Regioselective Formation of Peroxyquinolatocobalt(III) Complexes in the Oxygenation of 2,6-Di-t-butylphenols with Cobalt(II) Schiff-base Complexes[1]

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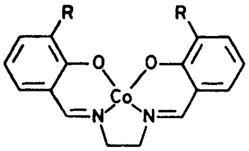
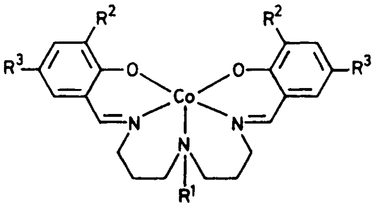
The oxygenation of 2,6-di-t-butylphenols with five-co-ordinate cobalt(II) Schiff-base complexes in aprotic solvents, such as CH_2Cl_2, thf, and dmf (thf = tetrahydrofuran, dmf = dimethylformamide), has been found to result in regioselective formation of peroxyquinolatocobalt(III) complexes. The regioselectivity depends on the nature of the substituent at the 4-position of the phenol used: 4-alkyl-2,6-di-t-butylphenols (1) afford peroxy-*p*-quinolatocobalt(III) complexes, whereas peroxy-*o*-quinolato-complexes are formed from 4-aryl-2,6-di-t-butylphenols (4). The initiation of the oxygenation is hydrogen abstraction by superoxocobalt(III) species from the phenols to give the corresponding phenoxy-radicals (10). Rapid reduction of (10) with cobalt(II) species follows giving rise to a phenolatocobalt(III) complex intermediate, within which dioxygen is incorporated. The regioselectivity of the oxygenation is attributable to the formation of the phenolatocobalt(III) complex intermediate. Crystals of the peroxy-*p*-quinolatocobalt(III) complex (2a) are orthorhombic, space group $P2_12_12_1$, with a = 33.749(11), b = 11.844(5), c = 9.329(4) Å, and Z = 4. The crystal structure has been refined from 3 018 diffractometer data to R = 0.067.

SELECTIVE oxidation of organic molecules with dioxygen catalysed by transition-metal complexes capable of binding dioxygen is of current interest from the standpoints of organic syntheses and biological oxidations.[2] Biological oxidations are mostly catalysed by iron and copper complexes involved in the reaction centre of relevant enzymes.[3] The catalysis by these iron and copper complexes in enzymes is considered to involve the activation of dioxygen in such a manner as to form reactive dioxygen complexes of the types Fe–O–O and Cu–O–O–Cu. These dioxygen complexes are formally equivalent to those of haeme- and copper-containing natural oxygen carriers, haemoglobin and haemocyanin.

On the other hand, many cobalt(II) complexes co-ordinated with *N*-bases have been demonstrated to reversibly interact with dioxygen to form CoO_2 and Co_2O_2 complexes depending on the nature of the ligand, exhibiting a model of the two types of natural oxygen carriers.[4]



[CoL¹]; R = H
[CoL²]; R = OMe



[CoL³]; $R^1 = R^2 = R^3 = H$
[CoL⁴]; R^1 = Me, $R^2 = R^3 = H$
[CoL⁵]; R^1 = Me, R^2 = OMe, R^3 = H
[CoL⁶]; R^1 = Me, $R^2 = R^3$ = Cl
[CoL⁷]; R^1 = Me, R^2 = H, $R^3 = NO_2$

Typical cobalt(II) complexes capable of binding dioxygen reversibly are the Schiff-base complexes [CoL¹] and [CoL³] and their derivatives. Since CoO_2 and Co_2O_2 complexes from cobalt(II) species are well characterized as superoxo- and μ-peroxo-complexes respectively, it is interesting to know whether these cobalt(II) complexes can catalyse the oxygenation of organic molecules related to biological systems.

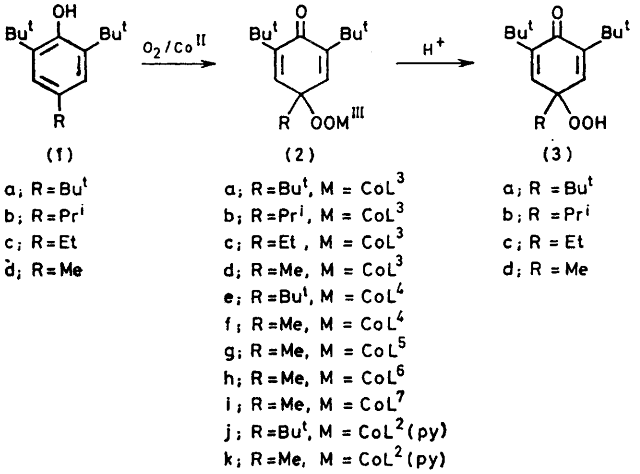
Although the electronic structures of FeO_2 complexes are considered to be of the superoxoiron(III) type,[5] the diamagnetic property of natural and synthetic FeO_2 complexes obscures their true electronic structure. With the cobalt dioxygen complexes, it should be possible to clarify the chemical reactivities of typical superoxo- and μ-peroxo-complexes. van Dort and Geursen[6] and Vogt *et al.*[7] have reported the oxygenation of some phenols to give *p*-benzoquinones and diphenoquinones catalysed by [CoL¹] and its derivatives. Recently, we have reported that [CoL¹] catalyses the oxygenolysis of the heterocyclic ring of 3-substituted indoles and 3-hydroxyflavones to give the same type of products as those obtained in the reactions of tryptophan-2,3-dioxygenase and quercetinase respectively.[8,9]

Herein we report that a five-co-ordinate cobalt(II) Schiff-base complex, [CoL³], and its derivatives mediate dioxygen incorporation into 2,6-di-t-butylphenols in aprotic solvents such as CH_2Cl_2, thf, py, and dmf (thf = tetrahydrofuran, py = pyridine, dmf = dimethylformamide) to result in the regioselective formation of peroxyquinolatocobalt(III) complexes (2) and (5) depending on the nature of the 4-substituent in the substrate. A plausible mechanism of the present unique oxygenation reaction involves hydrogen abstraction from the substrate by the superoxocobalt(III) complex initially formed followed by a rapid reduction of the resulting phenoxy-radical by the cobalt(II) species affording a phenolatocobalt(III) complex intermediate. The regioselectivity results from dioxygen incorporation into the intermediate.

RESULTS

Formation of Peroxy-p-*quinolatocobalt*(III) *Complexes* (2).—Dioxygen was bubbled through a solution of 2,4,6-tri-t-butylphenol (1a) and [CoL³] in CH_2Cl_2 at 0 °C for 2 h. The

^{1}H n.m.r. spectrum of the reaction mixture showed only signals from (1a) and the peroxy-*p*-quinolatocobalt(III) complex (2a). No signals from the hydroperoxide (3a) were observed, indicating the formation of complex (2a)



as the sole product, which was isolated as crystals. Similar results were obtained in the oxygenation with other phenols (1b)—(1d) and $[\mathrm{CoL^3}]$ derivatives (Table 1). Analytical and spectral data of (2) are in good agreement with the structure, which was further supported by the quantitative formation of hydroperoxides (3) on filtration of a solution of (2) in $\mathrm{CH_2Cl_2}$ through a short column of silica gel. When (2a) was treated with acetic acid, $[\mathrm{Co^{III}(O_2CMe)L^3}]$ was obtained along with hydroperoxide (3a). These results indicate that the peroxy-*p*-quinolato-complexes are susceptible to an acid–base exchange reaction. Two non-equivalent t-butyl signals were observed in the ^{1}H n.m.r. of (2) (Table 1) contrary to the case of (3) whose t-butyl groups are magnetically equivalent. The non-equivalency

TABLE 1

Peroxy-*p*-quinolatocobalt(III) complexes (2) isolated from oxygenation of phenols (1) [a]

Product	Yield [b]/ %	^{1}H n.m.r. (CDCl$_3$), δ [c]/p.p.m.			
		Bu^t	R	(R) [d]	Δδ(R) [e]
(2a)	64	1.28, 1.30	0.60	(0.96)	0.36
(2b)	60	1.18, 1.30	0.57 [f]	(0.86) [f]	0.29
(2c)	62	1.10, 1.27	0.50 [g]	(0.75) [g]	0.25
(2d)	68	1.07, 1.25	1.05	(1.37)	0.32
(2e)	3	1.28	0.60		
(2f)	0	1.17, 1.26	1.01 [h]		
(2g)	81	0.98, 1.05	0.72		
(2h)	73	1.00, 1.06	0.82		
(2i)	60	1.23, 1.27	0.91		
(2j)	3	0.98	0.55		

[a] Dioxygen was bubbled through a solution of (1) (20 mmol) and cobalt complex (10 mmol) in $\mathrm{CH_2Cl_2}$ (150 cm^3) at 0 °C for 2—4 h. [b] Of pure, isolated product. The ^{1}H n.m.r. spectrum of the reaction mixture showed the quantitative formation of (2). [c] Other signals: amine region, 1.8—4.4 (m); aromatic region, 6.0—7.6 (m). [d] R in hydroperoxides (3). [e] Difference in chemical shifts of R in (2) and (3). [f] Me group; d, $J = 7$ Hz. [g] Me group; t, $J = 7.5$ Hz. [h] In CD$_3$OD.

