Thermodynamic Studies on the Addition of Molecular Oxygen to Cobalt(II) Complexes. Part 3.[1] The Cobalt(II)–Tetraethylenepenta-amine–O_2 System in Aqueous Solution at 25 °C †

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Calorimetric measurements have been carried out on the heat evolved when O_2 is bubbled into KNO_3 (0.1 mol dm^{-3}) aqueous solutions of $Co(NO_3)_2$, tetraethylenepenta-amine (tetren) and HCl, or when a $Co(NO_3)_2$ stock solution is added to a KNO_3 (0.1 mol dm^{-3}) aqueous solution of tetren and HCl under both anaerobic (p_{N_2} = 1 atm) or aerobic (p_{O_2} = 1 atm) conditions. An acceptable agreement is found between the value for the enthalpy change of formation of $[Co_2L_2O_2]^{4+}$ (L = tetren) when it is obtained through direct measurements of oxygen addition to $[CoL]^{2+}$ or by using the enthalpy changes relative to the formation of $[CoL]^{2+}$ and $[Co_2L_2O_2]^{4+}$ starting from Co^{2+}. The thermodynamic data for the binding of oxygen to complexes of Co^{II} with tetren and other linear polyamines are compared and discussed.

As a part of a systematic study [1,2] on oxygen-carrier complexes the thermodynamic aspects of oxygen addition to Co^{II} complexes with tetraethylenepenta-amine (tetren) are considered herein. Tetraethylenepenta-amine is a quinquedentate ligand which with Co^{II} forms complexes capable of adding reversibly molecular oxygen in order to give a singly bridged μ-peroxo-compound, $[Co_2(tetren)_2O_2]^{4+}$.[3-9] For this peroxo-compound spectral studies [4,8] have been carried out and the kinetic [3] and equilibrium [5-7,9] data for its formation from $[Co(tetren)]^{2+}$ and O_2 have been reported. But, as far as we know, enthalpy values for the oxygenation reaction are lacking.

This paper reports the results of calorimetric measurements on the formation of $[Co_2(tetren)_2O_2]^{4+}$ from $[Co(tetren)]^{2+}$. Some calorimetric measurements have also been performed on the formation of $[Co(tetren)]^{2+}$ and $[Co_2(tetren)_2O_2]^{4+}$ starting from Co^{2+}, and also on the tetren–H^+ system, in order to verify the internal consistency of the results.

Experimental

Commercial tetren (Strem) was distilled under reduced pressure and precipitated as a hydrochloride by addition of concentrated HCl solution. The pentahydrochloride was recrystallized from aqueous ethanol and its purity checked by elemental analysis.

The stock solution of $Co(NO_3)_2$ was standardized as previously described.[1,2] All solutions were prepared with deionized water and contained KNO_3 (0.1 mol dm^{-3}).

The calorimetric measurements were carried out using several methods: (*i*) by bubbling O_2 gas into N_2-saturated aqueous solutions containing known amounts of tetren, $Co(NO_3)_2$, and HCl; (*ii*) by adding known amounts of cobalt stock solution to aqueous solutions of tetren under both anaerobic (N_2 at 1 atm) and aerobic (O_2 at 1 atm) conditions. Experiments have also been carried out where (*iii*) known amounts of HCl stock solution were added to aqueous solutions containing tetren and HCl. We determined the heat of dilution of the $Co(NO_3)_2$ stock solution in aqueous KNO_3 (0.1 mol dm^{-3}). The heat of dilution of the HCl stock solution in KNO_3 (0.1 mol dm^{-3}) was calculated using the data of ref. 10 and by assuming Young's rule to be valid.[11] The heat of solution of O_2 gas in aqueous KNO_3 (0.1 mol dm^{-3}) was assumed to be equal to -12.06 kJ mol^{-1} (see refs. 1 and 2). The enthalpy of formation of water in the same solvent medium was taken to be equal to -56.57 kJ mol^{-1}, as previously [1] reported (in ref. 1 the quoted value of 13 250 cal mol^{-1} is a misprint for 13 520 cal mol^{-1}).

