aqueous solution. [f] Obtained from data of Powell and Nancollas.[6] In this case the values refer to reaction (2) and the values in the first column are the total amounts of en in the ' ethylenediamine buffer ' used.

$$[en] = (c_H{}^0 - [H]^+ + c_{O_2}{}^0 - [O_2])/\Sigma i\beta_i{}^H[H^+]^i \quad (3)$$

$$[Co^{2+}] = \{c_{Co}{}^0 - 2(c_{O_2}{}^0 - [O_2])\}/(1 + \Sigma\beta_i{}^{Co}[en]^i) \quad (4)$$

and the cobalt(II) ion concentrations were employed. Values of the stability constants for $H_i en^{i+}$ (log $\beta_1{}^H$ = 10.19 and log $\beta_2{}^H$ = 17.63) and for $[Co(en)_i]^{2+}$ (log $\beta_1{}^{Co}$ = 5.94, log $\beta_2{}^{Co}$ = 10.66, and log $\beta_3{}^{Co}$ = 13.68) in KCl (1 mol dm^{-3}) aqueous solution at 25 °C were taken from the literature.[12] The concentration of molecular oxygen ($c_{O_2}{}^0 = 9.44 \times 10^{-4}$ mol dm^{-3} at 1 atm O_2) was calculated using the Henry constant in pure water ($K_H{}^0 = 8.0 \times 10^2$ dm^3 mol^{-1} atm) together with the Sechenov coefficients for the oxygen salting-out.[10]

The value $K = (1.2 \pm 0.6) \times 10^{26}$ dm^{15} mol^{-5} for reaction (2) was calculated as the weighted mean of several data on the hypothesis that the μ-peroxo-μ-hydroxo-species is the sole oxygenated complex. The equilibrium constant of reaction (5)

$$2[Co(en)_2]^{2+} + O_2(aq) + H_2O \rightleftharpoons [Co_2(en)_4(O_2)(OH)]^{3+} + H^+ \quad (5)$$

was found to be $(5.7 \pm 2.3) \times 10^4$ dm^3 mol^{-1} while the values reported by Nakon and Martell[5] and Powell and Nancollas[6] are 2.5×10^6 and 6.9×10^{10} dm^3 mol^{-1} respectively.

The presence of the sole olate complex at pH > 7.4 does not exclude the possibility of a monobridged complex at lower pH values. In order to verify from a thermodynamic viewpoint the possibility of an equilibrium between the μ-peroxo-monobridged (O_2) and the μ-peroxo-μ-hydroxo-species (O_2,OH), it is convenient to consider equation (6)

$$\frac{[O_2,OH]}{[O_2] + [O_2,OH]} = \frac{1}{1 + K_R[H^+]} \quad (6)$$

which gives the fraction of the olate form with respect to the total oxygenated species and where $K_R = K'/K$ and $K' = [Co_2(en)_4(O_2)^{4+}]/[Co^{2+}]^2[en]^4[O_2]$.

The presence at pH > 7.5 of the sole O_2,OH form means that K_R must be less than 5×10^5 dm^3 mol^{-1}; at pH ≈ 6, therefore, where the oxygen uptake begins, the olate form is prevalent and the concentration of the non-olate may not be analytically significant. This seems to be confirmed by the spectral data, no absorption bands being observed in the range 300—310 nm where, according to Sasaki *et al.*,[13] the monobridged species should absorb.

Calorimetric Measurements.—The enthalpy change corresponding to the formation of the Co^{II}–en oxygenated adduct, ΔH (O_2 adduct), was determined by using the isoperibol calorimeter as described in the Experimental section. It was charged with about 380 g KCl(1 mol dm^{-3}) oxygen-saturated solution containing known amounts of ethylenediamine dihydrochloride and adjusted, with NaOH, to pH ranging from 7.3 to 8.5. After thermal equilibrium had been attained, reaction was started by breaking a thin glass bulb containing a weighed amount of $Co(NO_3)_2$ stock solution. In some experiments successive additions of the cobalt(II) solution were carried out using a precision microburette. A summary of the calorimetric experiments and results is given in Table 2. The ΔH(O_2 adduct) values were calculated according to equation (7) where $q_{obs.}$ is the measured heat, c_{ox} the concentration of

$$\Delta H(O_2\ adduct) = -(q_{obs.}/c_{ox}V) - (\Sigma\Delta c_i\Delta H_i/c_{ox}) \quad (7)$$

the oxygenated adduct, Δc_i the change of concentration of the ith species, ΔH_i the relative enthalpy changes, and V the volume of the solution. The ΔH_i relative to the formation of $[Co(en)_i]^{2+}$ species were always negligible under our experimental conditions. The distribution of the individual species in solution before and after the oxygenation reaction was calculated using for Hen^+, H_2en^{2+}, and $[Co(en)_i]^{2+}$ (i = 1—3) the β_i values taken from ref. 12. The heats of dilution of the stock cobalt nitrate solution were determined in separate experiments.