TABLE 2

Interatomic distances and bond angles in (2a)

(*a*) Bond distances (Å)

Co–O(3)	1.854(9)	Co–N(2)	2.053(14)
Co–O(4)	1.894(9)	Co–O(5)	1.929(11)
Co–N(1)	1.949(12)	Co–N(3)	1.944(11)
N(1)–C(25)	1.27(2)	N(3)–C(32)	1.28(2)
N(1)–C(26)	1.50(2)	N(3)–C(31)	1.50(2)
N(2)–C(28)	1.45(2)	N(2)–C(29)	1.47(2)
C(26)–C(27)	1.52(3)	C(31)–C(30)	1.54(2)
C(27)–C(28)	1.44(3)	C(30)–C(29)	1.49(3)
O(4)–C(19)	1.30(2)	O(5)–C(38)	1.33(1)
C(19)–C(20)	1.39(2)	C(38)–C(37)	1.42(2)
C(20)–C(21)	1.46(2)	C(37)–C(36)	1.40(2)
C(21)–C(22)	1.42(3)	C(36)–C(35)	1.43(2)
C(22)–C(23)	1.39(3)	C(35)–C(34)	1.45(2)
C(23)–C(24)	1.47(3)	C(34)–C(33)	1.37(2)
C(24)–C(19)	1.43(2)	C(33)–C(38)	1.41(2)
C(24)–C(25)	1.45(2)	C(33)–C(32)	1.50(2)
O(2)–O(3)	1.50(1)	O(2)–C(4)	1.42(1)
C(1)–O(1)	1.24(2)	C(4)–C(9)	1.63(2)
C(1)–C(2)	1.51(2)	C(1)–C(6)	1.46(2)
C(2)–C(3)	1.33(2)	C(6)–C(5)	1.35(2)
C(2)–C(8)	1.55(2)	C(6)–C(7)	1.51(2)
C(3)–C(4)	1.53(2)	C(5)–C(4)	1.54(2)

(*b*) Intramolecular short contacts (Å)

C(2) ··· C(31)	4.08(2)	C(10) ··· C(19)	4.07(2)
C(3) ··· C(31)	4.06(2)	C(10) ··· C(20)	3.77(2)
C(5) ··· C(19)	3.98(2)	C(10) ··· O(4)	3.52(2)
C(5) ··· C(31)	3.87(2)	O(2) ··· N(1)	2.88(1)
C(5) ··· O(4)	3.05(1)	O(2) ··· O(4)	3.04(1)
C(6) ··· C(31)	3.93(2)	O(2) ··· C(26)	3.23(2)
C(10) ··· $\mathrm{C(21^{I})}$	3.86(3)	C(11) ··· $\mathrm{C(35^{II})}$	3.86(2)
C(10) ··· $\mathrm{C(22^{I})}$	3.86(3)	C(12) ··· $\mathrm{C(25^{III})}$	3.99(2)
C(10) ··· $\mathrm{C(36^{I})}$	3.81(2)	C(18) ··· $\mathrm{C(28^{IV})}$	3.63(2)
C(11) ··· $\mathrm{C(34^{II})}$	3.98(2)	C(18) ··· $\mathrm{C(30^{IV})}$	3.92(2)

(*c*) Bond angles (°)

N(1)–Co–N(2)	96.8(5)	N(3)–Co–N(2)	85.8(4)
N(1)–Co–O(4)	91.3(4)	N(3)–Co–O(5)	90.2(4)
O(3)–Co–O(5)	172.8(4)	N(3)–Co–O(4)	86.0(4)
Co–N(1)–C(26)	119.2(10)	Co–N(3)–C(31)	117.7(8)
N(1)–C(26)–C(27)	110.1(15)	N(3)–C(31)–C(30)	106.1(11)
C(26)–C(27)–C(28)	121.8(18)	C(31)–C(30)–C(29)	114.9(13)
C(27)–C(28)–N(2)	123.9(20)	C(30)–C(29)–N(2)	117.9(14)
C(28)–N(2)–Co	117.3(11)	C(29)–N(2)–Co	114.0(9)
C(28)–N(2)–C(29)	106.5(14)		
C(26)–N(1)–C(25)	118.1(12)	C(31)–N(3)–C(32)	117.2(11)
Co–N(1)–C(25)	122.7(10)	Co–N(3)–C(32)	125.1(9)
N(1)–C(25)–C(24)	124.0(13)	N(3)–C(32)–C(33)	123.5(13)
C(25)–C(24)–C(19)	123.2(14)	C(32)–C(33)–C(38)	121.0(11)
C(24)–C(19)–O(4)	120.6(12)	C(33)–C(38)–O(5)	123.2(11)
C(19)–O(4)–Co	123.1(8)	C(38)–O(5)–Co	121.4(7)
Co–O(3)–O(2)	114.3(6)	O(3)–O(2)–C(4)	105.6(8)
O(1)–C(1)–C(2)	120.7(12)	C(5)–C(4)–C(9)	110.7(10)
O(1)–C(1)–C(6)	120.2(12)	O(2)–C(4)–C(9)	102.5(9)
C(2)–C(1)–C(6)	119.0(10)	O(2)–C(4)–C(3)	109.6(10)
		O(2)–C(4)–C(5)	109.7(10)
C(1)–C(2)–C(3)	119.1(12)		
C(8)–C(2)–C(1)	118.5(10)	C(1)–C(6)–C(5)	119.8(11)
C(8)–C(2)–C(3)	122.4(12)	C(7)–C(6)–C(1)	119.6(11)
C(2)–C(3)–C(4)	121.7(12)	C(7)–C(6)–C(5)	120.7(12)
		C(6)–C(5)–C(4)	120.8(11)
C(3)–C(4)–C(5)	113.5(10)		
C(3)–C(4)–C(9)	110.4(10)		

Superscripts refer to the following equivalent positions: I $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; II $1 - x, \frac{1}{2} + y, 1.5 - z$; III $x, 1 + y, z$; IV $x, y, -1 + z$.

of the two t-butyl groups and the higher-field shift of the alkyl group R in (2) compared to (3) ($\Delta\delta$ = 0.25—0.36) may be due to a ring-current effect caused by the aromatic ring of one of the salicylideneiminato-moieties, as judged by the *X*-ray analysis of (2a) (see below). The oxygenation of (1a) and (1d) with [CoL^2], a square-planar complex, in pyridine also gave (2j) and (2k) respectively, although (2k) was too unstable to isolate and decomposed even under the conditions for n.m.r. measurement.

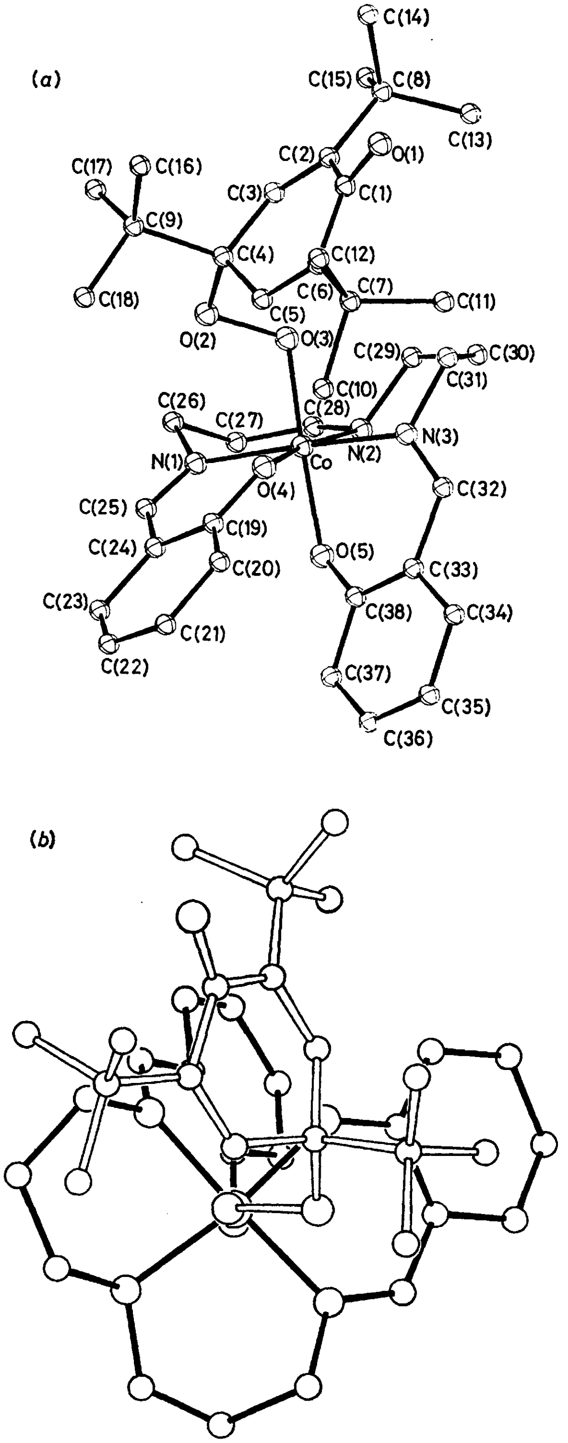
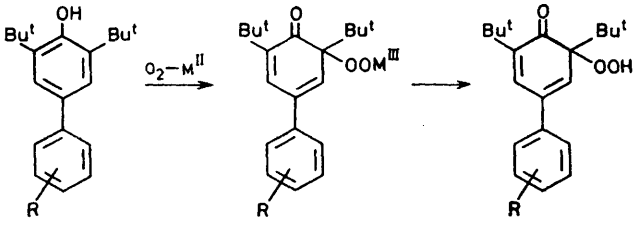


FIGURE 1 (*a*) Molecular structure showing atom numbering. (*b*) A view of the molecule showing the orientation of the peroxyquinolato-group (open bonds) relative to the parent [CoL^3] (filled bonds)

Structure of Peroxy-p-*quinolatocobalt*(III) *Complex* (2a).—The structure of (2) was confirmed by the *X*-ray analysis of (2a). The molecular parameters are listed in Table 2 and the atomic numbering is shown in the ORTEP [10] drawing of the molecule (Figure 1). As seen from Figure 1, three N and three O atoms co-ordinate octahedrally to the Co atom with the *mer* configuration. The Co–N bond lengths are typical ones for cobalt(III) complexes, indicating that the metal ion is in a +III oxidation state. This agrees well with the fact that complexes (2) display sharp ^{1}H n.m.r. signals. The Co–O(3) bond is slightly shorter than that in μ-peroxo-cobalt(III) complexes.[11] The observed configuration of the Schiff-base ligand is similar to that of the binuclear μ-peroxo-cobalt(III) complex obtained from [CoL^3].[12] Interestingly, however, in contrast to the μ-peroxo-complex, the N–H group of the quinquedentate ligand in (2a) projects to the side of the O(5) atom. The different Co–N–H bonding mode is attributable to the configurational change in the Schiff-base ligand. With the present complex (2a), the six-membered chelate ring composed of N(2), C(29), C(30), C(31), N(3), and Co has a chair form and the other ring comprising C(26)—C(28) assumes an envelope conformation. By contrast, of the two six-membered rings including the three N atoms and Co in the μ-peroxo-cobalt(III) complex [(CoL^3)$_2$(O$_2$)], one corresponding to the chair form in (2a) has a skew conformation whereas the other assumes a flattened chair form,[12] although the origin of the difference is unclear.



