Intramolecular Charge-transfer Decomposition of the μ-Peroxo-bis[penta-amminecobalt(III)] Complex in Acidic Solutions. Stabilization by Protonation and the Effect of Chloride and Sulphate

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The kinetics of the decomposition of the μ-peroxo-bis[penta-amminecobalt(III)] complex, $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+} \xrightarrow{H^+} 2Co^{2+} + O_2 + 10\ NH_4^+$, generated by fast one-electron reduction of the μ-superoxo-complex, $[(NH_3)_5{\cdot}Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+}$, have been studied using the stopped-flow technique at $[H^+] = 0.005$—0.100M, $I = 0.10$M($LiClO_4$). The $[H^+]$ dependence of first-order rate constants, $k_{obs} = kK/([H^+] + K)$, is consistent with the formation of a protonated non-reactive form. At 25 °C the rate constant for decomposition of the unprotonated (brown) form is $k = 84\ s^{-1}$, and $\Delta H^‡ = 17.5 \pm 1.0$ kcal mol^{-1}, $\Delta S^‡ = 8.7 \pm 3.7$ cal K^{-1} mol^{-1}, in excellent agreement with previous data for solutions $[NH_3] = 4.3$—15.0M, $I = 2.0$M (NH_4NO_3). The acid dissociation constant K of the protonated (red) complex (25 °C) is 0.084M, with $\Delta H = 6.0 \pm 2.5$ kcal mol^{-1}, $\Delta S = 15.2 \pm 9.0$ cal K^{-1} mol^{-1}. Chloride < sulphate further stabilize the complex, and with $[Cl^-] > 0.6$M the effect of $[H^+]$ and $[Cl^-]$ on the rate of decomposition was studied by conventional spectrophotometry, $I = 2.3$M (Cl^-/ClO_4). Solid samples of the brown and red complexes interconvert rapidly in solution to give identical spectra. The protonated red complex does not react with iodide during the *ca.* 30 min period required for decomposition. Implications regarding the structure of the protonated complex are considered.

ALTHOUGH the chemistry of cobalt–oxygen carriers is now fairly well understood,[1] the solution properties of one of the simplest binuclear species, $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+}$, have still to be fully evaluated. Decomposition in ammoniacal solutions at high pH values has been studied by Simplicio and Wilkins.[2] An investigation of the decomposition in acidic solutions, and stability of a protonated form provide the subject of the present study. A variety of properties are consistent with a μ-peroxo-dicobalt(III) assignment.[3] Decomposition occurs by intramolecular electron transfer from the peroxo-bridge to Co^{III}.

EXPERIMENTAL

Reactants.—A sample of the chloride salt of the μ-superoxo-bis[penta-amminecobalt(III)] complex, $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]Cl_5{\cdot}H_2O$, was prepared with one modification of the literature procedure.[4] This involved addition of 12 g and not 6 g of ammonium peroxodisulphate in the oxidation step, and leaving the resultant solution for 30 min. The chloride was converted into the perchlorate salt as described.[4] This was made up in 0.1M-$HClO_4$ within 15 min of preparation, standardized spectrophotometrically $\lambda_{max.}$ 670 nm (ε 890M^{-1} cm^{-1}), and stored at 0 °C in a flask covered with aluminium foil.

Synthesis of the brown μ-peroxo-complex $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5](SO_4)_2{\cdot}xH_2O$ was as described by Charles and Barnartt.[5] An *X*-ray crystallographic study has been carried out on the tetrahydrate.[6] Rohm and Nyman [7] find that decomposition in $HClO_4$, HCl, H_2SO_4, and HBr gives $2Co^{II} + O_2$ in 97—100% yields. Samples contain up to 5% of the μ-superoxo-complex as impurity. The latter could be identified spectrophotometrically at 670 nm. The solid was stored over silica gel *in vacuo*.

