Reactivity of Different Forms of the µ-Amido-µ-peroxo-bis[bis(ethylenediamine)cobalt(III)] Complex: Oxidation with Tris(1,10-phenanthroline)-iron(III)

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The kinetics of oxidation of the µ-amido-µ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complex with tris(1,10-phenanthroline)iron(III) have been studied, pH 0—2, with a view to obtaining further information regarding reactivities of the different forms of the µ-amido-µ-peroxo-complex. The unprotonated complex, B, is the only reactive form. At 25 °C and $I = 0\cdot245$M ($LiClO_4$): $k_B = (8\cdot1 \pm 0\cdot8) \times 10^5$ l mol^{-1} s^{-1}; $\Delta H_B^\ddagger = -1\cdot1 \pm 0\cdot08$ kcal mol^{-1}, and $\Delta S_B^\ddagger = -35\cdot1 \pm 0\cdot85$ cal K^{-1} mol^{-1}. Possible structures for the protonated, BH, form of the complex are considered.

MOLECULAR oxygen can bond to cobalt in a number of different ways.[1] An extensive series of 2 : 1 cobalt–oxygen complexes has been prepared by the uptake of oxygen by cobalt(II) complexes in solution,[1,2] and, for the amine complexes in this series at least, a µ-peroxo-terminology with both cobalt atoms in oxidation state III is appropriate.[1] Related µ-superoxo-complexes have been prepared by direct oxidation of the peroxo-species. Bailes and Calvin[3] were the first to obtain evidence for a 1 : 1 cobalt to oxygen complex; more recently other 1 : 1 complexes with Schiff's base ligands have been prepared by Floriani and Calderazzo,[4] and Crumbliss and Basolo.[5] E.s.r. spectra[6] for a series of such complexes are consistent with end-on bonding, Co–O–O, and are probably best regarded as superoxo-adducts of cobalt(III). Finally Vaska and his co-

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[1] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, ed. J. O. Edwards, Wiley, New York, 1970, **13**, pp. 1—106.

[2] R. G. Wilkins, Advances in Chemistry Series No. 100, Bio-inorganic Chemistry, Amer. Chem. Soc., 1970, pp. 111—134.

[3] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

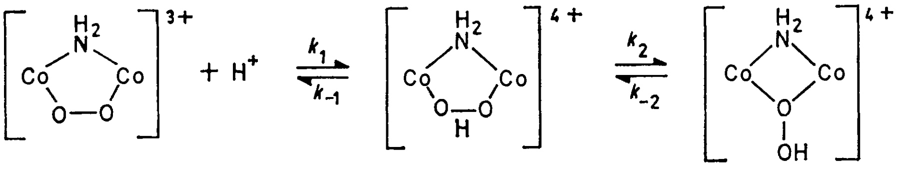
[4] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[5] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55.

[6] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

workers[7] have prepared the 1 : 1 complex [Co(O_2)-(P-P)$_2$] [P-P is the ligand *cis*-(Ph)$_2$PCH=CHP(Ph)$_2$] in which the O_2 group has been shown to be bonded sideways on to the cobalt. Assignment of oxidation states is less clear-cut, and possibly inappropriate for this type of compound.

The μ-peroxo-dicobalt(III) complexes are known to protonate and then isomerize.[8] The relative redox reactivities of the different forms of the μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complex are considered in this paper. In the pH range 0—2, three forms of the complex (hereafter B, BH, and AH) are present in equilibrium [equation (1)]. Mori and Weil[8] have determined values of K_1 ($=k_{-1}/k_1$) and K_2 ($= k_2/k_{-2}$) at 25 °C and $I = 0{\cdot}245$M; these are 0·141 mol l^{-1} and 1·11 respectively. The structures of B[9] and AH[10] have been determined, but the complex BH has not been isolated and its structure is not known with certainty. The assumption that BH has the same ring size as B is based on observations that k_1 and k_{-1} are both fast, and k_2 and k_{-2} are much slower, both *ca.* 0·05 s^{-1} at 25 °C.[8] If this assumption is correct then both B and BH, but not AH, have the correct ring size for oxidation to the corresponding μ-amido-μ-superoxo-complexes.



(1)

(B) (BH) (AH)

Earlier studies with cerium(IV) as the oxidant,[8] while excluding AH as a reactant, did not enable a distinction to be made between B and BH, since cerium(IV) is extensively hydrolysed and Ce^{4+} and CeOH^{3+} are both possible oxidants. The form of the rate law does not differentiate between the reaction paths B + Ce^{4+} ⟶ and BH + CeOH^{3+} ⟶. The same ambiguity holds for other aquo-metal ions. We have therefore chosen the complex tris(1,10-phenanthroline)-iron(III) as a suitable oxidant to investigate further the relative reactivities of B and BH.