Table 1. Calorimetric data for the addition of oxygen to $[Co(tetren)]^{2+}$ at 25 °C in KNO_3 (0.1 mol dm^{-3}) aqueous solution [a]

$10^4 m_{Co}^0$/mol	$10^4 m_L^0$/mol	pH [b]	q_r [c]/J	$-\Delta H_{Co_2L_2O_2}^{CoL}$ [d]/kJ mol^{-1}
4.481	15.66	7.96	40.75	181.9
4.481	14.36	8.18	39.96	178.3
4.978	14.65	8.14	43.18	173.5
4.978	14.05	8.40	44.06	177.0
5.476	12.31	7.94	49.00	178.9
5.178	8.40	8.80	47.53	183.6
				-178.9 ± 1.5 [e]

[a] The experiments were conducted by bubbling O_2 into solutions containing m_{Co}^0 moles of Co^{II}, m_L^0 moles of tetren, and whose pH was adjusted to the value given in the third column. [b] pH Refers to the molar concentration of H^+ ions. [c] $q_r = q_{obs.} - q_s^{O_2}$; $q_{obs.}$ = the heat measured, $q_s^{O_2} = (m_{Co}^0/2) \times 12\,016$ J = the heat of solution of oxygen. [d] $\Delta H_{Co_2L_2O_2}^{CoL} = -(2q_r/m_{Co}^0)$ = the enthalpy change relative to the reaction $2[CoL]^{2+} + O_2(aq) \longrightarrow [Co_2L_2O_2]^{4+}$. [e] Average value of $\Delta H_{Co_2L_2O_2}^{CoL}$; standard deviation $\sigma = [\sum_{j=1}^{n} (\Delta H_j - \Delta\bar{H})^2/n(n-1)]^{\frac{1}{2}}$, where n = number of measurements.

The heats measured in experiments (*i*), (*ii*), and (*iii*), corrected for the appropriate dilution or solution heats, are reported in Tables 1, 2, and 3 respectively.

The calorimetric apparatus and the procedure followed have been described elsewhere.[1,2] The calorimeter vessel contained *ca.* 360 g of solution (V = solution volume). The concentration of $Co(NO_3)_2$ ranged from 5×10^{-4} to 1.5×10^{-3} mol dm^{-3}, and the ratios of tetren : cobalt from 1.5 : 1 to 12 : 1.

The pH of the solutions was measured before and after each experiment by means of a Radiometer PHM 84 pH-meter, equipped with a GK 2351 B combined glass electrode, and standardized against known hydrogen-ion concentrations. (Throughout this paper pH refers to the molar concentration of H^+ ions.)

The formation and stability with time of the oxygenated complex was monitored through spectrophotometric measurements (ε = 13 980 dm^3 mol^{-1} cm^{-1} at λ = 308 nm) performed on a Pye-Unicam SP8-150 UV/VIS spectrophotometer.

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† *Non-S.I. units employed:* atm = 101 325 N m^{-2}, cal = 4.184 J.

Table 2. Calorimetric data for the reaction of Co^{II} with tetren under anaerobic (p_{N_2} = 1 atm) and aerobic (p_{O_2} = 1 atm) conditions [T = 25 °C; aqueous KNO_3 (0.1 mol dm^{-3})] [a]

