Dioxygen Adducts of Cobalt(II) Complexes of 6,6′-Bis(*p*-substituted benzoylamino)-2,2′-bipyridines and Their Catalytic Activities in Oxygenation of 2,6-Di-*tert*-butylphenol†

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The oxygen affinities and properties of oxygen adducts of complexes [CoL] [H_2L = 6,6′-bis(benzoylamino)-2,2′-bipyridine and its 4-methyl-, -*tert*-butyl or -chloro-benzoylamino analogues] has been studied by cyclic voltammetry and IR, electronic and ESR spectroscopy. The complexes exhibited oxygen-binding ability in the presence of an appropriate axial base ligand (B), and the oxygen adducts were of the end-on bonded $Co^{III}(O_2^-)$ type [CoL(B)(O_2)]. More complete electron transfer from the metal centre to the oxygen was indicated compared to that with [Co(salen)] [H_2salen = *N,N*′-ethylenebis(salicylideneimine)]. Electron-donating substituents gave higher concentrations of the oxygen adducts. The superior catalytic activity of these complexes, especially the Me- and Bu^t-substituted derivatives, in the oxygenation of 2,6-di-*tert*-butylphenol to the corresponding quinone is interpreted in terms of the reactivity of the co-ordinated oxygen and the oxygen affinity of the complexes.

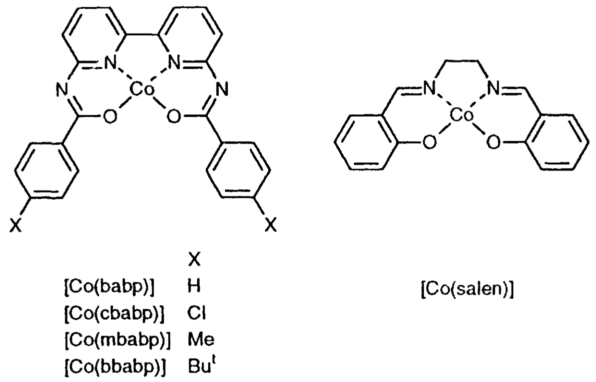
Square-planar cobalt(II) complexes are the subject of continuing studies because of their ability to form oxygen adducts and their monooxygenase-like activity in oxidation of phenols.[1] Among them, porphyrins, phthalocyanines, and Schiff-base complexes like [Co(salen)] [salen = *N,N*′-ethylenebis(salicylideneiminate)] have been studied extensively.[2–4] Recently we reported that a cobalt(II) complex of deprotonated 6,6′-bis(benzoylamino)-2,2′-bipyridine (H_2babp), [Co(babp)], served as an excellent catalyst for oxygenation of 2,6-di-*tert*-butylphenol to 2,6-di-*tert*-butyl-*p*-benzoquinone.[5] The complex has the same N_2O_2 square-planar structure as that of [Co(salen)], but the ligand has been replaced in order to give high stability under oxidative conditions. The durability and selectivity of the complex as a catalyst is much higher than that of [Co(salen)], yielding less than 1% of a dimeric by-product, 3,3′,5,5′-tetra-*tert*-butyl-4-(4-oxocyclohexa-2,5-dien-l-ylidene)cyclohexa-2,5-dien-l-one.

Though reversible formation of oxygen adducts in the presence of an appropriate base was evidenced by ESR study, the nature of the complex was not well understood. In this paper we clarify the properties of cobalt(II) complexes of H_2babp and its *p*-substituted derivatives with reference to those of [Co(salen)], and discuss their catalytic activities in oxidation of 2,6-di-*tert*-butylphenol.

Experimental

Materials.—The compound H_2babp and [Co(babp)] were prepared in a similar manner to those reported previously.[6] Solvents and other chemicals were obtained commercially, and were purified by routine methods if necessary.