PROCEDURE AND RESULTS

A 1 : 1 stoicheiometry as in (2) was demonstrated by reacting an excess of the μ-amido-μ-peroxo-complex with

$$\mu(O_2^{2-}) + Fe(phen)_3^{3+} \longrightarrow \mu(O_2^{-}) + Fe(phen)_3^{2+} \quad (2)$$

Fe(phen)$_3^{3+}$ and determining spectrophotometrically the amount of the μ-amido-μ-superoxo-complex formed (ε = 490 l mol^{-1} cm^{-1} at 687 nm;[11] none of the other reactants absorb at this wavelength). Preliminary experiments demonstrated that the reaction was fast and approaching the limit of the stopped-flow method.

It was possible to use more dilute reactant solutions by recording absorption changes at 510 nm for the formation of Fe(phen)$_3^{2+}$ (ε = 10·9 × 10^3 l mol^{-1} cm^{-1}) from Fe(phen)$_3^{3+}$ (ε = 300 l mol^{-1} cm^{-1}). The μ-amido-μ-peroxo-complex was in a large excess, and the background absorbance (ε_B = *ca.* 350, ε_{BH} = *ca.* 250, and ε_{AH} = *ca.* 160 l mol^{-1} cm^{-1} at 510 nm) was assumed constant throughout. The ionic strength of reactant solutions was adjusted to $I = 0{\cdot}245$M (LiClO$_4$). Values of the final absorbance OD$_\infty$ were obtained from oscilloscope traces and plots of log (OD$_\infty$ − OD$_t$) against time were linear for at least three half-lives. First-order rate constants were evaluated and, from these, second-order rate constants k_{exp} were obtained, assuming a first-order dependence on the total concentration of the μ-amido-μ-peroxo-complex, c_0. No significant variation in k_{exp} was observed at 3·5 °C on varying c_0 from 1·6 × 10^{-4} to 5·4 × 10^{-4}M and [Fe(phen)$_3^{3+}$] from 6·03 × 10^{-6} to 12·1 × 10^{-6}M (Table 1). These findings are consistent with the rate law (3).

$$d[Fe(phen)_3^{2+}]/dt = k_{exp}c_0[Fe(phen)_3^{3+}] \quad (3)$$

Two experimental procedures were adopted to determine the dependence of k_{exp} on the hydrogen-ion concentration. In the first, X, solutions of the μ-amido-μ-peroxo-complex were prepared with the concentration of perchloric acid the same as that in the solution of Fe(phen)$_3^{3+}$. Equilibration of B, BH, and AH is complete within the time required (*ca.* 15 min) for thermostatting the solutions prior to a run. In the second method, Y, solutions of the μ-amido-μ-peroxo-reactant were made up in water with no perchloric acid present initially. On mixing with an equal volume of Fe(phen)$_3^{3+}$ containing perchloric acid, $I = 0{\cdot}49$M, protonation of B to BH was assumed to occur instantly, but the redox process was sufficiently rapid to exclude formation of AH. If now it is assumed that for procedure X, B and BH, but not AH, are oxidized to the μ-amido-μ-superoxo-complex, a possible rate dependence is as in (4). Substituting for [B] and [BH],

$$\text{Rate} = k_B[B][Fe(phen)_3^{3+}] + k_{BH}[BH][Fe(phen)_3^{3+}] \quad (4)$$

using equations previously derived,[12] equation (5) is obtained. Values of K_1 and K_2 as determined by Mori and

$$k_{exp}(K_1 + [H^+] + K_2[H^+]) = k_BK_1 + k_{BH}[H^+] \quad (5)$$

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[7] N. W. Terry, E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, 1972, **94**, 653.

[8] M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, 1967, **89**, 3732.

[9] U. Thewalt, *Z. Naturforsch.*, 1970, *B*, **25**, 5169.

[10] U. Thewalt and R. E. Marsh, *J. Amer. Chem. Soc.*, 1967, **89**, 6364.

[11] A pure sample of μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] nitrate was prepared as described in M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2293.

[12] R. Davies, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1261.