$10^4 m_L^0$/ mol	$10^4 m_H^0$/ mol	V_i/cm^3	pH$_i$	$\bar{n}_{H,i}$ [b]	$10^4 m_{Co}^0$/ mol	pH$_f$	$\bar{n}_{H,f}$ [b]	q [c]/J	q_w [d]/J	q_{prot} [e]/J	$-\Delta H$ [f]/ kJ mol^{-1}
15.66	28.30	360.3	9.05	1.811	4.481	7.96	2.532	26.99	0.33	−0.27	60.10
12.31	16.55	369.6	9.52	1.360	5.478	7.96	2.422	32.80	1.05	−0.86	59.53
15.20	31.00	359.9	8.82	2.042	2.987	8.10	2.539	18.12	0.17	−0.14	60.56
14.65	23.25	373.2	9.28	1.595	4.979	8.15	2.405	30.25	0.59	−0.47	60.51
14.36	23.80	355.7	9.21	1.664	4.481	8.18	2.410	25.86	0.46	−0.38	57.53
14.05	20.25	368.6	9.40	1.452	4.979	8.41	2.234	30.17	0.75	−0.60	60.29
8.40	5.01	365.4	9.97	0.660	5.178	8.80	1.565	31.09	2.85	−2.28	58.94
								$\Delta H_{CoL} = -59.64 \pm 0.41$ kJ mol^{-1} [g]			
10.05	20.26	360.1	8.83	2.019	2.751	7.15	2.774	39.66	0.21	−0.17	288.0
8.18	10.92	361.8	9.48	1.355	3.658	7.94	2.414	51.67	0.96	−0.76	281.4
21.92	49.60	343.8	8.49	2.264	1.990	8.09	2.489	29.92	0.04	−0.05	300.8
16.00	35.03	351.2	8.60	2.190	1.470	8.25	2.410	21.88	0.08	−0.06	297.4
9.57	7.85	365.1	9.88	0.866	5.175	8.65	1.792	75.27	2.30	−1.87	289.2
8.84	9.22	367.1	9.68	1.074	1.809	9.35	1.329	26.36	0.84	−0.67	289.6
11.48	12.38	367.9	9.68	1.103	1.441	9.50	1.252	20.67	0.54	−0.43	285.4
								$\Delta H_{Co_2L_2O_2}{}^{Co} = -290.3 \pm 2.6$ kJ mol^{-1} [g]			

[a] The experiments were conducted by adding a stock $Co(NO_3)_2$ solution (0.4979 mol dm^{-3}) to a solution containing known amounts of tetren·5HCl and NaOH under N_2 or under O_2. Initial and final states of the reaction are indicated by subscripts i and f respectively. [b] $\bar{n}_H = (c_H{}^0 - [H^+] + P_w/[H^+])/c_L{}^*$, where P_w is the ionic product of water in 0.1 mol dm^{-3} aqueous KNO_3 (1.56×10^{-14} mol^2 dm^{-6}), $c_H{}^0$ the concentration of HCl, $[H^+]$ the concentration of hydrogen ion, and $c_L{}^*$ the concentration of tetren not involved in complexes with cobalt ion. [c] $q = q_{obs.} - q_{dil}{}^{Co} - q_s{}^{O_2}$. The heat of dilution of the $Co(NO_3)_2$ solution, $q_{dil}{}^{Co}$, was determined in separate experiments, $q_s{}^{O_2}$ as in Table 1. [d] Heat of formation of water. [e] Heat effect associated with the redistribution of protons on the ligand molecules, calculated as $q_{prot} = -\Delta\bar{H}_{HL}(\bar{n}_{H,f}\, m_{L,f} - \bar{n}_{H,i}\, m_{L,i})$; the moles of ligand at the end of each run were taken as those remaining available for protonation equilibria, *i.e.* $m_L = m_L{}^0 - m_{Co}{}^0$. $\Delta\bar{H}_{HL} = -45.5$ kJ mol^{-1} (see Table 3). [f] $\Delta H = -q_r$/moles of complex formed, where $q_r = q - q_w - q_{prot}$. [g] Standard deviation $\sigma = [\sum_{j=1}^{n} (\Delta H_j - \Delta\bar{H})^2/n(n-1)]^{\frac{1}{2}}$.