Preparation of the p-*Substituted Benzoylamino Compounds.*—These were prepared according to the procedure reported for H_2babp with slight modification if necessary.[6] 6,6′-Bis(4-methylbenzoylamino)-2,2′-bipyridine (H_2mbabp): yield 68% (white plates), m.p. 308 °C (Found: C, 73.65; H, 5.25; N, 13.40. $C_{26}H_{22}N_4O_2$ requires C, 73.90; H, 5.25; N, 13.25%) IR (KBr): ν_{max} 3316s (NH), 1657vs (amide I), 1528vs (amide II) and 1254s cm^{-1} (amide III). 6,6′-Bis(4-chlorobenzoylamino)-2,2-bipyridine (H_2cbabp): yield 77% (white powder), m.p. 325 °C (Found: C, 62.45; H, 3.25; N, 11.80. $C_{24}H_{16}Cl_2N_4O_2$ requires C, 62.20; H, 3.50; N, 12.10%) IR (KBr): ν_{max} 3310s (NH), 1650vs (amide I), 1531vs (amide II) and 1258s cm^{-1} (amide III). 6,6′-Bis(4-*tert*-butylbenzoylamino)-2,2′-bipyridine (H_2bbabp): yield 86% (white powder), m.p. 273 °C (Found: C, 76.10; H, 6.60; N, 10.85. $C_{32}H_{34}N_4O_2$ requires C, 75.90; H, 6.70; N, 11.05%) IR (KBr): ν_{max} 3283s (NH), 1658vs (amide I), 1529vs (amide II) and 1257s cm^{-1} (amide III).



Scheme 1

Preparation of the Complexes.—[Co(mbabp)]. The compound H_2mbabp (42 mg, 0.1 mmol) and Co(O_2CMe)$_2$·4H_2O (25 mg, 0.1 mmol) were dissolved in methanol (15 cm^3) under a nitrogen atmosphere. After 1 h, 0.5 mol dm^{-3} ethanolic KOH solution (0.5 cm^3) was added and stirred for another hour. The solvent was evaporated to dryness and the resultant red solid was dried at 200 °C in vacuum for 8h. It was recrystallized from toluene as red needles (yield 82%), m.p. 324 °C (Found: C, 65.10; H, 3.55; N, 11.85. $C_{26}H_{20}CoN_4O_2$ requires C, 65.15; H, 4.20; N, 11.70%) IR (KBr): ν_{max} 1556s (amide I) and 1387s cm^{-1} (amide II). [Co(cbabp)]: yield 72% (red needles), m.p. 369 °C (Found: C, 55.45; H, 2.25; N, 11.25. $C_{24}H_{14}CoN_4O_2$ requires

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† *Non-SI units employed:* G = 10^{-4} T, mmHg ≈ 133 Pa.

C, 55.40; H, 2.70; N, 10.75%) IR (KBr): ν_{max} 1557s (amide I) and 1386s cm^{-1} (amide II). [Co(bbabp)]·2H_2O: yield 47% (red powder), m.p. 342 °C (Found: C, 64.30; H, 5.70; N, 9.65. $C_{32}H_{36}CoN_4O_4$ requires C, 64.10; H, 6.05; N, 9.35%) IR (KBr): ν_{max} 1554s (amide I) and 1385s cm^{-1} (amide II).

Preparation of the Oxygen Adducts.—The cobalt(II) complexes (0.01 mmol) and 4-dimethylaminopyridine (dmap; 6 mg, 0.05 mmol) were dissolved in toluene (2 cm^3). After 30 s of oxygen bubbling the solution was allowed to stand for 1 h and hexane (10 cm^3) was added. The black precipitates were collected and dried in a desiccator at room temperature.

Measurements.—Infrared spectra were measured with a JASCO IR-700 spectrophotometer, and electronic spectra with JASCO Ubest-50 and Ubest-35 spectrophotometers at 20 °C.

The ESR spectra were measured with a JEOL JES-FE3X spectrometer operated at X band. Samples under anaerobic conditions were prepared as follows. To the cobalt(II) complexes (0.01 mmol) in an ESR sample tube, were added degassed anhydrous toluene (0.4 cm^3) and pyridine (approximately 5% v/v with respect to toluene) by vacuum distillation. Then the ESR tube was melt-sealed under vacuum. The concentration of the complexes was approximately 25 mmol dm^{-3}. The ESR parameters obtained are with reference to Mn^{II} in MgO.