Weil,[8] $I = 0{\cdot}245$M (NaClO$_4$), were used. For procedure Y, K_2 will not be effective since no isomerization to AH is occurring in the time of the reaction, and (5) may be modified to give (6).

$$k_{\mathrm{exp}}(K_1 + [\mathrm{H}^+]) = k_{\mathrm{B}}K_1 + k_{\mathrm{BH}}[\mathrm{H}^+] \qquad (6)$$

The terms on the left-hand side of both (5) and (6) are defined as k'. Values of k' (Table 1) are seen to be in agreement whether procedure X or Y is employed. Moreover k' is independent of hydrogen-ion concentration, $[\mathrm{H}^+] = 0{\cdot}010$—$0{\cdot}244$M. It is concluded therefore that reaction of BH with Fe(phen)$_3{}^{3+}$ makes negligible contribution, and that the reaction proceeds solely by the oxidation of B; at 25 °C, $k_{\mathrm{B}} = 8{\cdot}1 \times 10^5$ l mol^{-1} s^{-1}. From the temperature dependence of k_{B} (Table 2) and using a least-squares treatment with each data point given equal weighting, activation parameters are $\Delta H_{\mathrm{B}}^{\ddagger} = -1{\cdot}1 \pm 0{\cdot}08$ kcal mol^{-1} and $\Delta S_{\mathrm{B}}^{\ddagger} = -35{\cdot}1 \pm 0{\cdot}85$ cal K^{-1} mol^{-1}.* No allowance was made for errors in K_1 and K_2.

TABLE 1

Second-order rate constants, k_{exp}, for the reaction of the μ-amido-μ-peroxo-complex with Fe(phen)$_3{}^{3+}$, concentrations $5{\cdot}4 \times 10^{-4}$ and $6{\cdot}03 \times 10^{-6}$M respectively, except where stated [$I = 0{\cdot}245$M (LiClO$_4$)]

t/°C	[H$^+$]/M	Procedure	$10^{-5}k_{\mathrm{exp}}$ [a]/l mol^{-1} s^{-1}	$10^{-5}k'$ [b]/l mol^{-1} s^{-1}
3·5	0·20	X	0·79(2)	0·56
	0·20 [c]	X	0·84(3)	0·59
	0·20 [d]	X	0·78(3)	0·55
	0·20 [e]	X	0·89(5)	0·63
	0·10	X	1·47(4)	0·57
	0·10	Y	3·46(2)	0·59
	0·040	X	3·32(4)	0·63
10·2	0·244	X	1·00(5)	0·75
	0·244	Y	2·43(5)	0·81
	0·100	X	2·06(6)	0·74
	0·100	Y	3·94(5)	0·74
17·7	0·244	X	1·25(6)	0·83
	0·244	Y	2·81(4)	0·93
	0·100	X	2·62(5)	0·91
	0·100	Y	4·98(4)	1·07
25·0	0·244	X	1·60(7)	1·04
	0·244	Y	3·63(4)	1·44
	0·20	X	1·86(3)	1·04
	0·20	Y	4·05(2)	1·41
	0·10	X	3·11(7)	1·10
	0·10	Y	5·61(4)	1·39
	0·08	X	3·23(5)	1·00
	0·04	X	4·92(5)	1·13
	0·01	X	8·37(5)	1·41

[a] Number of runs averaged indicated in parentheses. [b] Evaluated from equation (5) for procedure X, from (6) for Y. [c] [Complex] = $1{\cdot}61 \times 10^{-4}$M. [d] [Complex = $2{\cdot}68 \times 10^{-4}$M. [e] [Complex] = $2{\cdot}68 \times 10^{-4}$M; [Fe(phen)$_3{}^{3+}$] = $12{\cdot}1 \times 10^{-6}$M.

TABLE 2

Rate constants, k_{B}, for the reaction of the μ-amido-μ-peroxo-complex, B form, with Fe(phen)$_3{}^{3+}$ ($I = 0{\cdot}245$M)

t/°C	$10^{-5}k'$ [a]/l mol^{-1} s^{-1}	K_1 [b]/l mol^{-1}	$10^{-5}k_{\mathrm{B}}$/l mol^{-1} s^{-1}
3·5	0·594 ± 0·045	0·069	8·61 ± 0·65
10·2	0·760 ± 0·035	0·089	8·54 ± 0·39
17·7	0·947 ± 0·091	0·115	8·23 ± 0·80
25·0	1·19 ± 0·18	0·147	8·10 ± 1·23

[a] Obtained from an unweighted least-squares treatment of data in Table 1. [b] Obtained from a plot of log K_1 against $1/T$, experimental data as in ref. 8.