The brown μ-peroxo-complex was converted into the protonated red μ-hydroperoxo-bis[penta-amminecobalt(III)] complex, $[(NH_3)_5Co{\cdot}O_2H{\cdot}Co(NH_3)_5](HSO_4)_3(SO_4)$ by the procedure described by Mori and Weil.[8] A pestle and mortar were used to grind the brown μ-peroxo-complex with 3M-H_2SO_4. Analyses found: H, 5.05; Co, 16.5; NH_3, 24.1; SO_4^{2-}, 52.7. Calc. for $Co_2(NH_3)_{10}(O_2H)(HSO_4)_3(SO_4)$: H, 4.84; Co, 16.6; NH_3, 24.0; SO_4^{2-}, 54.2%. A gas burette was used to determine the O_2 released on treatment with HCl, when similar results to those obtained by Rohm and Nyman for the brown peroxo-compound were obtained (*i.e. ca.* 96% O_2 evolution). Cobalt(II) was identified as a product from the absorbance peak at *ca.* 508 nm (ε 4.8 l mol^{-1} cm^{-1}). I.r. ν_3 and ν_4 bands of SO_4^{2-} and HSO_4^- mask ν(O–O) bands.[9] Attempts to prepare a crystalline sample for an *X*-ray crystal study were unsuccessful.

Solutions of V^{2+} were prepared by electrolytic reduction of vanadium(IV) perchlorate in *ca.* 0.5M-$HClO_4$. The preparation of $[Ru(NH_3)_6]^{2+}$ has been described previously.[10] AnalaR $FeSO_4{\cdot}7H_2O$ was used as a source of Fe^{2+} and was made up by weight as required. Solutions of V^{2+} and $[Ru(NH_3)_6]^{2+}$ were kept under air-free conditions (N_2 and Ar respectively) at all times.

Kinetic Studies.—The μ-peroxo-complex was generated by outer-sphere reduction of the μ-superoxo-complex [equation (1)], with V^{2+} or $[Ru(NH_3)_6]^{2+}$ as reductant,[11,12] $[HClO_4] >$

$$[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+} + e^- \longrightarrow [(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+} \quad (1)$$

0.005M, $I = 0.10$M ($LiClO_4$). Decomposition of the μ-peroxo-complex [equation (2)] was observed as the second

$$[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+} \longrightarrow 2Co^{2+} + O_2 + 10\ NH_4^+ \quad (2)$$

stage. Although significantly slower than reaction (1), the stopped-flow technique was required for reaction (2). Reaction (1) can be monitored at the μ-superoxo-absorbance peaks at 297 nm (ε 24 500 l mol^{-1} cm^{-1}) and 670 (890),[11,12] whereas (2) is best monitored at wavelengths *ca.* 297 nm. At 297 nm the μ-peroxo-complex has ε *ca.* 2×10^3 l mol^{-1} cm^{-1}, and absorbance contributions from other species are small. Plots of absorbance (A) changes $\log(A_t - A_\infty)$ against time for (2) were linear to >95% completion. From the slopes (×2.303) rate constants k_{obs} were obtained.

With Fe^{2+} as reductant chloride (or sulphate) is required to catalyse reaction (1), thus maintaining the required difference in rates of (1) and (2). For a range of conditions $[H^+] > 0.6$M, $I = 2.3$M (NaCl), with Fe^{2+} in large excess reaction (1) is rapid, but (2) is appreciably slower and at *ca.* 5 °C can be monitored at 495 nm by conventional spectrophotometry. Rate constants, k_{obs}, were evaluated as described above.

RESULTS

Decomposition of the μ-Peroxo-complex $[H^+] < 0.10$M.—First-order rate constants, k_{obs}, for the decomposition of the μ-peroxo-complex (2), $[H^+] = 0.005$—0.100M, $I = 0.10$M ($LiClO_4$), are independent of the identity and concentration of the reactant in (1), V^{2+} or $[Ru(NH_3)_6]^{2+}$ (Table 1). A linear dependence of $1/k_{obs}$ against $[H^+]$ is observed at each temperature, Figure 1, consistent with relation (3). This