Table 3. Thermodynamic data pertaining to the Co^{II}–en and Co^{II}–en–O_2 systems in KCl (1 mol dm^{-3}) aqueous solution at 25 °C

Reaction	$\Delta G^\ominus$/ kJ mol^{-1}	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}	log K_{eq} [a]	Ref.
$en + H^+ \rightleftharpoons Hen^+$	−58.15	−51.04	23.85	10.19	12, *b*
$Hen^+ + H^+ \rightleftharpoons H_2en^{2+}$	−42.48	−44.35	−6.28	7.44	12, *b*
$Co^{2+} + en \rightleftharpoons [Co(en)]^{2+}$	−33.86	−28.87	16.74	5.94	12, 15
$[Co(en)]^{2+} + en \rightleftharpoons [Co(en)_2]^{2+}$	−27.00	−29.50	−8.37	4.72	12, 15
$[Co(en)_2]^{2+} + en \rightleftharpoons [Co(en)_3]^{2+}$	−17.22	−34.31	−57.32	3.02	12, 15
$2[Co(en)_2]^{2+} + O_2 (aq) + H_2O \rightleftharpoons [Co_2(en)_4(O_2)(OH)]^{3+} + H^+$	−27.11	−116.31	−299.16	4.76	This work
$2Co^{2+} + 4en + O_2 (aq) + H_2O \rightleftharpoons [Co_2(en)_4(O_2)(OH)]^{3+} + H^+$	−148.84	−233.05	−282.42	26.08 [c]	This work
O_2 (ideal gas; 1 atm) $\rightleftharpoons$ O_2 (Hypothetical solution unit mole fraction)	26.48	−12.01	−129.08	−4.64 [d]	14
O_2 (ideal gas; 1 atm) $\rightleftharpoons$ O_2 (Hypothetical ideal 1 mol dm^{-3} aqueous solution) [e]	16.52	−12.01	−95.69	−2.89 [f]	14
O_2 (ideal gas; 1 mol dm^{-3}) $\rightleftharpoons$ O_2 (Hypothetical ideal 1 mol dm^{-3} aqueous solution)	8.57	−12.01	−69.04	1.50 [g]	14

[a] The symbol K_{eq} indicates a generic equilibrium constant; its units are dm^3 mol^{-1} unless otherwise stated. [b] M. Ciampolini and P. Paoletti *J. Phys. Chem.*, 1961, **65**, 1224. [c] K_{eq} in dm^{15} mol^{-5}. [d] K_{eq} in atm^{-1}. [e] The entropy of O_2 gas (1 atm, 25 °C) is 205.06 J K^{-1} mol^{-1}; partial molar entropy of O_2 (hypothetical ideal 1 mol dm^{-3} aqueous solution 25 °C) 109.37 J K^{-1} mol^{-1}. [f] K_{eq} in mol dm^{-3} atm^{-1}. [g] K_{eq} has no units.

The ΔH(O_2 adduct) values listed in Table 2 include the heat of solution of gaseous oxygen. This has to be taken into account in order to obtain the enthalpy change according to equation (2). By using a value of −12.058 kJ mol^{-1} for the enthalpy of solution of oxygen in pure water [14] a mean value ΔH(O_2 adduct) = −233.0 ± 10.5 kJ mol^{-1} was obtained. A value of $\Delta H = -116.3 \pm 10.5$ kJ mol^{-1} corresponding to reaction (5) was calculated using $\Delta H = -58.37$ kJ mol^{-1} (ref. 15) for the formation reaction of $[Co(en)_2]^{2+}$.

Our results cannot be directly compared with data reported by Powell and Nancollas [6] because those authors calculated the enthalpy of formation of the oxygenated complex by neglecting the change in the Hen^+ and H_2en^{2+} distribution following the oxygenation reaction. Their experimental calorimetric data, treated according to our procedure and reported in Table 2, provide a value of ΔH(O_2 adduct) = −102.1 ± 2.1 kJ mol^{-1} which is in fair agreement with our result.

For the sake of convenience, thermodynamic data relative to the aqueous Co^{II}–en system at 25 °C under both aerobic and anaerobic conditions are summarized in Table 3. Also shown are data for proton addition to ethylenediamine, which are very important in accounting for the competition for the ligand between the proton and Co^{2+}, and for transfer of molecular oxygen from the ideal gas to the ideal aqueous solution for different standard states which are useful when heterogeneous systems involving gaseous oxygen have to be considered. It is better, however, to consider the reaction in a homogeneous system so that it can be compared with usual solution reactions where, except for the solvent, all species are referred to the same standard state, usually ideal 1 mol dm^{-3} solution.