DISCUSSION

Previous studies have indicated that the standard electrode potential for the μ-amido-μ-peroxo/μ-amido-μ-superoxo couple, (en)$_2$Co·μ(NH$_2$,O$_2$)·Co(en)$_2{}^{3+/4+}$, is *ca.* 0·9 V.[13] This value is consistent with observations that the μ-amido-μ-superoxo-complex is reduced by Fe^{2+} (standard electrode potential Fe^{2+}/Fe^{3+} = 0·77 V)[14] and that the μ-amido-μ-peroxo-complex is oxidized by tris(1,10-phenanthroline)iron(III) [standard electrode potential Fe(phen)$_3{}^{2+}$/Fe(phen)$_3{}^{3+}$ = 1·06 V].[14] Tris(1,10-phenanthroline)iron(III) is inert to substitution and, since oxidation of the peroxo-bridge is fast, electron transfer must occur by an outer-sphere process without bonding of the O$_2$ group to the oxidant.

The form of the rate law allows a clear distinction to be made between B, BH, and AH as reactants. The AH form does not undergo oxidation directly, which is as expected in view of the smaller ring size. There is also no evidence for a contribution from the BH form, and B appears to be the sole reactant. Similar results were obtained for the oxidation of the μ-amido-μ-peroxo-complex by four superoxo-species.[13] This raises the question as to whether BH has in fact a five-membered ring as in (1), or whether structurally it is more similar to AH. The interpretation centering around equations (5) and (6) requires the $\mathrm{B} + \mathrm{H}^+ \rightleftharpoons \mathrm{BH}^+$ equilibrium to be established rapidly, and the constancy of values of k' (Table 1) would seem to support this assumption. Minor structural changes accompanying protonation cannot necessarily be ruled out however. Data for redox reactions of the μ-amido-μ-peroxo-complex are summarized in Table 3. The reduction with Cr^{2+}[15] is different in kind from that with iodide,[12] since in the first stage Cr^{2+} reduces a cobalt(III) atom whereas

TABLE 3

Reactivity of B, BH, and AH forms of the μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complex

	B	BH	AH	Reference
Oxidant				
Fe(phen)$_3{}^{3+}$	Yes	No	No	This work
Superoxo-complexes	Yes	No	No	13
Ce$^{\mathrm{IV}}$ [a]	Possibly [b]	Possibly [b]	No	8
Reductant				
I$^-$ [c]	No	Yes [d]	Yes (fast)	12
Cr^{2+}	Yes [e]	Small [f]	No	15

[a] The reaction with HOCl shows similar features, R. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1968, 2840. [b] An ambiguity exists in interpretation depending on whether Ce^{4+} oxidizes B, and/or CeOH^{3+} oxidizes BH. [c] Reduces the peroxo-bridge and not cobalt(III). [d] Dependence on [I$^-$]^2 for this path. [e] Reduction of cobalt(III) occurs in the first stage. [f] The extent of the contribution from this reaction is uncertain. From a least-squares treatment a rate constant *ca.* 16 l mol^{-1} s^{-1} at 25 °C and $I = 2{\cdot}0$M (LiClO$_4$) is obtained, but this is small compared with the value of 2100 l mol^{-1} s^{-1} which is observed for the reduction of B.

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* 1 cal = 4·2 J.

[13] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1423.

[14] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall Inc., New York, 1952. The I.U.P.A.C. sign convention is used.

[15] M. R. Hyde and A. G. Sykes, to be submitted.

iodide reduces the peroxo-bridge. With iodide both BH and AH are reactants and the μ-amido-μ-hydroxo-product has a four-membered ring. It is tempting therefore to conclude that BH may also have a four-membered ring. However the dependence on iodide for this path is $[I^-]^2$ and the reduction is probably not a simple concerted process. With Cr^{2+} as reductant B is the principal reactant and this is consistent with the proton of BH hindering approach of the reductant. Similarly in the present study this could be a perfectly adequate explanation for the absence of a path in which BH is oxidized. The non-involvement of BH can also be accounted for by the reluctance of the μ-amido-μ-superoxo-complex to protonate, thus giving rise to a higher energy barrier in the oxidation of BH. To summarize, the most likely structure for BH remains one closely similar to B, where the presence of the proton (which may be shared by both oxygens) very much reduces the reactivity.