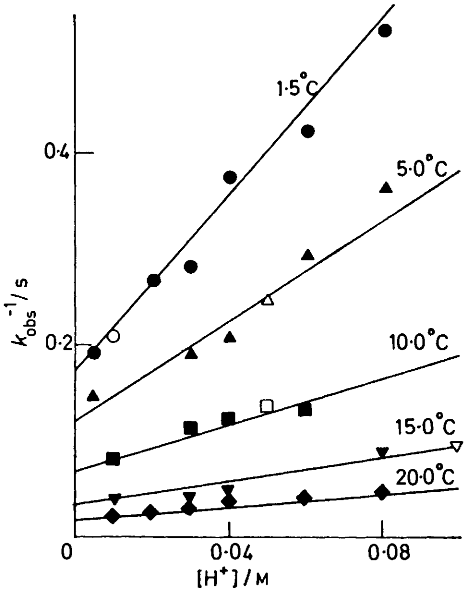


FIGURE 1 Plot of $1/k_{obs}$ against $[H^+]$ for the decomposition of the μ-peroxo-complex $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+}$ generated by V^{2+} (closed points) and $[Ru(NH_3)_6]^{2+}$ (open points) reduction of the μ-superoxo-complex, $I = 0.10$M ($LiClO_4$)

$$k_{obs} = \frac{Kk}{K + [H^+]} \qquad (3)$$

TABLE 1

First-order rate constant, k_{obs} (s^{-1}), for the decomposition of μ-peroxo-bis[penta-amminecobalt(III)], $I = 0.10$M ($LiClO_4$), λ = 296 nm. The μ-peroxo-complex was generated *in situ* by reduction of the μ-superoxo-complex in a rapid first stage [a]

$[H^+]$/M	t/°C 1.5	5.0	10.0	15.0	20.0
0.005	5.32 [b]	6.85 [b]			
0.010	4.71 [c]		12.46	27.2	37.0
0.020	3.74				34
0.030	3.62	5.15	8.94	23.8	33.5
0.040	2.65	4.35	8.15	21.2	31.9
0.050		4.03 [d]	7.33 [d]		
0.060	2.36	3.37	7.59		25.6
0.080	1.88	2.72		11.1	20.4
0.100				10.9 [d]	

[b] Vanadium(II) used to reduce μ-superoxo-complex in first stage. Concentrations are $[\mu(O_2^-)] = 5.50 \times 10^{-6}$M, $[V^{2+}] = 3.35 \times 10^{-3}$M, except as stated. [b] $[\mu(O_2^-)] = 2.75 \times 10^{-6}$M, $[V^{2+}] = 1.68 \times 10^{-3}$M. [c] Hexa-ammineruthenium(II) used as reductant in first stage, $[\mu(O_2^-)] = 3.3 \times 10^{-6}$M, $[Ru(NH_3)_6^{2+}] = 3.5 \times 10^{-5}$M. [d] $[\mu(O_2^-)] = 6.9 \times 10^{-6}$M, $[Ru(NH_3)_6^{2+}] = 6.2 \times 10^{-5}$M.

implicates a stabilised μ-hydroperoxo (*i.e.* protonated μ-peroxo) species, where K and k are as defined in equations (4) and (5). Values of K and k (Table 2) were obtained by a non-linear least-squares fit to (3).[13] Activation parameters for k are $\Delta H^\ddagger = 17.5 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = 8.7 \pm 3.7$ cal K^{-1} mol^{-1}. Thermodynamic parameters for K are $\Delta H = 6.0 \pm 2.5$ kcal mol^{-1}, $\Delta S = 15.2 \pm 9.0$ cal K^{-1} mol^{-1}. These give $k = 84$ s^{-1} and $K = 0.084$M at 25 °C.

$$\mu(O_2H^-) \overset{K}{\rightleftharpoons} \mu(O_2^{2-}) + H^+ \qquad (4)$$

$$\mu(O_2^{2-}) \xrightarrow{k} \text{products} \qquad (5)$$

Effect of Anions on the Decomposition of the μ-Peroxo-complex $[H^+] < 2.3$M.—Under more strongly acidic conditions ($[H^+] > 0.1$M), and in the presence of chloride, the rate of decomposition of the μ-peroxo-complex is very much slower. When V^{2+} is used to generate the μ-peroxo-complex it is involved in subsequent reactions. With the weaker Fe^{2+} reductant there is no similar involvement, and the effect of chloride and sulphate can be studied. These anions also have the effect of catalysing reaction (1), which would otherwise be slow compared with (2).