Cyclic voltammetry was performed in tetrabutylammonium tetrafluoroborate solution (0.1 mol dm^{-3}), with glassy carbon and platinum wire as working and counter electrodes, respectively.[7] Nitrogen gas was bubbled through the solution for 15 min prior to measurements. The scan rate was varied from 2 to 100 mV s^{-1}.

General Procedure for Oxidation of 2,6-*Di*-tert-*butylphenol.*—Oxidation of the phenol was carried out under similar conditions to those described previously.[5]

Results and Discussion

Electrochemical Properties and Oxygen Affinities of the Cobalt(II) *Complexes.*—Cyclic voltamograms of [Co(babp)] and its analogues in pyridine under a nitrogen atmosphere showed two pairs of quasireversible oxidation–reduction waves (ΔE < 90 mV) due to Co^I–Co^{II} ($E_{\frac{1}{2}} = -1.11$ to -1.28 V *vs.* saturated calomel electrode, SCE) and Co^{II}–Co^{III} ($E_{\frac{1}{2}}$ in Table 1) couples respectively. The axial base ligand has a large effect on the $E_{\frac{1}{2}}$(Co^{II}–Co^{III}), indicating that the electron is taken from the d_{z^2} orbital to form a cobalt(III) species.[9] An electron-donating Me or Bu^t group on the phenyl rings of [Co(babp)] only slightly decreases the $E_{\frac{1}{2}}$(Co^{II}–Co^{III}) which is thought to increase their oxygen affinity. In pyridine, [Co(salen)] showed irreversible waves. The $E_{\frac{1}{2}}$(Co^{II}–Co^{III}) of [Co(salen)] in dimethyl sulfoxide (dmso) is slightly lower than that of [Co(babp)],[10] suggesting a lower oxygen affinity of [Co(babp)] in dmso.[8]

The electronic spectra of [Co(cbabp)] or [Co(babp)] in the presence of an appropriate axial base at various oxygen pressures showed only modest changes. An appreciable change was observed only for [Co(mbabp)] in dimethylformamide at 20 °C in the presence of a strong base, 4-dimethylaminopyridine (dmap, pK_a = 9.7). The increase in absorbance at 500 nm was in good accord with a 1 : 1 stoichiometry, and the equilibrium constant, log K[O_2], was determined to be −2.11 mmHg^{-1} [equation (1)]. As log K[O_2] for the 1 : 1 oxygen adduct of

$$[\mathrm{Co(mbabp)(dmap)}] + \mathrm{O_2} \overset{K[\mathrm{O_2}]}{\rightleftharpoons} [\mathrm{Co(mbabp)(dmap)(O_2)}] \quad (1)$$

[Co(salen)] is not available, that of the α-methyl derivative of salen with 4-methylpyridine (pK_a = 6.0) as axial base was estimated at 20 °C from the reported thermodynamic parameters as −2.0.[11] Though direct comparison is difficult due to the different axial base, it is likely that oxygen affinity of the present complexes in the presence of an appropriate base is no better than that of the α-methyl derivatives of salen.

Table 1 Values of $E_{\frac{1}{2}}$ in V *vs.* SCE for the Co^{II}–Co^{III} couple of the cobalt complexes

Complex	Solvent	$E_{\frac{1}{2}}$/V
[Co(cbabp)]	py	−0.04
[Co(mbabp)]	py	−0.12
[Co(bbabp)]	py	−0.11
[Co(babp)]	py	−0.10
	dmap[a]	−0.41
	dmso	0.12
[Co(salen)][b]	dmso	−0.09

[a] 4-Dimethylaminopyridine (5 × 10^{-2} mol dm^{-3}) in acetonitrile. [b] Ref. 8.