Results

In the experiments (*i*) where O_2 gas was bubbled into solutions containing $[Co(tetren)]^{2+}$ no change of pH was observed and therefore no correction for proton redistribution was necessary. The heat evolved was therefore corrected only for the heat of solution of O_2, $q_s{}^{O_2}$, calculated by assuming that the number of moles of oxygen dissolved was equal to the number of moles of oxygenated complex. No correction was introduced for the substitution of N_2 by O_2. The enthalpy change corresponding to the reaction, *i.e.* equation (1) (L = tetren) gave $\Delta H_{Co_2L_2O_2}{}^{CoL} = -178.9 \pm 1.5$ kJ mol^{-1} (see Table 1).

$$2[CoL]^{2+} + O_2(aq) \longrightarrow [Co_2L_2O_2]^{4+} \qquad (1)$$

In the experiments (*ii*) carried out in order to obtain the enthalpy changes corresponding to reactions (2) or (3)

$$Co^{2+} + L \longrightarrow [CoL]^{2+} \qquad (2)$$

$$2Co^{2+} + 2L + O_2 \longrightarrow [Co_2L_2O_2]^{4+} \qquad (3)$$

according to anaerobic or aerobic experimental conditions respectively, noticeable changes of pH were observed (see Table 2) and corrections for the proton redistribution were necessary.* This was effected by calculating the proton distribution before and after the formation of the complex by using the average number of hydrogens bonded to tetren, $\bar{n}_H$ (see footnote of Table 2), obtained by direct calculation from experimental data alone, and by using for the enthalpy change in the proton addition to tetren a mean value of $\Delta\bar{H}_{HL} = -45.5$ kJ per mole of proton added. This was possible since in the pH range we explored the heat evolved per mole of proton added was almost independent of the number of hydrogens bonded to tetren (see data of Table 3), also in agreement with the values of ΔH_{H_iL} (i = 1—3) obtained by Paoletti and Vacca.[12]

For reaction (2) the value, $\Delta H_{CoL} = -59.6 \pm 0.4$ kJ mol^{-1} was obtained which agrees satisfactorily with the corresponding value of −57.9 kJ mol^{-1} obtained by Paoletti and Vacca,[12] who employed experimental conditions such that the correction for the proton redistribution was reduced to practically zero.

For reaction (3) the value, $\Delta H_{Co_2L_2O_2}{}^{Co} = -290.3 \pm 2.6$ kJ mol^{-1} was obtained which when combined with the value for ΔH_{CoL} from ref. 12 ($\Delta H_{Co_2L_2O_2}{}^{CoL} = \Delta H_{Co_2L_2O_2}{}^{Co} - 2\Delta H_{CoL}$) produced for reaction (1) a value of $\Delta H_{Co_2L_2O_2}{}^{CoL} = -174.5 \pm 2.7$ kJ mol^{-1}. This value agrees with that obtained in experiments (*i*) by the direct addition of oxygen to $[CoL]^{2+}$.

A satisfactory internal consistency is therefore attained despite the uncertainty in the equilibrium constants of proton addition to tetren.

Table 4 summarizes the more reliable thermodynamic data

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* The values of the equilibrium constants and heats of reaction reported in the literature for the system tetren–H^+ did not yield reliable corrections for the formation of the protonated species of tetren. In effect, the calorimetric data of experiments (*ii*) (see Table 2) yielded highly variable values of ΔH_{CoL} or $\Delta H_{Co_2L_2O_2}{}^{Co}$ when the protonation corrections were made using a given set of β_{H_iL} (i = number of protons bonded to L = 1—5), and quite different mean values of these enthalpy changes when different sources of β_{H_iL} (indicated in parentheses) were utilized: ΔH_{CoL} (kJ mol^{-1}) = -15.6 ± 5.3 (ref. 12), -22.2 ± 4.0 (ref. 5), -30.0 ± 2.9 (ref. 7), and -65.2 ± 0.9 (ref. 13); $\Delta H_{Co_2L_2O_2}{}^{Co}$ (kJ mol^{-1}) = -206.7 ± 8.9 (ref. 7), -180.6 ± 9.3 (ref. 12), -192.6 ± 7.8 (ref. 5), and -298.4 ± 6.6 (ref. 13). Only the data derived from ref. 13 approach the results obtained as described in the text and present an acceptable standard deviation. In all the above calculations we used the values for the enthalpy changes, ΔH_{H_iL}, for proton addition to tetren as reported in ref. 12. These are the only available data.