(4) (5) (6)

a; R = 4-OMe b; R = 3-OMe c; R = 2-OMe d; R = 4-Me
e; R = 3-Me f; R = 2-Me g; R = H h; R = 4-Cl
M = CoL^3

The O–O distance of the peroxy-group in (2a) is nearly the same as that in H$_2$O$_2$ but the Co–O–O–C(4) torsion angle (127.7°) is very different from the H–O–O–H angle. The dienone ring in the peroxyquinolato-group has a boat conformation and the t-butyl group involving C(9) assumes an axial position with respect to the ring.

Peroxy-o-*quinolatocobalt*(III) *Complexes* (5).—In contrast to 4-alkylphenols (1), the oxygenation of 4-arylphenols (4) with [CoL^3] in CH$_2$Cl$_2$ under the same conditions as for the formation of (2) gave peroxy-*o*-quinolatocobalt(III) complexes (5) exclusively (Table 3). Treatment of (5) with acetic acid or filtration of a solution of (5) in CH$_2$Cl$_2$ through a short column of silica gel gave the corresponding *o*-hydroperoxides (6) [13] in quantitative yield. Spectral and analytical data of (5) are in good agreement with the structure. The ^{1}H n.m.r. signal of one of the t-butyl groups in (5) shifts to considerably higher field compared to that of the corresponding hydroperoxides (6) ($\Delta\delta$ = 0.16—0.22 p.p.m.),

TABLE 3

Peroxy-*o*-quinolatocobalt(III) complexes (5) from oxygenation of phenols (4), and hydroperoxides (6) from (5) [a]

Product	Yield [b]/ %	^{1}H n.m.r. ($CDCl_3$), δ/p.p.m. Bu^t		Me	C=CH [c]		Aromatic	OOH
(5a)	27	0.83	1.23	3.80	5.85	6.89	6.7—7.6	
(5b)	18	0.82	1.21	3.83	6.00	*d*	6.6—7.6	
(5c)	44	0.88	1.26	3.81	5.80	6.82	6.7—7.6	
(5d)	30	0.83	1.24	2.35	5.99	6.88	6.7—7.6	
(5e)	58	0.84	1.25	2.40	5.97	*d*	6.7—7.6	
(5f)	4	0.85	1.25	2.16	5.45	6.63	6.7—7.6	
(5g)	4	0.83	1.24		6.03	*d*	6.7—7.6	
(5h)	37	0.87	1.25		5.97	6.88	6.7—7.6	
(6a)	80	1.03	1.28	3.83	6.60	7.06	6.7—7.6	9.00
(6b)	83	1.03	1.28	3.86	6.62	6.93	6.9—7.4	8.67
(6c)	76	1.04	1.27	3.80	6.45	6.84	7.5	8.63
(6d)	67	1.05	1.29	2.39	6.63	7.02	7.25	8.82
(6e)	62	1.03	1.28	2.22	6.63	7.02	7.22	9.06
(6f)	70	1.06	1.26	2.37	6.38	6.69	7.4	8.51
(6g)	72	1.03	1.29		6.04	7.02	7.2—7.4	8.96
(6h)	68	1.03	1.26		6.65	6.95		8.50

[a] Dioxygen was bubbled through a solution of (4) (0.5 mmol) and [CoL^3] (0.4 mmol) in CH_2Cl_2 (6 cm^3) at 0 °C for 1 h. Hydroperoxides (6) were obtained by filtration of a CH_2Cl_2 solution of (5) through a short column of silica gel (5 g). [b] Of pure, isolated product. The ^{1}H n.m.r. spectrum of the reaction mixture showed the quantitative formation of (5). Yields of (6) refer to the conversion of (4) into (5). [c] A pair of doublets with J = 2.8 Hz. [d] The signal is concealed behind the aromatic signals.

reflecting again the co-ordination effect. The magnitude of coupling between the two olefinic protons of the quinoid system (J = 2.8 Hz) in (5) is characteristic for that between H^3 and H^5 of cyclohexa-2,4-dienones.[13,14] The oxygenation of (4a) with [CoL^2] in pyridine followed by separation of the product on a silica gel column gave hydroperoxide (6a) quantitatively. This is also indicative of the formation of the corresponding peroxy-*o*-quinolatocobalt(III)–L^2 complex, although it was not isolated.

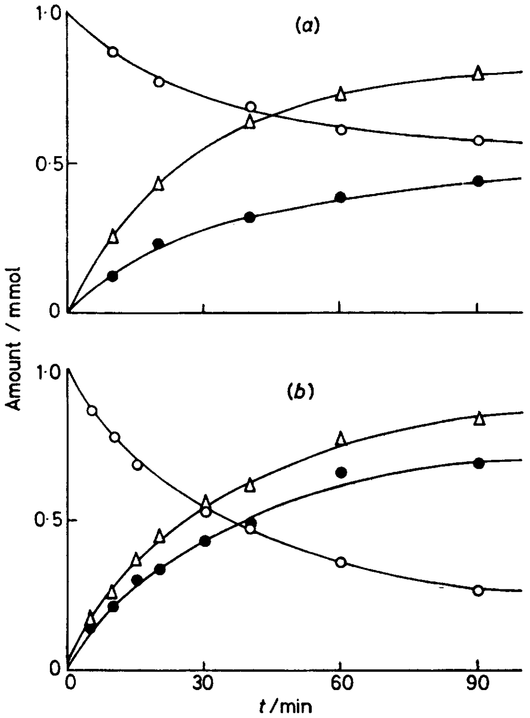


FIGURE 2 Time course of the oxygenation of (*a*) (1d) with [CoL^4] and (*b*) (1a) with [CoL^3]. Conditions: [(1)] = [Co] = 2.5 × 10^{-2} mol dm^{-3} in CH_2Cl_2 (40 cm^3), 5 °C. (●), Formation of (2f) (*a*), (2a) (*b*); (△), O_2 uptake; (○), formation of (1d) (*a*), (1a) (*b*)

The formation of (5) is of particular interest, because a similar type of peroxy-*o*-quinolato-complex intermediate has been postulated for the oxygenolysis of phenolic substrates catalysed by non-haeme iron-containing dioxygenases.[15]

Stoicheiometry of Formation of Peroxyquinolatocobalt(III) *Complexes*.—Peroxyquinolatocobalt(III) complexes (2) were not stable in alcohols, where they were converted into the corresponding *p*-quinols,[16] but fairly stable in aprotic solvents. Complexes (5) were also stable in aprotic solvents. The time course of the oxygenation of (1d) with [CoL^4] and of (1a) with [CoL^3] showed a molar ratio of (2f) : (1d) : O_2 uptake = 1 : 1 : 2 [Figure 2(*a*)] and that of (2a) : (1a) : O_2 uptake = 1 : 1 : 1.25 [Figure 2(*b*)]. These results suggest that the O_2-uptake ratio depends upon the nature of the ligand in the Schiff-base complex. Therefore, the relation between the formation of (2) [or (5)] and O_2 uptake with various combinations of the relevant reactants was examined. The results are summarized in Table 4 together with the half-conversion time ($t_{\frac{1}{2}}$ in min). The present oxygenation falls into two types of stoicheiometries: *i.e.* O_2 uptake : (2) [or (5)] = 2.0 or 1.25 : 1, although Table 4 shows some scatter attributable to unavoidable error in the method of product determination employed. No hydrogen peroxide was found in the oxygenation mixture in any run. However, where the stoicheiometry O_2 uptake : (2) = 2 : 1 was obtained, acidification of the oxygenation mixture gave H_2O_2, indicating the formation of hydroperoxide cobalt(III) species, $Co^{III}(OOH)$. Where the stoicheiometry O_2 uptake : (2) [or (5)] = 1.25 : 1 was obtained, on the other hand, no such $Co^{III}(OOH)$ was found. From these results, the following stoicheiometries can be depicted. For O_2 uptake : (2) =

$$2\,Co^{II} + 2\,O_2 + (1) \longrightarrow (2) + Co^{III}(OOH) \qquad (i)$$

2.0 : 1, equation (i) holds and for O_2 uptake : (2) [or (5)] = 1.25 : 1, equation (ii) holds.

$$Co^{II} + \tfrac{5}{4}\,O_2 + (1)\ [\text{or } (4)] \longrightarrow (2)\ [\text{or } (5)] + \tfrac{1}{2}\,H_2O \qquad (ii)$$

The stability of $Co^{III}(OOH)$ is dependent on the nature of the ligand and it decomposes to give hydroxo-cobalt(III)

TABLE 4

Oxygen uptake in the formation of peroxyquinolatocobalt(III) complexes (2) and (5) [a]