Infrared Spectra of Oxygen Adducts.—Addition of hexane to an oxygenated toluene solution of [Co(babp)] in the presence of dmap yielded black precipitates, which were presumably mixtures of the oxygenated and unoxygenated complexes. The IR spectra of the precipitates in KBr pellets at room temperature showed a $\nu(O_2)$ peak characteristic of an end-on bonded monomeric Co^{III}(O_2^-) complex at 1142 cm^{-1},[12,13] which disappeared irreversibly upon heating above 130–150 °C. No absorption bands in the μ-peroxo range (790–884 cm^{-1})[1a] were observed, confirming the absence of the μ-peroxo dimer. This is a marked difference from [Co(salen)], for which substantial formation of the μ-peroxo adduct has been reported.[14] The *para* substituents on the phenyl ring had little effect on the peak position but did substantially alter the intensities of $\nu(O_2)$ of the precipitates. Thus the mbabp derivative showed a much stronger $\nu(O_2)$ absorption than did those of babp and cbabp, indicating preferential formation of the monomeric O_2^- complex for [Co(mbabp)].

The ESR Spectra of the Cobalt Complexes.—The spectra of the complexes in frozen toluene–pyridine (py) under anaerobic conditions at −196 °C showed eight-line patterns due to ^{59}Co ($I = \frac{7}{2}$) and five equivalent superhyperfine lines due to two ^{14}N nuclei [Fig. 1(*a*)], which indicates the formation of six-co-ordinate complexes (two axial pyridines).[15] The ESR parameters do not show any definite correlation with the substituent group. The spectra of oxygenated solutions of the complexes at −196 °C showed signals with much smaller A_{iso}^{Co} and $g_{\parallel} > g_{\perp}$ [Fig. 1(*b*), Table 2], which are characteristic of an end-on bonded monomeric Co^{III}(O_2^-)(py) complex.[16–18] The A_{iso}^{Co} values are smaller than those of the oxygen adducts of well known Schiff-base complexes like [Co(salen)(py)(O_2)]. The observed anisotropy, $A_{\parallel}^{Co} - A_{iso}^{Co}$, is a good measure of the residual spin density on the 3d orbital,[16,18] and the extent of electron transfer from Co^{II} to O_2 of [Co(babp)(py)(O_2)] is estimated semiquantitatively to be 0.6 based on the procedure of Drago and co-workers[18] [$2(1 - \alpha^2) - 1$, where α^2 is the fractional occupation of the d orbital]. This value is larger than that for [Co(salen)(py)(O_2)] (0.5[18a]) and the same as that (0.6[18b]) of [Co(tmpp)(py)(O_2)] [tmpp = 5,10,15,20-tetra(*p*-methoxyphenyl)porphyrinate]. The ESR parameters of the oxygen adducts of the *p*-substituted derivatives were little different from those of [Co(babp)], confirming more complete electron transfer to the co-ordinated dioxygen compared to those in [Co(salen)(py)(O_2)].

The ESR spectra of toluene solutions of the complexes in the presence of various axial bases were measured at −71 °C under aerobic conditions [Fig. 1(*c*), Table 3]. Highly basic axial ligands decrease the A_{iso}^{Co} value, while the *para* substituents on the phenyl ring only slightly affect the ESR parameters. However, the intensities of the signals were quite different from each other. Relative intensities of the signals ([Co(babp)] = 1) in pyridine at room temperature are also included in Table 3. Introduction of a more electron-donating group results in a higher signal intensity, which is a direct indication of the higher concentration of the O_2^- complex. The results are consistent with those of the IR study.

Based on the above studies, the oxygen affinity and properties of the oxygen adducts can be summarized as follows. At room temperature in the presence of appropriate axial bases, the complexes form end-on bonded monomeric $Co^{III}(O_2^-)$ adducts even in the presence of a highly basic ligand like dmap. The *para* substituents of the phenyl ring have little effect on the properties of the complexes and their oxygen adducts, but the electron-donating Me or Bu^t quantitatively increases the concentration of the O_2^- adducts. The oxygen affinities of these complexes are no better than that of [Co(salen)], but the extent of electron transfer to the co-ordinated dioxygen is higher.