An ionic strength of 2.3M was used to enable a range of anion concentrations to be investigated. With $[H^+]$ and $[Cl^-] > 0.6$M the decomposition can be monitored by conventional spectrophotometry. Protonation of the μ-peroxo-complex (4) is extensive and the red colour of the μ-hydroperoxo-complex is clearly visible prior to decomposition as in (2). The decomposition, monitored at 495 nm, gave rate constants (5.9 °C) of 4.3×10^{-3} s^{-1} (2.3M-HCl), and 6.9×10^{-4} s^{-1} (2.3M-H_2SO_4), but in 2.3M-$HClO_4$ (V^{2+} used to generate the μ-peroxo-complex) remains in the stopped-flow range and 2—3 orders of magnitude faster.

The $[H^+]$-dependence of the decomposition was investigated, $[Cl^-] = 2.3$M, $I = 2.3$M (NaCl). At 5.9 °C rate constants k_{obs} (Table 3) fit a dependence (6) (Figure 2).

$$k_{obs} = Kk[H^+]^{-1} \qquad (6)$$

From an unweighted least-squares treatment $Kk = 0.010\,5 \pm 0.006$ mol l^{-1} s^{-1}. The effect of varying chloride, $[Cl^-] = 0.6$—2.3M, $I = 2.3$M (Cl^-/ClO_4^-), with $[H^+] = 2.3$M, was also investigated briefly (see Table 3). The strong inhibition of the chloride is illustrated in Figure 3. A rate law

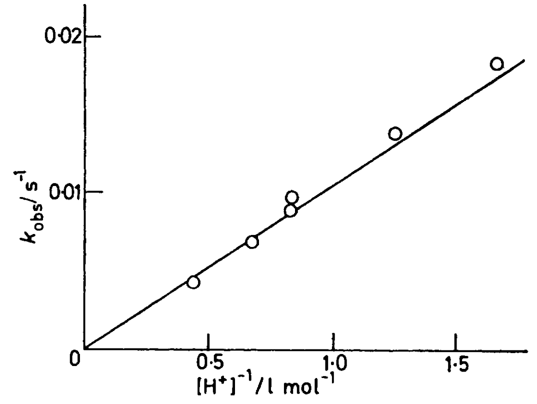


FIGURE 2 The dependence of first-order rate constants k_{obs} on $[H^+]^{-1}$ for the decomposition of the μ-peroxo-complex at 5.9 °C, $I = 2.3$M (NaCl).

with denominator terms in $[Cl^-]$ and $[Cl^-]^2$ is suggested, but the data were not sufficiently extensive to permit a fit to a multi-term rate law.

TABLE 2

Values of K and k obtained from fit of data in Table 1 to equation (3), $I = 0.10$M ($LiClO_4$)

t/°C	$\frac{K}{\text{M}}$	$\frac{k}{\text{s}^{-1}}$
1.5	0.036	6.3
5.0	0.041	9.4
10.0	0.049	17.1
15.0	0.060	29.5
20.0	0.071	51.0
25.0	0.084	84.0

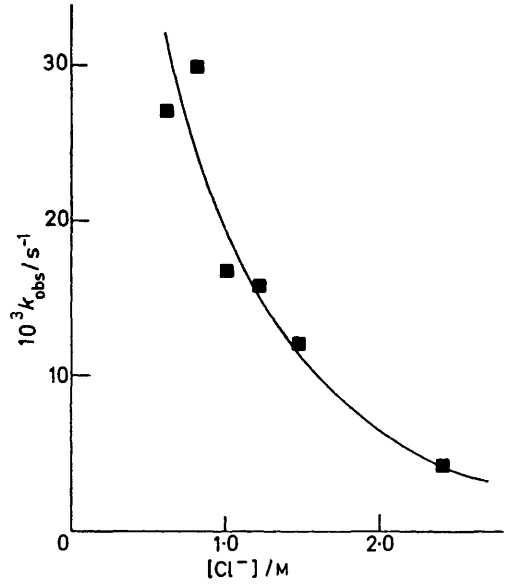


FIGURE 3 Plot of first-order rate constants k_{obs} against $[Cl^-]$ for the decomposition of the μ-peroxo-complex at 5.9 °C, $[H^+] = 2.3$M, $I = 2.3$M (Cl^-/ClO_4^-)