Phenol	Complex [b]	Solvent	Product	Yield [c]/ mmol	O_2 uptake/ mmol	O_2 uptake : (2) [or (5)]	$t_{\frac{1}{2}}$ [d]/ min
(1a)	[CoL^3]	CH_2Cl_2	(2a)	0.84	1.04	1.24	11
(1d)	[CoL^3]	CH_2Cl_2	(2d)	0.83	0.97	1.17	14
		thf	(2d)	0.92	1.12	1.22	4
		dmf	(2d)	0.81	1.00	1.23	12
	[CoL^3]	py	(2d)	0.85	1.05	1.23	14
	[CoL^4]	CH_2Cl_2	(2f)	0.46	0.96	2.1	11
	[CoL^5]	CH_2Cl_2	(2g)	0.47	0.98	2.1	12
	[CoL^6]	CH_2Cl_2	(2h)	e	0.93	e	10
	[CoL^7]	CH_2Cl_2	(2i)	0.91	1.19	1.31	10
	[CoL^2]	py	(2k)	0.89	1.11	1.25	13
(4a)	[CoL^3]	CH_2Cl_2	(5a)	0.78	0.97	1.24	4

[a] Conditions: (1) [or (4)] (10 mmol), cobalt(II) complex (1 mmol), solvent (80 cm³); 5 °C; P_{O_2} 780 mmHg. [b] Synthesized by method A (see Experimental section). [c] Determined by iodometry of the corresponding hydroperoxides obtained by filtration of the oxygenated mixture through a short column of silica gel (runs in CH_2Cl_2 and thf) or extraction from acidified mixtures (runs in dmf and py) after 1 h in which O_2 uptake was complete. Selectivity: 100% as judged by t.l.c. [d] Half-conversion time obtained from time course of O_2 uptake. [e] Not determined due to difficulty in removal of the metal complex, but O_2 uptake : (2h) should be around 2 : 1.

species, $Co^{III}(OH)$, and O_2 [equation (iii)].* Further oxygenation of (1) [or (4)] with $Co^{III}(OH)$ [equation (iv)]

$$Co^{III}(OOH) \longrightarrow Co^{III}(OH) + \tfrac{1}{2}\,O_2 \qquad \text{(iii)}$$

gives the stoicheiometry (ii). In fact, the oxygenation of (1d) and (4a) in the presence of an equimolar amount of

$$\text{(1) [or (4)]} + Co^{III}(OH) + O_2 \longrightarrow \text{(2) [or (5)]} + H_2O \qquad \text{(iv)}$$

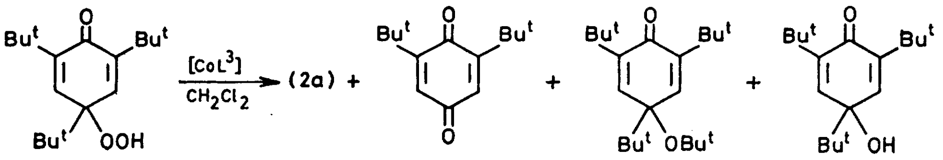
[$Co^{III}(OH)L^3$] in CH_2Cl_2 gave (2d) and (5a) in quantitative yield respectively. Furthermore, when the reaction with [CoL^4] or [CoL^5], which gave the stoicheiometry (i) in a short reaction time, was allowed to continue for several hours the stoicheiometry changed from (i) to (ii) due to the slow decomposition of the $Co^{III}(OOH)$ species.

DISCUSSION

In general, autoxidation of carbon compounds with cobalt(II) species involves redox of the hydroperoxide products and of the Co^{II}–Co^{III} system.[17] If the autoxidation mechanism (see equation below) is operative in the

$$2\ ROOH \xrightarrow{Co^{II}\text{–}Co^{III}} RO\cdot + ROO\cdot + H_2O$$

present oxygenation, the resulting mixture should include products resulting from the reaction of hydroperoxide (3) [or (6)] and the cobalt(II) complex. Thus, the reaction of (3a) and [CoL^3] was examined and found to afford (2a) (30%), 2,6-di-t-butyl-*p*-benzoquinone (7) (32%), 4-t-butoxy-2,4,6-tri-t-butylcyclohexa-2,5-dienone (8) (32%), and 2,4,6-tri-t-butyl-*p*-quinol (9) (6%). The products (7)—(9) were ones resulting from further reactions of the quinoxy-radical primarily formed by one-electron reduction of (3a) by [CoL^3], and (2a) resulted from a neutralization reaction between [$Co^{III}(OH)L^3$], thus formed, and (3a). In fact, the reaction of (3a) with [$Co^{III}(OH)L^3$] separately prepared gave (2a) quantitatively (see below). It is therefore concluded that hydroperoxide (3a) can be reduced by [CoL^3] but not oxidized by the [$Co^{III}L^3$]$^+$ species. In any run of the present oxygenation, no products derived from one-electron reduction of hydroperoxide (3) [or (6)] by the cobalt(II) species were found. Therefore, a novel mechanism other than the usual autoxidation process must be operative in the present regioselective peroxyquinolatocobalt(III) complex formation.



(3a) (7) (8) (9)

Since phenols (1) and (4) are quite stable in the presence of dioxygen without a catalyst, the present oxygenation obviously requires the activation of dioxygen by [CoL^3] and its derivatives. The activation results from the reversible formation of the superoxo-complex (CoO_2) or the μ-peroxo-complex (Co_2O_2). These species are therefore included in an aerated solution of the cobalt(II)–Schiff-base complex,[18,19] in which CoO_2 can actually be detected by e.s.r. spectroscopy even at room temperature.[1c] The concentration of CoO_2 is dependent on the nature of the solvent used and the ligand in the cobalt(II) complex. A higher concentration was obtained in dmf and pyridine and a lower concentration in methanol and CH_2Cl_2 as judged from the magnitude of the e.s.r. signals. The complex [CoL^3] gave the highest concentration of CoO_2 among its derivatives while [CoL^7] gave the least, reflecting a substitution effect. The μ-peroxo-complex (Co_2O_2) may not be the

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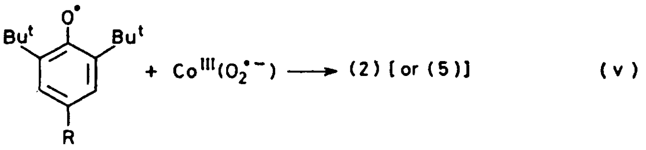
* Such a decomposition of $Co^{III}(OOH)$ has been reported with [$Co(CN)_5(OOH)$]$^{3-}$: G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discuss. Faraday Soc.*, 1968, **46**, 110.

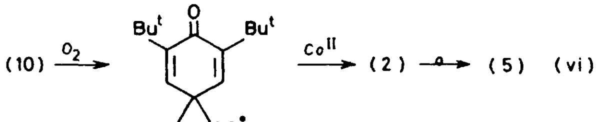
reactive species in the dioxygen incorporation into the phenols, because the interaction of this species with the phenols is sterically hindered as judged by a molecular model. Thus, CoO_2 is reasonably considered to initiate the reaction.

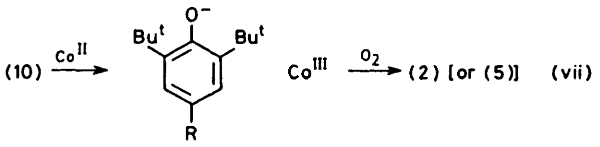
As the superoxo-species possesses radical and anionic natures, two initiation processes are theoretically possible: (*a*) hydrogen abstraction from the phenol by CoO_2 and (*b*) proton transfer from the phenol to CoO_2. The following facts seem to suggest that process (*b*) is favoured. Phenolate anions of (1) and (4) undergo oxygenation to give hydroperoxides (3) and (6) with the same regioselectivity as that observed in the present oxygenation,[20] and $[\mathrm{Co(CN)_5(O_2)}]^{3-}$, a stable superoxo-complex irreversibly formed, acts as a base toward phenols (1) allowing the stoicheiometric formation of hydroperoxides (3) under a dioxygen atmosphere.[21] On the other hand, the oxygenation of $[\mathrm{CoL^2}]$ in pyridine leads to complete formation of $[\mathrm{Co^{III}(O_2{}^{\bullet-})L^2(py)}]$ (a_{Co} = 12.8 G*)[4] whereas the concentration of $[\mathrm{Co^{III}(O_2{}^{\bullet-})L^3}]$ (a_{Co} = 13.5 G) formed in the oxygenation of $[\mathrm{CoL^3}]$ in solution is estimated to be less than 10% as judged by O_2-uptake and e.s.r. measurements. The hyperfine splitting constant, a_{Co}, reflects the basicity of $O_2{}^{\bullet-}$ in the CoO_2 complex. Thus, the CoO_2 complex from $[\mathrm{CoL^2(py)}]$ is more basic than that from $[\mathrm{CoL^3}]$. However, the apparent rate of the oxygenation of (1) with $[\mathrm{CoL^3}]$ was nearly the same as that with $[\mathrm{CoL^2(py)}]$, although the same mechanism should be operative in the oxygenation with these complexes. Furthermore, the rate of the oxygenation of (1) with $[\mathrm{CoL^3}]$ was only slightly affected by the polarity of the solvent (Table 4). These results exclude the proton-transfer mechanism (*b*). It is therefore considered reasonable that the dioxygen incorporation into the phenol is initiated by a process involving hydrogen abstraction by CoO_2 from the phenol which affords the corresponding phenoxy-radical and $\mathrm{Co^{III}(OOH^-)}$. In fact, when a small amount of (1a) was added to a solution of $[\mathrm{CoL^3}]$ in CH_2Cl_2 containing CoO_2 in the presence of dioxygen, the signal of CoO_2 was diminished with simultaneous appearance of a signal attributed to the phenoxy-radical of (1a). Upon bubbling dioxygen through the resulting solution, the signal of the phenoxy-radical disappeared and that of the CoO_2 complex reappeared. This e.s.r. observation could be repeated several times, and (2a) was obtained from the final solution.[1a,c] Similar results were also obtained with (4a) and $[\mathrm{CoL^3}]$ in CH_2Cl_2.