Oxidation of 2,6-*Di*-tert-*butylphenol*.—Oxidations of the phenol (0.5 mol dm^{-3}) catalysed by cobalt(II) complexes (2.5 × 10^{-3} mol dm^{-3}) were carried out in pyridine, through which oxygen was bubbled in a thermostat (Table 4, Fig. 2). The reactions at 20 and 40 °C were completed within 24 h. Yields of the diphenoquinone by-product were less than 0.6 and 1.7% respectively, demonstrating high selectivity for 2,6-di-*tert*-butyl-*p*-benzoquinone. The substituent groups had little effect on the selectivity and the reaction rates, except for [Co(cbabp)] with which the reaction rate was slightly lower. Reactions catalysed by [Co(salen)] under the same conditions were not completed in 24 h, though the initial reaction rates were higher than those with the present complexes.

At 60 °C, only the reaction catalysed by [Co(bbabp)] or [Co(mbabp)] was practically completed within 24 h, suggesting that inactivation of the catalyst took place at this temperature. However, [Co(salen)] showed much poorer performance yield-

Table 2 The ESR parameters of the oxygen adducts of the complexes under aerobic conditions

Complex	$g_\perp$	$g_\parallel$	$A_\perp^{Co}$/G	$A_\parallel^{Co}$/G	A_{iso}^{Co}/G
[Co(babp)(py)(O$_2$)][a]	1.991[b]	2.071	9.1[c]	15.1	11.1
[Co(cbabp)(py)(O$_2$)][a]	1.990[b]	2.071	9.1[c]	15.2	11.2
[Co(mbabp)(py)(O$_2$)][a]	1.991[b]	2.071	9.1[c]	15.3	11.2
[Co(bbabp)(py)(O$_2$)][a]	1.990[b]	2.071	9.0[c]	15.4	11.1
[Co(salen)(py)(O$_2$)][d]	1.997[b]	2.079	10.2[c]	17.7	12.7
[Co(salen)(py)(O$_2$)][e]	1.997	2.080	10.4	17.9	12.9

[a] In 0.4% v/v pyridine–toluene. [b] Calculated from $g_{iso} = \frac{1}{3}(g_\perp + 2g_\parallel)$. [c] Calculated from $A_{iso}^{Co} = \frac{1}{3}(A_\perp^{Co} + 2A_\parallel^{Co})$. [d] This work, in 5% v/v pyridine–toluene. [e] Ref. 16.

Table 3 The ESR parameters of the oxygen adducts of the complexes under aerobic conditions at −71 °C

	Axial base ligand (pK_a)					
	py(5.2)[a]		4Me-py(6.0)[b]		dmap(9.7)[c]	
Complex	A_{iso}^{Co}/G	g_{iso}	A_{iso}^{Co}/G	g_{iso}	A_{iso}^{Co}/G	g_{iso}
[Co(babp)]	11.1 (≡1)[d]	2.018	10.9	2.019	10.6	2.020
[Co(cbabp)]	11.2 (0.78)[d]	2.017	10.8	2.018	10.7[e]	2.023[e]
[Co(mbabp)]	11.2 (2.76)[d]	2.018	10.9	2.019	10.7	2.020
[Co(bbabp)]	11.1 (2.75)[d]	2.017	—		—	
[Co(salen)]	12.7[f] (6.08)[d]		—		—	

[a] 0.4% v/v. [b] 0.1 mol dm^{-3}. [c] 0.01 mol dm^{-3}. [d] Relative intensity of the signal in pyridine at room temperature. [e] Measured in dimethylformamide because of the formation of a black precipitate in toluene solution. [f] In 5% v/v pyridine–toluene, see text.

Table 4 Oxidation of 2,6-di-*tert*-butylphenol catalysed by cobalt(II) complexes

Complex	T/°C	Phenol conversion (%)	Quinone yield (%)	By-product: quinone molar ratio
[Co(babp)]	20	100	99	<0.01 : 1
	40	100	97	0.02 : 1
	60	83	67	0.11 : 1
[Co(cbabp)]	20	100	99	<0.01 : 1
	40	100	98	0.01 : 1
	60	71	56	0.14 : 1
[Co(mbabp)]	20	100	99	<0.01 : 1
	40	100	97	0.01 : 1
	60	97	87	0.06 : 1
[Co(bbabp)]	20	100	100	<0.01 : 1
	60	100	90	0.06 : 1
[Co(salen)]	20	83	78	0.03 : 1
	40	50	47	0.11 : 1
	60	50	29	0.37 : 1

0.5 mol dm^{-3} Substrate, 2.5 × 10^{-3} mol dm^{-3} catalyst.