Finally the values obtained for the activation parameters $\Delta H_B^\ddagger = -1{\cdot}1 \pm 0{\cdot}08$ kcal mol^{-1} and $\Delta S_B^\ddagger = -(35{\cdot}1 \pm 0{\cdot}85)$ cal K^{-1} mol^{-1} warrant comment. The rate constant k_B may be regarded as composite and equal to kK_0, where K_0 is the equilibrium constant for outer-sphere association of B and $Fe(phen)_3^{3+}$ and k is the rate constant for electron transfer. Direct measurement of outer-sphere association constants has been possible in only a few instances, and in general values of K_0 have to be estimated. Equations derived by Fuoss and Eigen[16] can be used for this purpose. For interactions between two 3+ ions K_0 is small and, for an interatomic separation of 5 Å, ΔH_0 and ΔS_0 are both negative, with ΔS_0 dominant. Using expression (7) derived by Fuoss [where N_A is Avogadro's number, a = the centre to centre separation

$$K_0 = \frac{4\pi N_A a^3}{3000} \exp\left[\frac{-z_1 z_2 e^2}{aDkT} + \frac{z_1 z_2 e^2 \kappa}{DkT(1+\kappa a)}\right] \qquad (7)$$

of the ions at closest distance of approach, e the electronic charge, z_1 and z_2 the charges on the ions (with appropriate sign), D the macroscopic dielectric constant, k Boltzmann's constant, and κ the Debye–Hückel parameter], $K_0 = 10^{-3{\cdot}7}$ l mol^{-1} at 25 °C and, from the temperature dependence of K_0, $\Delta H_0 = ca.\ -4{\cdot}1$ kcal mol^{-1} and $\Delta S_0 = ca.\ -30{\cdot}4$ cal K^{-1} mol^{-1} [$I = 0{\cdot}245$M $(LiClO_4)$].* Activation parameters for k are accordingly $\Delta H^\ddagger = ca.$ 3 kcal mol^{-1} and $\Delta S^\ddagger = ca.\ -4{\cdot}7$ cal K^{-1} mol. Enthalpies of activation for two other reactions, the V^{2+} reductions of $(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5^{5+}$ (ref. 17) and $(trenen)Co{\cdot}O_2{\cdot}Co(trenen)^{5+}$ (trenen = 4-aminoethyl-1,4,7,10-tetra-azadecane)[18] are also negative (*ca.* −1 kcal mol^{-1}). After making allowances for outer-sphere complexing, positive enthalpies of activation (*ca.* 3 kcal mol^{-1}) are likewise obtained for the electron-transfer process.

EXPERIMENTAL

The μ-amido-μ-superoxo-bis[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,O_2){\cdot}Co(NH_3)_4](NO_3)_4$, was prepared as described in ref. 19. This was converted to the μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complex [B form, see equation (1)] by heating the μ-amido-μ-superoxo-ammine complex (2 g) with ethylenediamine (10%, 25 cm^3) at 60 °C for *ca.* 2 h. To obtain pure B, conc. HNO_3 was first added to a concentrated solution of complex (both at 0 °C), until the solution turned red. The latter was then kept at *ca.* −5 °C to complete crystallization of the red AH form of the complex The AH so obtained was recrystallized twice under similar conditions. To convert to B the AH form was dissolved in a minimum of cold 7M-ammonia and acetone (*ca.* 150 cm^3) added to initiate precipitation. The solution was left at *ca.* 0 °C to complete precipitation {Found: C, 15·4; H, 5·95; N, 26·1. Calc. for $[(en)_2Co{\cdot}\mu(NH_2,O_2){\cdot}Co(en)_2](NO_3)_3,2{\cdot}5H_2O$: C, 15·1; H, 6·15; N, 26·35%}.

The tris(1,10-phenanthroline)iron(III) complex was prepared as described in the literature[20] [Found: C, 47·85; H, 3·0; N, 9·4. Calc. for $Fe(C_{12}H_8N_2)_3(ClO_4)_3,H_2O$: C, 47·4; H, 2·85; N, 9·20%]. Perchloric acid was of AnalaR grade purity. Lithium perchlorate was prepared by neutralization of lithium carbonate, the product being recrystallized until free of anionic impurities. Stock solutions of $Fe(phen)_3^{3+}$ were freshly prepared each day by dissolving the complex in 5M-$HClO_4$ and storing at 0 °C. Aqueous solutions of the μ-amido-μ-peroxo-complex were also freshly prepared and treated in a similar manner. Prior to each run the latter was diluted with $HClO_4/LiClO_4$ for procedure X and with water for procedure Y.

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* An allowance has been made for the variation of D with temperature and ionic strength; for further details see M. R. Hyde and A. G. Sykes, to be published. Values of ΔH_0 and ΔS_0 become numerically smaller for distances of closest approach up to 10 Å. The procedure must be regarded as very approximate and particularly so for binuclear complexes. It does however clearly indicate a negative value for ΔH_0 and help to rationalize the negative value which has been attained for the experimental enthalpy of activation.

[16] M. Eigen, *Z. phys. Chem.*, 1954, **1**, 176; R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

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[19] R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, 1970, **12**, 203.

[20] A. A. Schilt and R. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.