For the formation of peroxyquinolatocobalt(III) complexes (2) and (5) from the phenoxy-radicals (10), there are three possible mechanisms: (v) direct combination of (10) and CoO_2; (vi) combination of (10) with dioxygen followed by complexation by the cobalt(II) species, where phenoxy-radicals (10) combine with dioxygen predominantly at the *para* position, so the formation of (5) should involve the migration of the peroxy-group in a peroxyquinolato-complex of type (2) formed as an intermediate; and (vii) reduction of (10) by the cobalt(II) species to the corresponding phenolatocobalt(III) complex into which dioxygen is incorporated. The e.s.r. observations seem to suggest that the formation of the peroxyquinolatocobalt(III) complex results from a radical combination between (10) and CoO_2 [mechanism (v)]. However, this does not explain the regioselectivity in the formation of (2) and (5) from (1) and (4) respectively, since the superoxo-complex $[\mathrm{Co(CN)_5(O_2)}]^{3-}$ can combine directly with (10; R = $\mathrm{Bu^t}$), with no regioselectivity, giving rise to a mixture of (2; R = $\mathrm{Bu^t}$) and (5; R = $\mathrm{Bu^t}$). Furthermore, in the reaction of this superoxo-complex with (10; R = C_6H_4-OMe-4) at −70 °C, only (2) but no (5) (R = C_6H_4OMe-4) was formed, and at 0 °C only electron transfer took place from the superoxo-complex to the phenoxy-radical.[1c,22] These results are incompatible with the present regioselective peroxyquinolatocobalt(III) complex formation, thus excluding the mechanism (v).



(10)





(11)

Mechanism (vi) can also be excluded on the basis of kinetic observations that the combination of (10; R = C_6H_4OMe-4) with dioxygen was very slow ($k_{\mathrm{obs.}}$ = $3.5 \times 10^{-4}\ \mathrm{s^{-1}}$, 5 °C), which is not consistent with the rate observed for the formation of (5a) from (4a) ($k_{\mathrm{obs.}}$ = $3.3 \times 10^{-3}\ \mathrm{s^{-1}}$, 5 °C).* Therefore, mechanism (vii) involving the reduction of (10) by the cobalt(II) species to a phenolate intermediate is the most probable. It was found that phenoxy-radicals (10) (R = $\mathrm{Bu^t}$ or C_6H_4-OMe-4) were rapidly reduced by the $[\mathrm{CoL^3}]$ derivatives to the corresponding phenolate species (11) when the

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* Throughout this paper: 1 G = 10^{-4} T; 1 mmHg ≈ 13.6 × 9.8 Pa.

* In the reaction of (10; R = C_6H_4OMe-4) with O_2, the coupling between the radical and O_2 should be rate determining since no other radicals besides (10) were observable (e.s.r.). The rate constant was determined under the following conditions: a solution of (10; R = C_6H_4OMe-4) (20 mmol $\mathrm{dm^{-3}}$) in CH_2Cl_2 (100 $\mathrm{cm^3}$ containing 5% C_6H_6) was oxygenated (P_{O_2}, 780 mmHg). Decrease of (10) was determined by iodometry. The rate constant for the formation of (5a) from (4a) was determined by O_2 uptake at a constant O_2 pressure (780 mmHg) in CH_2Cl_2. Considering the concentration of (10) (estimated below 1 mmol $\mathrm{dm^{-3}}$) under the reaction conditions, the apparent rate of this reaction is at least 200-fold larger than that of the reaction of (10) with O_2.

complex was in excess, and subsequent dioxygen bubbling through the resulting solution led to the quantitative regioselective formation of the peroxyquinolatocobalt(III) complex. Figure 3 shows the time span of the reduction of (10; R = Bu^t) with 3 equivalents of [CoL^4] followed by dioxygen incorporation. Under the conditions for the oxygenation of (1) with [CoL^4], since the concentration of (10) is less than 1% of the [CoL^4] employed (see below), the rate of the reduction should become much faster than that shown in Figure 3.

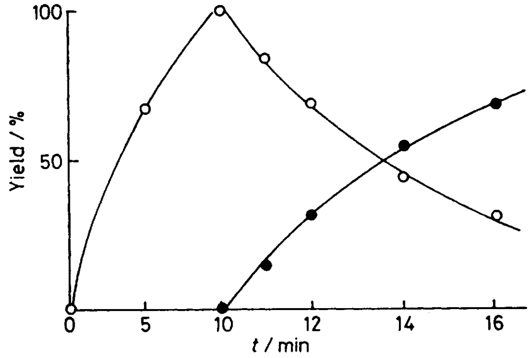

FIGURE 3 Reduction of (10; R = Bu^t) with [CoL^4] (10 min under N_2) followed by oxygenation (P_{O_2} 780 mmHg). [(10)] = 1.7 × 10^{-2} mol dm^{-3}, [Co] = 5.1 × 10^{-2} mol dm^{-3}; in CH_2Cl_2–C_6H_6 (2 : 1) (30 cm^3). (○), (1a); (●), (2e). Product determination: an aliquot (5 cm^3) was taken up at intervals and filtered through a silica gel column (3 g). The resulting (3a) and unreacted (1a) were determined by ^{1}H n.m.r. spectroscopy

The rate of formation of (2) [or (5)] depended on the concentration of the phenol. The reaction with a tenfold excess of (1d) followed pseudo-first-order kinetics with respect to [CoL^4] up to more than 90% conversion with a rate constant of 7.8 × 10^{-4} s^{-1} at 5 °C.

These results are rationalized by the following reaction mechanism, equations (1)—(6), involving rate-determining step (2). From reactions (1), (2), (4), and (6), the

$$\mathrm{Co^{II}} + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CoO_2}\ [\mathrm{Co^{III}}(\mathrm{O_2}^{\bullet-})] \qquad (1)$$

$$\mathrm{CoO_2} + (1)\ [\text{or } (4)] \xrightarrow{k_2} \mathrm{Co^{III}(OOH)} + (10) \qquad (2)$$

$$\mathrm{Co^{III}(OOH)} \xrightarrow{k_3} \mathrm{Co^{III}(OH)} + \tfrac{1}{2}\,\mathrm{O_2} \qquad (3)$$

$$(10) + \mathrm{Co^{II}} \xrightarrow{\text{fast}} (11) \qquad (4)$$

$$(1)\ [\text{or } (4)] + \mathrm{Co^{III}(OH)} \xrightarrow{\text{fast}} (11) + \mathrm{H_2O} \qquad (5)$$

$$(11) + \mathrm{O_2} \xrightarrow{k_6} (2)\ [\text{or } (5)] \qquad (6)$$

stoicheiometry (i) is obtained and from (1)—(6), the stoicheiometry (ii). Since the concentration of CoO_2 from [CoL^4] in CH_2Cl_2 is estimated to be less than 1% as judged from O_2 uptake (*ca.* 1%), a steady-state approximation is applicable for reactions (1) and (2). An assumption that step (2) is a fast reaction is inconsistent with the O_2 uptake curve (Figure 2). Reaction (3) is negligible with [CoL^4] (see above). Therefore, under conditions of excess of phenol, the kinetic law (7) can be derived. Therefore, a plot of $k_{\text{obs.}}$ against $k_{\text{obs.}}$/[phenol]

$$\text{Rate} = k_{\text{obs.}}[\mathrm{Co^{II}}] = \frac{k_1 k_2[\mathrm{O_2}][\mathrm{Co^{II}}][\text{Phenol}]}{k_{-1} + k_2[\text{Phenol}]} \qquad (7)$$

$$\text{where } k_{\text{obs.}} = \frac{k_1' k_2[\text{Phenol}]}{k_{-1} + k_2[\text{Phenol}]} = k_1' - \frac{k_{-1}k_{\text{obs.}}}{k_2[\text{Phenol}]}$$

$$k_1' = k_1[\mathrm{O_2}]$$

at different phenol concentrations should give a straight line; this is obtained (Figure 4). From the intercept, k_1' is estimated as 9.95 × 10^{-4} s^{-1} and from the slope, k_{-1}/k_2 as 3.59 × 10^{-2} mol dm^{-3}.

Phenolate species formed in reactions (4) and (5) should not be in a free state but in a co-ordinated form (11), since the oxygenation of free phenolate anions gives only epoxy-*p*-quinols and the free anions of (4) are quite stable in the presence of dioxygen. These free anions are formed in dmf. The phenolate anions of (4) are oxygenated to give *o*-hydroperoxides (6) only when they are associated with metal ions.[20,23] No significant information about the structure of (11) is available, although a π complex may be suggested from the results of the base-catalysed reaction of hydroperoxides (3) and (6),[23] and those of the reaction of [Co(CN)$_5$(O$_2$)]$^{3-}$ with (10).[22]

A rate constant, k_6, for (11) derived from (10; R = Bu^t) and [CoL^4], was estimated as *ca.* 3.35 × 10^{-3} s^{-1} under the conditions shown in Figure 3, which is about 23 times larger than the rate constant for dioxygen incorporation into free phenolate anions.[13] Since dioxygen incorporation into free phenolate anions has been shown to be a reversible process where the equilibrium is strongly shifted towards the phenolate species,[23] the apparent acceleration of dioxygen incorporation into (11) may be due to stabilization of the resulting peroxyquinolate anion by co-ordination with the cobalt(III) species. Thus, reaction (6) becomes irreversible as observed. Formation of stable cobalt(III) complexes with organic peroxides has also been known in the oxygenation of alkylcobaloximes.[24,25]