Nakon and Martell [5] used $\beta_{O_2,OH}$ values for comparing the poorly defined 'stability' of μ-peroxo-μ-hydroxo-dicobalt complexes of linear polyamines $H_2N(CH_2CH_2NH)_nCH_2CH_2NH_2$ (n = 0—2). Such a comparison is invalid because the $\beta_{O_2,OH}$ values have different dimensions depending on the number of nitrogen atoms of the considered polyamine. This criticism has also to be applied to the comparison that Crawford *et al.*[8] made between the β_{O_2} constants of $[Co_2(tepa)_2(O_2)]^{4+}$ (tepa = tetraethylenepenta-amine) and $[Co_2(en)_5(O_2)]^{4+}$ species, which was supposed to demonstrate the stabilizing effect on the peroxo-species of co-ordination involving five nitrogen atoms. It would be useful to compare the enthalpy changes for the formation of the peroxo-compounds starting from cobalt and free polyamine, but unfortunately these data are not available.

The possibility of a valid direct comparison between the free energy and entropy functions for the formation of μ-peroxo-μ-hydroxo-dicobalt complexes does however exist for the reaction of the parent complexes according to equation (5). By using values $\beta_{O_2,OH}$ and β_{CoL} for L = diethylenetriamine (dien) and triethylenetetramine (trien) reported in refs. 5 and 16 respectively and our data for en, the stability constants corresponding to the formation of μ-peroxo-μ-hydroxo-species starting from the parent non-oxygenated complexes are $10^{1.04}$ dm^3 mol^{-1} for n = 1 (dien), $10^{4.76}$ dm^3 mol^{-1} for n = 0 (en), and $10^{7.3}$ dm^3 mol^{-1} for n = 2 (trien). In the near future we hope to be able to determine the effects of the enthalpic and the entropic terms on this order of stability. Particularly interesting is the dramatic entropy decrease observed when oxygen is added to aqueous solutions of $[Co(en)_2]^{2+}$. The partial molar entropy of this gas in aqueous solution, 109.2 J K^{-1} mol^{-1}, can account only for a third of the entropy loss observed upon formation of the dibridged complex according to equation (5).

A comparison between the Co^{II}–en–O_2 and the Co^{II}–trien–O_2 system is made elsewhere.[16] A more general discussion on the thermodynamic characteristics of the peroxo-complexes of Co^{II} in aqueous solution will be possible only when more information about the enthalpy changes has been collected. In order to investigate systems in which difficulties arise from kinetic reasons, we are now developing a calorimeter suitable for studying slow reactions. This will allow us to complete the thermodynamic and kinetic study on the system Co^{II}–en–O_2 at low $c_{en}^0 : c_{Co}^0$ ratios.

Acknowledgements

This work was supported by Ministero della Pubblica Istruzione (Rome).

References

1 (*a*) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1; (*b*) S. Cabani, N. Ceccanti, G. Conti, and P. Gianni, *Gazz. Chim. Ital.*, 1982, **112**, 159; (*c*) J. H. Timmons, A. E. Martell, W. R. Harris, and I. Murase, *Inorg. Chem.*, 1982, **21**, 1525; (*d*) A. E. Martell, *Acc. Chem. Res.*, 1982, **15**, 155.

2 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

3 F. Miller, J. Simplicio, and R. G. Wilkins, *J. Am. Chem. Soc.*, 1969, **91**, 1962.

4 M. Zehnder, H. Macke, and S. Fallab, *Helv. Chim. Acta*, 1975, **58**, 2306.

5 R. Nakon and A. E. Martell, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1365.

6 H. K. Powell and G. H. Nancollas, *J. Am. Chem. Soc.*, 1972, **94**, 2664.

7 S. W. Foong, J. D. Miller, and F. D. Oliver, *J. Chem. Soc. A*, 1969, 1725.

8 M. Crawford, S. A. Bedell, R. J. Patil, L. W. Young, and R. Nakon, *Inorg. Chem.*, 1979, **18**, 2075.

9 S. Cabani and G. Conti, *Gazz. Chim. Ital.*, 1965, **95**, 533; S. Cabani, G. Conti, and P. Gianni, *J. Chem. Soc. A*, 1969, 923.

10 A. Schumpe, I. Adler, and W. D. Deckwe, *Biotechnol. Bioeng.*, 1978, **20**, 147.

11 S. Fallab, M. Zehnder, and U. Thewalt, *Helv. Chim. Acta*, 1980, **63**, 1491.

12 L. J. Edwards, Ph.D. Dissertation, University of Michigan, 1950.

13 Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3373.

14 B. B. Benson, D. Krause, and M. A. Peterson, *J. Solution Chem.*, 1979, **8**, 655.

15 M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4553.

16 R. Nakon and A. E. Martell, *J. Am. Chem. Soc.*, 1972, **94**, 3026.

Received 19*th July* 1982; *Paper* 2/1233