TABLE 3

Rate constants for the decomposition of the μ-peroxo-complex obtained by Fe^{2+} reduction of the μ-superoxo-complex, λ = 495 nm, temperature 5.9 ± 0.2 °C, $I = 2.3$M (NaCl)

$\frac{[H^+]}{\text{M}}$	$\frac{[Cl^-]}{\text{M}}$	$\frac{10^3[Fe^{2+}]}{\text{M}}$	$\frac{10^3[\mu(O_2^-)]}{\text{M}}$	$\frac{10^3 k_{obs}}{\text{s}^{-1}}$
2.3	2.3	10.0	4.2	4.20
2.3	2.3	20.0	4.2	4.08
2.3	2.3	20.0	2.1	4.42
2.3	2.3	20.0	8.4	4.40
2.3	2.3	80.0	4.0	4.32
1.5	2.3	20.0	4.2	7.0
1.2	2.3	40.0	4.0	9.2
1.2	2.3	20.0	4.2	9.7
0.80	2.3	20.0	4.2	13.8
0.60	2.3	20.0	4.2	18.3
2.3	1.5 *	20.0	4.2	11.0
2.3	1.2 *	20.0	4.2	15.9
2.3	1.0 *	20.0	4.2	16.9
2.3	0.80 *	20.0	4.2	30.2
2.3	0.60 *	20.0	4.2	26.9

* Anion concentration made up to 2.3M with ClO_4^-.

Solutions from μ-Peroxo- and μ-Hydroperoxo-solids.— Samples of the brown μ-peroxo, $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+}$, and red μ-hydroperoxo-, $[(NH_3)_5Co{\cdot}O_2H{\cdot}Co(NH_3)_5]^{5+}$, complexes interconvert rapidly in solution with subsequent slower changes. Thus both solids yield identical spectra of (unprotonated) μ-peroxo-complex in 8M-NH_3 ($\lambda_{max.}$ 353, ε 1.4 × 10^3 l mol^{-1} cm^{-1})[14] and of the μ-hydroperoxo-complex in acid solutions ($\lambda_{max.}$ 492 nm, ε 119 l mol^{-1} cm^{-1}; $\lambda_{min.}$ 421 nm, ε 50.9 l mol^{-1} cm^{-1}). Absorption coefficients (ε) were obtained by extrapolating absorption data (over a period of minutes) for reaction occurring (*ca.* 0 °C) to time $t = 0$.* The spectrum of the μ-hydroperoxo-complex (Figure 4) is the same in 2.3M-HCl and *ca.* 1M-H_2SO_4. Stopped-flow experiments in which the μ-superoxo-complex was reduced by V^{2+} in 1M-$HClO_4$ also generated a spectrum, peak 495 ± 5 nm, ε 120 ± 10 l mol^{-1} cm^{-1}, in agreement with Figure 4. Corrections were made for other absorbants in these experiments. The μ-hydroperoxo-complex dissolves readily in 98% H_2SO_4 without decomposition giving a red solution $\lambda_{max.}$ 520 nm (ε 103 l mol^{-1} cm^{-1}), $\lambda_{min.}$ 410 nm (ε 23 l mol^{-1} cm^{-1}) which is stable for days. Solutions of the μ-peroxo-complexes in 2.3M-HCl (*i.e.* no Fe^{2+} present) decompose at the same rate as in the presence of Fe^{2+}. Solutions in 2.3M-NaCl and in 2.3M-$HClO_4$ decompose rapidly $t_{\frac{1}{2}} < 20$ s at 5.9 °C.

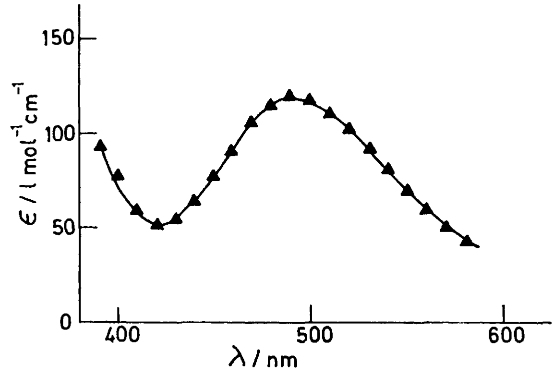


FIGURE 4 Spectrum of the μ-hydroperoxo-complex obtained by dissolving the (brown) μ-peroxo- and (red) μ-hydroperoxo-complexes in 2.3M-HCl or *ca.* 1M-H_2SO_4 and extrapolating kinetic plots (*ca.* 0 °C) to time $t = 0$