Table 3. Calorimetric data for addition of H^+ to tetren at 25 °C in KNO_3 (0.1 mol dm^{-3}) aqueous solution [a]

$10^4 m_L{}^0$/ mol	$10^4 m_H{}^0$ [b]/ mol	V/cm^3	pH	$\bar{n}_H$ [c]	$q_{obs.}$ [d]/J	q_{prot} [e]/J	$-\Delta\bar{H}_{HL}$ [f]/ kJ mol^{-1}
9.86	8.30	368.0	9.89	0.888	—	—	—
	14.30	368.3	9.39	1.465	29.12	26.11	45.89
7.82	8.10	358.5	9.74	1.075	—	—	—
	12.10	358.7	9.32	1.562	18.95	17.03	44.72
	16.10	358.9	8.81	2.064	19.33	17.99	45.83
	20.10	359.1	8.15	2.572	19.33	18.33	46.14
12.66	13.29	368.5	9.75	1.075	—	—	—
	18.29	368.7	9.42	1.457	24.81	22.76	47.06
	22.29	368.9	9.14	1.767	19.92	18.66	47.55
	28.29	369.2	8.63	2.236	30.08	28.49	47.98
	33.29	369.5	8.09	2.630	22.64	21.46	43.02
	38.29	369.7	6.32	3.023	22.64	21.51	43.23
30.71	15.54	360.8	10.12	0.530	—	—	—
	26.22	361.3	9.78	0.865	49.41	44.85	43.60
							-45.5 ± 0.6 [g]

[a] The experiments were conducted by adding successive amounts of a stock solution of HCl to solutions containing $m_L{}^0$ moles of tetren·5HCl and $m_{NaOH}{}^0$ moles of NaOH. [b] Moles of HCl present in solution $m_H{}^0 = 5m_L{}^0 - m_{NaOH}{}^0 + m_{HCl}$, where m_{HCl} is the total moles of HCl added as a titrant. The actual moles of HCl added per single step may be obtained as the difference between two consecutive steps of the titration. [c] See footnote *b* of Table 2. [d] Heat effect observed in each step. [e] $q_{prot} = q_{obs.} - q_{dil}{}^{HCl} - q_w$, where $q_{dil}{}^{HCl}$ is the heat of dilution of the stock solution of HCl and q_w the heat of formation of water from its ions (see Experimental section). [f] Mean enthalpy of formation of ligand–hydrogen bond calculated as: $\Delta\bar{H}_{HL} = -q_{prot}/(\Delta\bar{n}_H m_L{}^0)$ where $\Delta\bar{n}_H$ is the change of $\bar{n}_H$ in each step. [g] Average value of $\Delta\bar{H}_{HL}$; standard deviation $\sigma = [\sum_{j=1}^{n} (\Delta H_j - \Delta\bar{H})^2/n(n-1)]^{\frac{1}{2}}$.

for the reactions occurring in aqueous solutions of Co^{II} and tetren in both anaerobic and aerobic conditions. The mean values of the standard free energy of reaction have been calculated by using all the available equilibrium constant values, with no previous critical evaluation.