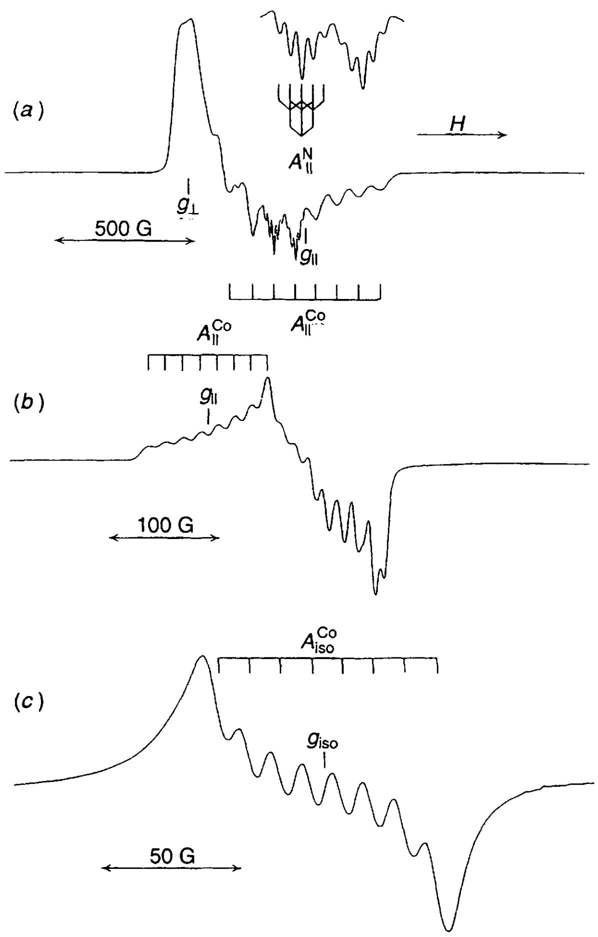


Fig. 1 The ESR spectra of [Co(mbabp)] in toluene-pyridine: (*a*) under anaerobic conditions at −196 °C {$g_\perp$ 2.31, $g_\parallel$ 2.032, $A_\parallel{}^{Co}$ 77.4 G, and $A_\parallel{}^{N}$ 14.0 G for [Co(mbabp)(py)$_2$]}, (*b*) under oxygenated conditions at −196 °C (ESR parameters in Table 2), and (*c*) under aerobic conditions at −71 °C

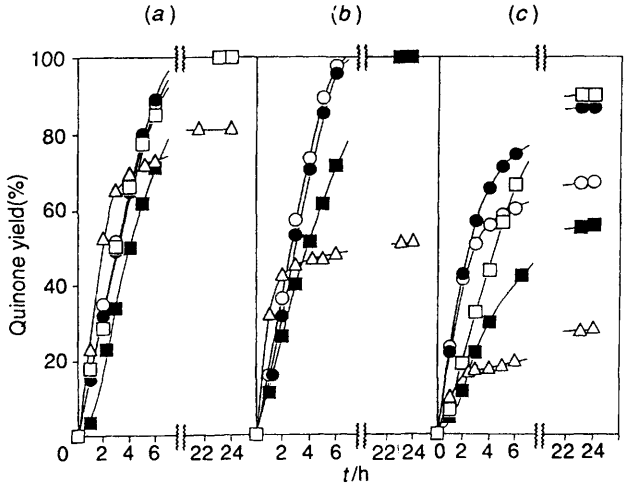


Fig. 2 Oxidation reactions catalysed by cobalt(II) complexes. Substrate: 0.5 mol dm^{-3}. Catalyst: 2.5 × 10^{-3} mol dm^{-3}. Temperature: (*a*) 20, (*b*) 40 and (*c*) 60 °C. Complexes: (○) [Co(babp)], (●) [Co(mbabp)], (□) [Co(bbabp)], (■) [Co(cbabp)] and (△) [Co(salen)]

ing only 29% of the quinone. Thus, it is demonstrated that the present complexes are superior catalysts for the oxidation of the phenol. Their high durability can be understood from the high thermal stability of the ligand moieties.[5]