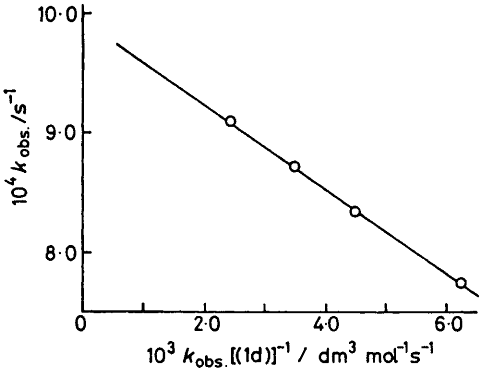

FIGURE 4 Plot of $k_{\text{obs.}}$ *vs.* $k_{\text{obs.}}$/[(1d)] in the reaction with [CoL^4]

Methylation of the NH group and introduction of an electron-withdrawing group into the aromatic ring of the Schiff-base ligand in [CoL^3] lead to a decrease in affinity toward dioxygen binding,[19] in accord with the general argument that dioxygen complex formation is subject to steric hindrance and influenced by the electron density of the co-ordinated metal ion.[4c] It was therefore suspected that peroxyquinolatocobalt(III) complex formation may be influenced by the nature of the ligand in the $[CoL^3]$ derivatives. However, the reaction rate was only slightly affected by the nature of the $[CoL^3]$ derivatives (Table 4). This may be rationalized by assuming that the ease of formation of CoO_2 is inversely proportional to its ability to abstract hydrogen atoms from phenols (1) [or (4)]. This assumption is supported by the fact that $[Co(CN)_5(O_2)]^{3-}$, a stable superoxo-complex irreversibly formed, cannot abstract hydrogen from the phenols.[21] The substitution effect appeared in the O_2-uptake stoicheiometry, which depended on the stability of $Co^{III}(OOH)$. It was observed that hydrogen peroxide was decomposed rapidly by a catalytic amount of $[CoL^3]$ in CH_2Cl_2 at 0 °C with vigorous evolution of O_2, whereas the decomposition by $[CoL^4]$ was very slow. These results also suggest that $[Co^{III}(OOH)L^3]$ is quite unstable whereas $[Co^{III}(OOH)L^4]$ is very stable. No clear explanation is available for the substitution effect of $[CoL^3]$ derivatives on the stability of $Co^{III}(OOH)$, although steric and electronic effects may be implicated. No significant solvent effect on the reaction rate was observed except in thf (Table 4). The reason why the reaction in thf is faster than that in other solvents is not clear. The reaction in methanol, where the peroxyquinolatocobalt(III) complex (2) [or (5)] was also quantitatively formed at 0 °C, was extremely slow. This suggests that hydrogen bonding between the hydroxy-group in (1) [or (4)] and CoO_2 is required for reaction (2) (hydrogen abstraction from the phenols). Solvation of CoO_2 in methanol through hydrogen bonding must hinder the interaction between CoO_2 and the substrate.

It was noted that the reactivity of $[CoL^3]$ in the formation of (2) strongly depended on its mode of synthesis. For example, apparent O_2 uptake in the formation of (2) with $[CoL^3]$ prepared by method B (see Experimental section) was faster ($t_{\frac{1}{2}}$ 6 min, 5 °C) than that with $[CoL^3]$ prepared by method A. This corresponds to the fact that in CH_2Cl_2, $[CoL_3]$ from method A absorbs dioxygen slowly with inactivation to some extent, whereas with $[CoL^3]$ from method B nearly 0.5 mol of dioxygen were taken up rapidly to form fairly stable dioxygen complexes. This remarkable difference may be rationalized by assuming that a different mode of synthesis of $[CoL^3]$ results in a different conformation of the Schiff-base ligand, as inferred from the results of X-ray analyses of the μ-peroxo-complex from $[CoL^3]$ prepared by method B,[12] and (2a) from $[CoL^3]$ prepared by method A. When $[CoL^3]$, regardless of the synthetic method, was crystallized from aqueous methanol, it did not absorb dioxygen and gave a low yield of (2). Details of these problems are currently being investigated.

EXPERIMENTAL

All melting points are uncorrected. Elemental analyses were performed by the Analytical Centre of the Pharmaceutical Department, Kyoto University. Infrared spectra were recorded on a Jasco IRA-1 spectrophotometer, ^1H n.m.r. spectra on a Varian T-60 spectrometer.

Starting Phenols.—Phenols (1), except for (1a) and (1d), were synthesized according to the method published by Rieker and Scheffler [26] and purified by repeated recrystallization from methanol.

Single-crystal X-*Ray Data of Peroxy*-p-*quinolatocobalt*(III)-L^3 (2a).—$C_{38}H_{52}CoN_3O_5$, $M = 689.8$, Orthorhombic, $a = 33.749(11)$, $b = 11.844(5)$, $c = 9.329(4)$ Å, $U = 3\,729$ Å^3, $D_m = 1.22$, $Z = 4$, $D_c = 1.229$ g cm^{-3}, $F(000) = 1\,460$, μ(Mo-K_α) = 5.24 cm^{-1}, space group $P2_12_12_1$ (D_2^4) from systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd.

The unit-cell dimensions and estimated standard deviations were determined by 2θ measurements of 12 carefully centred reflections, using a computer-controlled Philips PW1100 X-ray diffractometer, and refined by the method of least squares. A crystal of size 0.52 × 0.30 × 0.11 mm was mounted on a Philips PW1100 computer-controlled diffractometer operating with Mo-K_α radiation ($\lambda = 0.710\,7$ Å), filtered by a graphite monochromator. Integrated intensities were measured in the ω—2θ scan mode out to $2\theta = 46°$ for which the scan range was $0.9 + 0.3 \tan \theta$ and the scan rate was 2° min^{-1}. Background radiation was measured for one-half of the scan time on either side of the peak. Three reference reflections monitored every 180 min displayed neither systematic nor significant deviations from their initial intensities. Of the 3 018 reflections surveyed, 1 719 (57%) were judged observed $[I > 3\sigma(I)]$. The data were corrected for Lorentz and polarization effects but not for absorption.

The position of the Co atom was located by direct methods (MULTAN). Phases derived from the Co position were used to locate all other non-hydrogen atoms. The structure was refined by block-diagonal least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$; the weights were assigned as $w = 1.0/\sigma(F_o)^2$. Values of R and R' were 0.097 and 0.099 after three cycles of isotropic least-squares refinement. Six cycles of anisotropic least-squares refinement resulted in convergence with $R = 0.067$ and $R' = 0.072$.* Neutral atomic scattering factors [27] were used for all atoms. Fractional co-ordinates are listed in Table 5. Observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. SUP 23055 (8 pp.).†

Cobalt(II)-*Schiff-base Complexes*.—The $[CoL^3]$ and $[CoL^1]$ derivatives were synthesized by method A because it afforded good crystals; $[CoL^3]$ and $[CoL^4]$ were also synthesized by method B for comparison.

Method A. A reported method [28] involving reaction of bis(salicylaldehydato)cobalt(II) derivatives with diamines was modified. A typical run for $[CoL^3]$ is described. To a suspension of bis(salicylaldehydato)cobalt(II) dihydrate (16.9 g, 50 mmol), prepared from the reaction of Co-$[O_2CMe]_2 \cdot 2H_2O$ with a stoicheiometric amount of salicylaldehyde and alkali, in MeOH (500 cm^3) was added bis(3-aminopropyl)amine (6.6 g, 50 mmol) under nitrogen. The

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* All the calculations were performed on a FACOM 230/60 computer at the Computer Centre of Osaka City University. The principal programs used were: MULTAN–76, G. Germain, P. Main, and M. M. Woolfson; direct methods and the fast Fourier transforms, University of York, 1976; UNICS, The Universal Crystallographic Society of Japan, 1976.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 5

Positional parameters ($\times 10^4$) of (2a) with estimated standard deviations in parentheses

Atom	x	y	z
Co	5 996(1)	4 724(1)	6 462(2)
C(1)	6 749(4)	8 808(10)	5 795(15)
C(2)	7 025(4)	8 062(9)	6 647(15)
C(3)	7 064(4)	6 987(10)	6 278(15)
C(4)	6 847(4)	6 493(9)	4 982(13)
C(5)	6 482(4)	7 181(10)	4 529(13)
C(6)	6 450(4)	8 283(10)	4 872(13)
C(7)	6 105(4)	8 979(12)	4 331(16)
C(8)	7 238(5)	8 573(12)	7 970(16)
C(9)	7 152(4)	6 338(10)	3 636(16)
C(10)	5 781(4)	8 204(11)	3 606(22)
C(11)	5 890(5)	9 624(16)	5 593(19)
C(12)	6 251(5)	9 837(12)	3 202(16)
C(13)	6 915(6)	9 130(15)	8 945(17)
C(14)	7 538(5)	9 488(14)	7 526(20)
C(15)	7 462(5)	7 667(12)	8 848(16)
C(16)	7 301(4)	7 492(12)	3 178(15)
C(17)	7 504(4)	5 578(12)	4 121(15)
C(18)	6 921(5)	5 717(14)	2 453(17)
C(19)	5 695(3)	4 776(11)	3 643(16)
C(20)	5 416(4)	5 274(14)	2 753(15)
C(21)	5 239(4)	4 669(16)	1 554(20)
C(22)	5 358(5)	3 524(15)	1 401(22)
C(23)	5 637(5)	2 977(16)	2 250(19)
C(24)	5 801(4)	3 618(12)	3 456(20)
C(25)	6 104(4)	3 064(12)	4 293(16)
C(26)	6 555(4)	2 788(12)	6 217(23)
C(27)	6 443(8)	2 386(17)	7 710(22)
C(28)	6 316(8)	3 164(17)	8 808(23)
C(29)	6 278(5)	5 035(15)	9 456(16)
C(30)	6 071(6)	6 134(15)	9 641(17)
C(31)	5 994(5)	6 786(11)	8 242(15)
C(32)	5 375(4)	6 281(13)	7 218(15)
C(33)	5 079(4)	5 550(10)	6 465(17)
C(34)	4 719(4)	6 045(13)	6 223(18)
C(35)	4 415(4)	5 378(15)	5 536(17)
C(36)	4 503(4)	4 247(14)	5 121(16)
C(37)	4 867(4)	3 757(13)	5 461(16)
C(38)	5 160(3)	4 404(10)	6 190(16)
N(1)	6 224(3)	3 414(9)	5 507(13)
N(2)	6 092(3)	4 183(9)	8 524(15)
N(3)	5 743(3)	6 031(8)	7 332(11)
O(1)	6 782(3)	9 847(8)	5 834(11)
O(2)	6 732(2)	5 361(7)	5 281(9)
O(3)	6 486(2)	5 422(7)	6 613(9)
O(4)	5 845(2)	5 363(7)	4 682(8)
O(5)	5 501(2)	3 910(7)	6 531(11)