Discussion

The thermodynamic characteristics of the reaction of binding oxygen to Co^{II}–tetren, in particular the enthalpic effects, are very different from those presented by other oxygen binding reactions. As usual the entropy change is negative and similar in value to that obtained for the binding of O_2 to $[Co(en)_2]^{2+}$ (en = ethylenediamine) ($\Delta S = -297$ J K^{-1} mol^{-1}) [2] or to $[Co(trien)]^{2+}$ (trien = triethylenetetra-amine) ($\Delta S = -259$ J K^{-1} mol^{-1}).[1] In these latter cases, however, the formation of the double bridge requires the dissociation of one mole of water and consequently a loss of entropy of about 81 J K^{-1} mol^{-1} perhaps only partly balanced by the entrance of the hydroxide ion in the olate complex, $[Co_2L_2O_2(OH)]^{3+}$. On the basis of these considerations, the loss of entropy in the formation of the monobridged μ-peroxo-Co^{II}–tetren complex, although similar in value, is in effect much larger than that associated with the formation of μ-peroxo-μ-hydroxo-complexes. This large entropy loss may be only in part attributed to the loss of entropy of the oxygen dissolved in water $\{\Delta S[O_2(aq), 1\ \text{mol dm}^{-3}] = -109.2\ \text{J K}^{-1}\ \text{mol}^{-1}\}$ and in part to the formation of a dimeric compound.* It seems therefore that some specific effects should also be taken into consideration in order to justify the ΔS values found for the O_2 binding to Co^{II} complexes in aqueous solution. However, only a significant improvement in the determination of equilibrium constants and enthalpy changes would justify a deeper investigation of the causes of the observed entropy loss.

More than the entropy, the most peculiar feature of the $[Co_2(tetren)_2O_2]^{4+}$ species is the extremely large decrease in enthalpy associated with its formation from $[Co(tetren)]^{2+}$ and molecular oxygen. This change is much larger than twice the enthalpy change found in the formation of the 1 : 1 mononuclear oxygenated complexes which usually range from −40 to −65 kJ mol^{-1} and are independent of temperature and solvent.[20] But it is also very large with respect to the enthalpy changes in the addition of oxygen to $[Co(en)_2]^{2+}$ [$\Delta H_{Co_2(en)_4O_2(OH)}{}^{Co(en)_2} = -116$ kJ mol^{-1}] [2] and $[Co(trien)]^{2+}$ [$\Delta H_{Co_2(trien)_2O_2(OH)}{}^{Co(trien)} = -111$ kJ mol^{-1}] [1] in order to form binuclear dibridged μ-peroxo-μ-hydroxo-complexes. Since the energy spent for the dissociation of one mole of water is reasonably recovered in part in the formation of the hydroxo-bridge, it seems logical to assume a larger stabilizing enthalpic effect in the addition of O_2 to $[Co(tetren)]^{2+}$ with respect to the formation of the single oxygen bridge in the O_2 addition to the en or trien cobalt complex.

Such a behaviour is in contrast with the behaviour shown by

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* The entropy changes for reactions of dimerization of large non-charged molecules in aqueous solution are usually less negative than −100 J K^{-1} mol^{-1}. For instance, for the dimerization of some dyes ΔS values from 0 to −34 J K^{-1} mol^{-1} have been reported.[14] For the self-association of some pyrimidine derivatives ΔS ranges from −30 to −42 J K^{-1} mol^{-1} [15] and the heteroassociation between 2-aminopurine and thymidine produces an entropy decrease, $\Delta S = -25$ J K^{-1} mol^{-1}.[16] Only for the base stacking self-association of some purine nucleoside-5′-monophosphates [17] and various purine bases [18] are more negative ΔS values, ranging from −40 to −100 J K^{-1} mol^{-1}, found. The likeness between the dimerization of large non-charged molecules and the association of the charged $[Co(tetren)]^{2+}$ species into the binuclear μ-peroxo-complex seems to be justified by the fact that the thermodynamic behaviour of large cations, such as tetra-alkylammonium ions, is closer to that of non-ionic than of ionic species.[19] In any case, the interaction between two $[Co(tetren)]^{2+}$ cations and water should not substantially change when the two cations are held together through the oxygen bridge. The main factor responsible for the entropy change in the association process should be generally related with the decrease of the number of free species with loss of translational and rotational degrees of freedom.