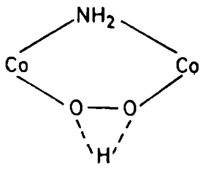
No iodine was obtained ($S_2O_3^{2-}$ test) when the μ-hydroperoxo-complex (10^{-3}M) was made up in 1M-H_2SO_4 in the presence of iodide (10^{-2}M).

DISCUSSION

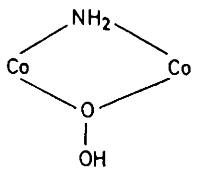
Decomposition of the μ-peroxo-complex $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{4+}$, which is known to have bonding Co–O–O–Co,[6] has been studied previously at alkaline pH values.[2] For the acidic pH range now considered the μ-peroxo-complex was generated *in situ* by V^{2+} or $[Ru(NH_3)_6]^{2+}$ reduction of the μ-superoxo-analogue, $I = 0.10$M ($LiClO_4$). The reductant plays no part in the decomposition, and the $[H^+]$-dependence (Figure 1) is

* S. Fallab (University of Basel), personal communication, has obtained spectrophotometric evidence for different μ-peroxo-species obtained on dissolving $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5](NO_3)_4$ in concentrated NH_4^+/NH_3 buffer at pH 10, and then decreasing the buffer concentration to $[NH_3] = 0.5$M. It is possible that a μ(OH,O_2) complex forms following loss of two ammonia ligands under these conditions. The slower changes observed in the present studies may correspond to formation of some μ(OH,O_2) complex.

consistent with a stable μ-hydroperoxo-complex [equations (4) and (5)]. From the kinetics $k = 84$ s^{-1} (25 °C), $\Delta H^{\ddagger} = 17.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 8.7$ cal K^{-1} mol^{-1} for decomposition of the μ-peroxo-form, in agreement with values $k = 56$ s^{-1} (25 °C), $\Delta H^{\ddagger} = 18$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9$ cal K^{-1} mol^{-1} with $[NH_3] = 4.3$—15.0M, $I = 2.0$M (NH_4NO_3).[2] Values of k thus appear to be remarkably insensitive to solution composition over a wide range of conditions in keeping with an intramolecular electron-transfer process. Charge neutralization occurs within the complex (initially the charge distribution approximates to +3, −2, +3 centres), and the resultant decrease in solvation is reflected in the positive $\Delta S^{\ddagger}$ term. Under conditions of $[Cl^-]$ and $[H^+] > 0.6$M when decomposition is much slower, no $[H^+]$-independent pathway corresponding to decomposition of the μ-hydroperoxo-complex is detected (Figure 2). Protonation by removing electron density from the O_2 bridge presumably decreases the tendency for charge transfer to occur. However it is remarkable that a single protonation brings about such a complete stabilization. One possible explanation is that isomerization to a second μ-hydroperoxo-complex is occurring as considered in the next paragraph.