resulting solution was refluxed for 30 min, concentrated *in vacuo* to *ca.* 150 cm³, and allowed to stand at room temperature to give long green prisms, which were collected by suction, washed with cold methanol, and dried in a vacuum desiccator. All other [CoL³] derivatives were obtained as greenish brown prisms. The complexes were recrystallized from methanol if necessary, but normally used without further purification. The following data were obtained: [CoL³], yield 76% (Found: C, 57.2; H, 6.50; Co, 12.55; N, 9.25. $C_{20}H_{23}CoN_3$·2CH_3OH requires C, 57.4; H, 6.80; Co, 12.8; N, 9.15%); [CoL⁴], yield 74% (Found: C, 61.15; H, 6.25; Co, 12.45; N, 10.25. $C_{21}H_{25}CoN_3O_2$ requires C, 61.45; H, 6.15; Co, 14.35; N, 10.25%); [CoL⁵], yield 75% (Found: C, 58.6; H, 6.35; Co, 12.25; N, 8.90. $C_{23}H_{29}CoN_3O_4$ requires C, 58.7; H, 6.20; Co, 12.55; N, 8.95%); [CoL⁶], yield 95% (Found: C, 45.7; H, 3.75; Cl, 26.0; Co, 10.75; N, 7.60. $C_{21}H_{21}Cl_4CoN_3O_2$ requires C, 46.0; H, 3.85; Cl, 25.85; Co, 10.75; N, 7.65%); [CoL⁷], yield 88% (Found: C, 50.1; H, 4.85; Co, 11.8; N, 14.25. $C_{21}H_{23}CoN_5O_6$ requires C, 50.4; H, 4.65; Co, 11.8; N, 14.0%).

Method B. This method is essentially the same as that reported by Bailes and Calvin,[29] involving complexation of bis(3-salicylideneaminopropyl)amine with Co[O_2CMe]$_2$ in aqueous MeOH solution. [CoL³], yield 69% (Found: C, 57.05; H, 6.35; Co, 13.5; N, 10.2. $C_{20}H_{23}CoN_3O_2$·1.5H_2O requires C, 56.75; H, 6.20; Co, 13.9; N, 9.90%). The complexes [CoL¹] and [CoL²] are known.[29]

Syntheses of Peroxy-p-*quinolatocobalt*(III) *Complexes* (2).—A solution of the [CoL³] derivative (10 mmol) and (1) (20 mmol) in CH_2Cl_2 (150 cm³) was stirred with oxygen bubbling at 0 °C for 2—4 h. The solution was concentrated *in vacuo* below 20 °C to *ca.* 30 cm³. Light petroleum (b.p. 40—60 °C) (80 cm³) was then added to the resulting solution which was allowed to stand in a refrigerator overnight. The resulting crystals were collected by suction, washed with a mixture of light petroleum and CH_2Cl_2 (3 : 1), and dried in a vacuum desiccator. Complexes (2a)—(2d) were synthesized by this method and obtained as yellow-green crystals. (2a), m.p. 160—161 °C, $\nu_{max.}$ (Nujol) at 3 240, 1 660, 1 635, and 1 630 cm⁻¹ (Found: C, 65.95; H, 7.45; N, 6.30. $C_{38}H_{52}CoN_3O_5$ requires C, 66.15; H, 7.60; N, 6.10%). (2b), m.p. 130—131 °C, $\nu_{max.}$ (Nujol) at 3 240, 1 665, 1 635, and 1 630 cm⁻¹ (Found: C, 65.8; H, 7.75; Co, 8.55; N, 6.40. $C_{37}H_{50}CoN_3O_5$ requires C, 65.75; H, 7.45; Co, 8.70; N, 6.20%). (2c), m.p. 110—112 °C, $\nu_{max.}$ (Nujol) at 3 240, 1 660, 1 640, and 1 630 cm⁻¹ (Found: C, 63.4; H, 7.40; Co, 8.60; N, 6.30. $C_{36}H_{48}CoN_3O_5$·H_2O requires C, 63.3; H, 7.40; Co, 8.65; N, 6.20%). (2d), m.p. 136—137 °C, $\nu_{max.}$ (Nujol) at 3 240, 1 660, 1 635, and 1 630 cm⁻¹ (Found: C, 64.0; H, 7.30; Co, 8.75; N, 6.45. $C_{35}H_{46}CoN_3O_5$·1.5H_2O requires C, 64.0; H, 7.20; Co, 8.95; N, 6.40%).

(2e). A solution of (1a) (0.262 g, 1 mmol) and [CoL⁴] (0.474 g, 1 mmol) in CH_2Cl_2 (30 cm³) was oxygenated at 0 °C. In 2 h, a 38% conversion with quantitative formation of (2e) based on the stoicheiometry [O_2 uptake : (2e) = 2 : 1] was observed by ¹H n.m.r. spectroscopy. After 15 h, conversion was 72% complete. From the mixture, (2e) was isolated as fine prisms (20 mg, 3%) by the usual work-up procedure, m.p. 130—131 °C, $\nu_{max.}$ (Nujol) at 1 660, 1 635, and 1 630 cm⁻¹ (Found: C, 66.4; H, 7.70; Co, 8.20; N, 6.10. $C_{39}H_{54}CoN_3O_5$ requires C, 66.55; H, 7.75; Co, 8.35; N, 5.95%). Further attempts to isolate (2e) in better yield were unsuccessful, probably due to contamination by [Co^{III}(OOH)L⁴], which could not be isolated either.

(2f). Synthetic conditions were the same as those for (2e). Attempts to isolate this peroxy-*p*-quinolato-complex were unsuccessful for the same reason as for (2e), although the ¹H n.m.r. spectrum of the mixture and the conversion into (3d) showed the quantitative formation of (2f).

(2g)—(2i). Dioxygen was bubbled through a solution of (1d) (0.11 g, 0.5 mmol) and the appropriate [CoL³] derivative (0.5 mmol) in CH_2Cl_2 (15 cm³) at 0 °C for 5 h. After the usual work-up, the resulting precipitates were filtered off and the filtrate was further concentrated to give yellow-green tabular crystals. (2g), m.p. 95—96 °C, $\nu_{max.}$ (Nujol) at 1 660, 1 640, and 1 630 cm⁻¹ (Found: C, 59.6; H, 7.35; Co, 6.80; N, 5.15. $C_{38}H_{52}CoN_3O_7$·2.5H_2O requires C, 59.5; H, 7.50; Co, 7.70; N, 5.50%). (2h), m.p. 103—105 °C, $\nu_{max.}$ (Nujol) at 1 655, 1 640, and 1 630 cm⁻¹ (Found: C, 50.15; H, 5.55; Co, 5.70; N, 4.65. $C_{36}H_{44}Cl_4CoN_3O_5$·3H_2O requires C, 50.65; H, 5.90; Co, 6.90; N, 4.90%). (2i), m.p. >200 °C, $\nu_{max.}$ (Nujol) at 1 660 and 1 635 cm⁻¹ (Found: C, 57.5; H, 6.25; Co, 7.65; N, 9.05. $C_{36}H_{46}CoN_5O_9$ requires C, 57.5; H, 6.15; Co, 7.85; N, 9.30%).

(2j). Dioxygen was bubbled through a solution of (1a)

(0.262 g, 1 mmol) and [CoL^2] (0.385 g, 1 mmol) in pyridine (50 cm^3) at 0 °C for 20 h. The solvent was evaporated *in vacuo* at 0 °C. The ^{1}H n.m.r. spectrum of the resulting residue showed the quantitative formation of (2j). Usual work-up, however, gave a low yield (20 mg, 2.6%) of (2j) as black prisms (Found: C, 63.15; H, 7.30; Co, 6.50; N, 5.85. $C_{36}H_{47}CoN_2O_7\cdot py\cdot H_2O$ requires C, 63.45; H, 7.00; Co, 7.60; N, 5.40%).

(2k). A mixture obtained in the reaction of (1d) with [CoL^2] in py followed by evaporation of the solvent showed nearly quantitative formation of (2k), but the compound was too unstable to isolate and decomposed under the conditions of n.m.r. measurement.

Acetic Acid Treatment of (2a).—To a solution of (2a) (0.2 g, 0.28 mmol) in CH_2Cl_2 (10 cm^3) was added acetic acid (0.02 g, 0.33 mmol) and the solvent was evaporated immediately. The ^{1}H n.m.r. spectrum of the residue showed the quantitative formation of (3a) and [Co^{III}(O$_2$CMe)L^3], which was isolated as black prisms by addition of a mixture of light petroleum and ethyl acetate (1 : 1), m.p. 198—199 °C (Found: C, 57.9; H, 5.95; N, 9.30. $C_{22}H_{26}CoN_3O_4$ requires C, 58.0; H, 5.75; N, 9.25%).