Table 4. Thermodynamic data for the formation of $[Co_2L_2O_2]^{4+}$ (L = tetren) in KNO_3 (0.1 mol dm^{-3}) aqueous solution at 25 °C

Reaction	$\bar{\beta}$ [a]	$-\Delta G^\ominus$/ kJ mol^{-1}	$-\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$/ J K^{-1} mol^{-1}
$Co^{2+} + L \longrightarrow [CoL]^{2+}$	$(2.7 \pm 1.3) \times 10^{13}$ dm^3 mol^{-1} [b]	76.6 ± 0.8	59.6 ± 0.4 [c]	57 ± 3
			57.9 [d]	63
$2Co^{2+} + 2L + O_2(aq) \longrightarrow [Co_2L_2O_2]^{4+}$	$(7.2 \pm 7) \times 10^{42}$ dm^{12} mol^{-4} [e]	244.3 ± 1.7	290.3 ± 2.6 [c]	-154 ± 11
$2[CoL]^{2+} + O_2(aq) \longrightarrow [Co_2L_2O_2]^{4+}$	$(9.9 \pm 8) \times 10^{15}$ dm^6 mol^{-2} [f]	91.2 ± 1.7	174.5 ± 2.7 [g]	-279 ± 12
	$(9.9 \pm 8) \times 10^{15}$ dm^6 mol^{-2} [f]	91.2 ± 1.7	178.9 ± 1.5 [h]	-294 ± 8

[a] Average values of equilibrium constants. [b] Calculated using refs. 5, 7, and 12. [c] This work. [d] From ref. 12. [e] Calculated using refs. 5 and 7. [f] Calculated from values of the two preceding reactions. [g] From $\Delta H^\ominus$ values of the two preceding reactions. For ΔH_{CoL} the value -57.9 kJ mol^{-1} was chosen since it was obtained in such conditions that the corrections for proton addition to tetren were not significant. [h] From direct calorimetric measurements of oxygen addition to $[CoL]^{2+}$ complex.

the parent non-oxygenated complexes of Co^{II}. As a matter of fact, the mean values of the enthalpy change per mole of single cobalt–nitrogen bonds in the cobalt complexes able to add molecular oxygen exhibit a trend which is opposite to the trend observed for the peroxo-complexes. Namely, the mean enthalpy changes for the formation of one mole of cobalt–nitrogen bond are: -14.6 kJ mol^{-1} for the Co^{II}–en complex [$\Delta H_{Co(en)_2} = -58.3$ kJ mol^{-1}],[21] -11.1 kJ mol^{-1} for the Co^{II}–trien complex [$\Delta H_{Co(trien)} = -44.6$ kJ mol^{-1}],[21] and -11.6 kJ mol^{-1} for the Co^{II}–tetren complex [$\Delta H_{Co(tetren)} = -57.9$ kJ mol^{-1}].[12]

Obviously, many other calorimetric values of enthalpy changes need to be reported, besides those now at our disposal,[1,2,22] in order to gain a significant picture of the thermodynamic behaviour of oxygen carrier complexes in aqueous solution. Nevertheless, the results obtained so far allow the correction of some points of view, for example that which identifies a particular stabilizing effect in the formation of the olate complex.[23,24] Actually, it is the bonding of O_2 in the monobridged complex which is associated with large negative enthalpic effects not observed in the formation of olate μ-peroxo-complexes. Curious, but significant, is the finding that the smaller the strength of the cobalt–nitrogen bond in the non-oxygenated complexes, the stronger is the reinforcement of this bond in the oxygenated complexes. It is in fact reasonable to associate the enthalpy change observed in the formation of $[Co_2(tetren)_2O_2]^{4+}$ mainly to a reinforcement of the cobalt–nitrogen bonding rather than to a very unusual strength of the cobalt–oxygen bond. In other words, it is reasonable to assume that there is a co-operative effect, increasing the strength of the cobalt–oxygen bond due to a charge transfer from cobalt to oxygen and increasing the strength of the cobalt–nitrogen bond due to a more pronounced character of Co^{III}. It is really a very acceptable hypothesis, even in the absence of relevant experimental data, to attribute an enthalpic nature to the huge increase in stability which the Co^{III} complexes show compared with the corresponding complexes of Co^{II}.

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