BH



AH

The kinetics also yield an acid dissociation constant for the μ-hydroperoxo-complex $K = 0.084$M (25 °C), $\Delta H = 6.0$ kcal mol^{-1}, $\Delta S = 15.2$ cal K^{-1} mol^{-1}. These parameters are similar to values obtained by Mori and Weil[8] for acid dissociation of the μ-amido-μ-hydroperoxo-complex, $[(en)_2Co{\cdot}(NH_2,O_2H){\cdot}Co(en)_2]^{4+}$, designated BH, $K = 0.141$M (25 °C), $\Delta H = 5.5$ kcal mol^{-1}, $\Delta S = 18$ cal K^{-1} mol^{-1}. A second μ-amido-μ-hydroperoxo-complex (AH) was identified by them, and the structure confirmed in an X-ray crystallographic study.[15] This raises the question as to whether complexes of the kind BH and/or AH are involved in the present study. No isomerization step was detected, but studies here are more difficult because of the incidence of decomposition and possible need to detect small absorbance changes. Mori and Weil[8] found that the isomerization, AH $\rightleftharpoons$ BH, is rapid with half-lives for the forward and reverse processes at 5 °C of 70 and 160 s respectively. For this reaction they report $\Delta H = 4.8$ kcal mol^{-1} and $\Delta S = 16$ cal K^{-1} mol^{-1}, so that the overall equilibration process $AH \rightleftharpoons B + H^+$ has $\Delta H = 10.3$ kcal mol^{-1} and $\Delta S = 34$ cal K^{-1} mol^{-1}. The present study yields ΔH and ΔS values close to those for the equilibration $BH \rightleftharpoons B + H^+$, which strongly suggests that the AH form is not involved. This is further supported by testing for redox activity. The μ-amido-μ-hydroperoxo-complex (AH form) is known to react rapidly with iodide (5.8 l mol^{-1} s^{-1} at 2 °C).[16] During the period required for decomposition of the μ-peroxo-complex in 1M-H_2SO_4 (*ca.* 30 min at 0 °C) no reaction with I^- was observed. Again the BH structure seems more probable therefore. Interestingly the μ-amido-μ-hydroperoxo-bis[ethylenediaminecobalt(III)] complex remains the only firmly established example of the AH structure.

Whereas chloride alone does not have an obvious stabilizing effect on the μ-peroxo-complex, it certainly enhances the effectiveness of H^+. Similarly sulphate, under conditions of H^+ where HSO_4^- predominates, has a stabilizing effect, which is an order of magnitude greater than for chloride. In terms of a single chloride association the data is consistent with equilibria in (7) [$K_1 = 1/K$, see equation (4)] where if only $\mu(O_2^{2-})$ decomposes (8) follows. When no Cl^- is present (8) reduces to (3). With $[H^+]$ and $[Cl^-] > 0.6$M, so that $[H^+]\,(K_2 + [Cl^-]) > K_1K_2$, (8) reduces to (9). With involvement of a second chloride these equations can be further modified. Binding of the anion to the μ-hydroperoxo-group and/or outer-sphere association to both Co^{III} co-ordination spheres (pseudo bridging) is possible. However no differences in the μ-hydroperoxo visible spectrum were detected in chloride and sulphate solutions (Figure 4). The acid dissociation constant $K = 0.084$M (25 °C) of the protonated complex is small compared to values for other similar complexes with chelating ligands,[17] and may be influenced by the dihedral angle of the Co–O–O–Co group. It is known that the sulphate but not the thiocyanate salt of the μ-peroxo-deca-ammine is bent out of the transoid planar arrangement by 34°,[6] and this influence of lattice anions may also hold for solution medium (anion) effects. Thus anions such as chloride and sulphate may influence and enhance protonation by affecting the dihedral angle.*

$$\mu(O_2^{2-}) \underset{K_1}{\overset{H^+}{\rightleftharpoons}} \mu(O_2H^-) \underset{K_2}{\overset{Cl^-}{\rightleftharpoons}} \mu(O_2H^-),Cl^- \qquad (7)$$

$$k_{obs} = \frac{k_1K_1K_2}{K_1K_2 + K_2[H^+] + [H^+][Cl^-]} \qquad (8)$$

$$k_{obs} = \frac{k_1K_1K_2}{[H^+](K_2 + [Cl^-])} \qquad (9)$$

It was also shown that decomposition under conditions of $[H^+] > 0.6$M, and in the presence of chloride or sulphate was strictly according to equation (1). Hydrogen peroxide does not reduce $[Co(NH_3)_5H_2O]^{3+}$ under the conditions of our experiments. The behaviour observed does not therefore resemble that of the μ-hydroxo-μ-peroxo-complexes where, with triethylenetetra-amine as ligand, an additional pathway (10) is reported, and the balance between (10) and the de-

$$Co^{III}{\cdot}O_2^{2-}{\cdot}Co^{III} + 2H^+ \longrightarrow 2Co^{III} + H_2O_2 \qquad (10)$$

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* We thank Professor S. Fallab for drawing our attention to this possibility.

composition as in (1) is known to be influenced by anions.[17]

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