Hydroperoxides (3) *from* (2).—A solution of (2) (0.5 mmol) in CH_2Cl_2 (5 cm^3) was filtered through a short column of silica gel (5 g) followed by elution with the same solvent. Evaporation of the eluate gave (3) as crystals in quantitative yield. Hydroperoxides (3a)—(3d) thus obtained were identical with authentic samples (i.r. and ^{1}H n.m.r.).[30]

Synthesis of Peroxy-o-*quinolatocobalt*(III) *Complexes* (5).—Dioxygen was bubbled through a solution of (4) (0.5 mmol) in CH_2Cl_2 (6 cm^3) containing [CoL^3] (0.4 mmol) at 0 °C for 1 h. The mixture was concentrated (3 cm^3) to induce the precipitation of unreacted [CoL^3], which was filtered off. The filtrate was kept at -20 °C overnight to give (5) as black prisms. The yields and ^{1}H n.m.r. data of (5a)—(5h) thus obtained are given in Table 3. (5a), m.p. 131—132 °C, $\nu_{max.}$ (Nujol) at 3 190, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 66.4; H, 7.10; Co, 8.15; N, 5.65. $C_{41}H_{50}CoN_3O_6$ requires C, 65.55; H, 6.80; Co, 7.95; N, 5.70%). (5b), m.p. 123—125 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 66.45; H, 7.10; Co, 7.80; N, 5.60. $C_{41}H_{50}CoN_3O_6$ requires C, 65.55; H, 6.80; Co, 7.95; N, 5.70%). (5c), m.p. 125—127 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 66.4; H, 7.15; Co, 7.70; N, 5.60. $C_{41}H_{50}CoN_3O_6$ requires C, 66.55; H, 6.80; Co, 7.95; N, 5.70%). (5d), m.p. 131—133 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 67.85; H, 7.25; Co, 7.95; N, 5.80. $C_{41}H_{50}CoN_3O_5$ requires C, 68.0; H, 6.95; Co, 8.15; N, 5.85%). (5e), m.p. 122—124 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 63.5; H, 7.05. $C_{41}H_{50}CoN_3O_5\cdot 3H_2O$ requires C, 63.55; H, 7.25%). Percentages of N and Co were not determined. (5f), m.p. 125—126 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 67.75; H, 7.50; Co, 7.80; N, 5.50. $C_{41}H_{50}CoN_3O_5$ requires C, 68.0; H, 6.95; Co, 8.15; N, 5.85%). (5g), m.p. 118—119 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 630 cm^{-1} (Found: C, 67.15; H, 6.10; Co, 8.45; N, 6.00. $C_{40}H_{48}CoN_3O_5$ requires C, 67.65; H, 6.80; Co, 8.30; N, 5.95%). (5h), m.p. 126—127 °C, $\nu_{max.}$ (Nujol) at 3 180, 1 660, 1 640, and 1 625 cm^{-1} (Found: C, 65.25; H, 6.85; Cl, 4.40; N, 5.40. $C_{40}H_{47}ClCoN_3O_5$ requires C, 64.55; H, 6.35; Cl, 4.75; N, 5.65%). The percentage of Co was not determined.

Hydroperoxides (6) *from* (5).—A solution of (5) in CH_2Cl_2 obtained in a separate run under the same conditions as described above was filtered through a short column of silica gel (6 g) followed by elution with the same solvent. Evaporation of the eluate *in vacuo* gave crystals of (6) which were recrystallized from light petroleum to give colourless prisms. The yields and ^{1}H n.m.r. data of (6b)—(6h) thus obtained are given in Table 3. Hydroperoxide (6a) was identical with an authentic sample (m.p., i.r., and ^{1}H n.m.r.).[20] (6b), m.p. 80—82 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 73.2; H, 8.10. $C_{21}H_{28}O_4$ requires C, 73.2; H, 8.20%). (6c), m.p. 100—102 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 73.15; H, 8.35. $C_{21}H_{28}O_4$ requires C, 73.2; H, 8.20%). (6d), m.p. 105—107 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 76.7; H, 8.85. $C_{21}H_{28}O_3$ requires C, 76.8; H, 8.60%). (6e), m.p. 81—83 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 76.7; H, 8.85. $C_{21}H_{28}O_3$ requires C, 76.8; H, 8.60%). (6f), m.p. 111—113 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 76.55; H, 8.65. $C_{21}H_{28}O_3$ requires C, 76.8; H, 8.60%). (6g), m.p. 101—103 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 76.45; H, 8.30. $C_{20}H_{26}O_3$ requires C, 76.4; H, 8.35%). (6h), m.p. 105—107 °C, $\nu_{max.}$ (Nujol) at 3 360 and 1 660 cm^{-1} (Found: C, 69.15; H, 7.15; Cl, 10.25. $C_{20}H_{25}ClO_3$ requires C, 68.85; H, 7.20; Cl, 10.15%).

Stoicheiometry and Kinetics.—Oxygen-uptake measurements were performed at a constant O_2 pressure (780 mmHg) on a gas volumetric apparatus with a pressure sensor and a pressure-regulating valve synchronized automatically with O_2 consumption. The reaction was initiated by dropping a small thin glass basket containing an appropriate [CoL^3] derivative suspended in the reaction vessel over a solution of (1) [or (4)] in a prescribed solvent at constant temperature.

The consumption of (1d) and the formation of (2f) [Figure 2(*a*)] were determined in a separate run as follows. An aliquot (4 cm^3) of the reaction mixture was taken at intervals and filtered through a short column of silica gel (5 g) followed by elution with diethyl ether. The eluate was evaporated below 10 °C *in vacuo*. The amounts of (3d) thus obtained and unreacted (1d) were determined by ^{1}H n.m.r. spectroscopy employing 1,4-dibromobenzene as a reference. The determination of (1a) and (2a) [Figure 2(*b*)] was made as follows. An aliquot (1 cm^3) taken at intervals was filtered through a silica gel column (3 g), eluted with diethyl ether, and treated with an excess (2 cm^3) of Me_2S, thus converting the resulting (3a) into the corresponding *p*-quinol, 4-hydroxy-2,4,6-tri-t-butylcyclohexa-2,5-dienone, which as well as unreacted (1a) was determined by g.l.c. (SE-30, 3 m, 150 °C) employing biphenyl as a reference. The yields of (2) and (5) in Table 4 were determined as follows. When the reaction was carried out in CH_2Cl_2, an aliquot (10 cm^3), after reaction for 1 h, was filtered through a silica gel column (5 g) and eluted with diethyl ether. Hydroperoxide (3) [or (6)] in the eluate was determined by iodometry according to a published method.[31] For the reaction in thf, an aliquot (10 cm^3) was evaporated at 0 °C *in vacuo* and the residue was dissolved in CH_2Cl_2; the above procedure was then followed. In cases with other solvents (dmf, pyridine), an aliquot (10 cm^3) was acidified with acetic acid, diluted with water, and extracted with light petroleum. The product (3) was determined by the method described above.

Determination of [Co^{III}(OOH)L^4].—The reaction mixture obtained from the oxygenation of (1d) (2 mmol) with [CoL^4] (0.2 mmol) in CH_2Cl_2 (16 cm^3) at 5 °C for 1 h was evaporated *in vacuo* (below 5 °C) to *ca.* 5 cm^3, poured into cold water (90 cm^3) containing acetic acid (10 cm^3), and extracted with light petroleum (50 cm^3). Iodometric titration of the organic layer as described above showed the formation of (2d) (0.093 mmol) (46% yield based on [CoL^4] used; theoretical conversion, 92%). The aqueous layer was diluted with water (300 cm^3), extracted with CH_2Cl_2 to remove the metal species, and the H_2O_2 thus obtained was titrated by iodometry; yield 0.067 mmol {34% based on [CoL^4] used, 74% based on (2d) formed}.

[Co^{III}(OH)L^3].—To a solution of [CoL^3] (3 mmol) in CH_2Cl_2 (55 cm^3) was added H_2O_2 (6 mmol) at 0 °C under nitrogen. Immediately dark green crystals were precipitated which gradually dissolved with vigorous gas evolution. The resulting solution was dried over $Na_2[SO_4]$ and evaporated to give [Co^{III}(OH)L^3] as a black solid. Crystallization of the solid from methanol gave greenish prisms (Found: C, 56.7; H, 6.45; Co, 12.5; N, 9.40. $C_{20}H_{24}CoN_3O_3{\cdot}CH_3OH$ requires C, 56.65; H, 6.35; Co, 13.25; N, 9.45%). Yield 1.12 g (84%).

Peroxyquinolato-complex (2d) *from Reaction of* (1d) *with* [Co^{III}(OH)L^3].—Dioxygen was bubbled through a solution of (1d) (0.2 mmol) and [Co^{III}(OH)L^3] (0.2 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C for 1.5 h. The ^{1}H n.m.r. spectrum of the mixture showed the quantitative formation of (2d).

Reaction of Hydroperoxide (3a) *with* [CoL^3].—Hydroperoxide (3a) [30] (0.75 mmol) and [CoL^3] (0.5 mmol) were dissolved in CH_2Cl_2 (15 cm^3) at 0 °C under N_2, and allowed to stand at 0 °C for 40 min. The ^{1}H n.m.r. spectrum and t.l.c. of the mixture showed the formation of (2a) (30%), 2,6-di-t-butyl-*p*-benzoquinone (32%), 4-t-butoxy-2,4,6-tri-t-butylcyclohexa-2,5-dienone (8) (32%), and 2,4,6-tri-t-butyl-*p*-quinol (9) (6%). Compound (8) was isolated by t.l.c. (developed with a 1 : 1 mixture of CH_2Cl_2 and light petroleum) as pale yellow crystals, m.p. 43—45 °C, δ($CDCl_3$) 0.89 (s, 9 H), 1.17 (s, 9 H), 1.23 (s, 18 H), and 6.73 (s, 2 H) (Found: C, 79.05; H, 11.5. $C_{22}H_{38}O_2$ requires C, 79.0; H, 11.45%).

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