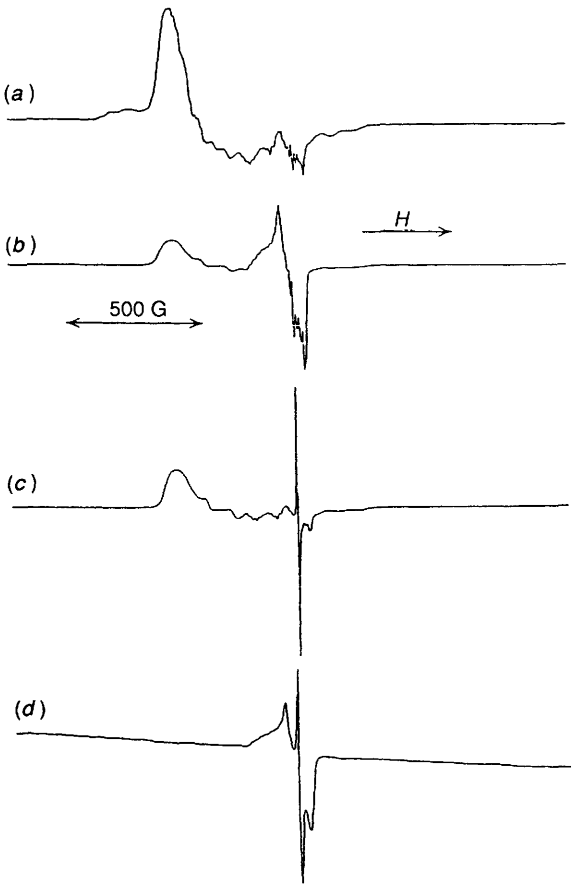
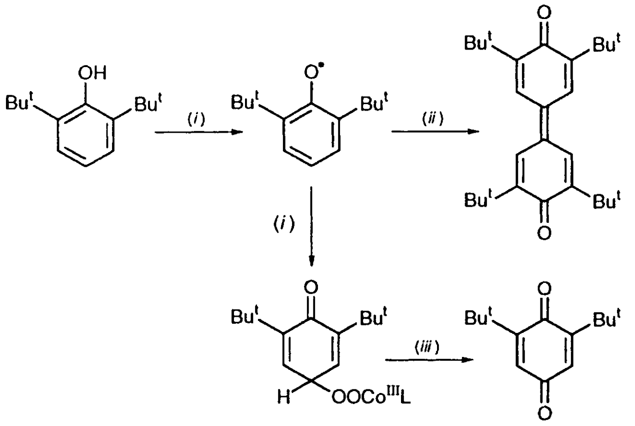


Fig. 3 The ESR spectra of the reaction mixture after 1 h at −196 °C. The reaction was catalysed by [Co(babp)] at (*a*) 20, (*b*) 40 and (*c*) 60 °C and by [Co(salen)] at 40 °C (*d*)

We also measured the ESR spectra of the reaction mixtures. Aliquots (0.4 cm^3) of the samples were withdrawn after 1 h of reaction and immediately frozen in liquid nitrogen (Fig. 3). The ESR spectra of the [Co(babp)]-catalysed reaction mixture exhibited mainly three signals, assigned to the $O_2{}^-$ adduct, phenoxy radicals (g = 2.004), and a six-co-ordinate complex [Co(babp)(py)$_2$]. The proportions of these species vary considerably with the reaction temperature. Therefore, the spectra can be used as an indication of the steady-state composition of the reaction mixture, though it may not be an exact reflection because of a possible change during the freezing process. The spectrum of the [Co(salen)]-catalysed solution at 40 °C, where the selectivity for the quinone was markedly decreased, showed signals due to phenoxy radicals and the $O_2{}^-$ adduct, and the intensity of the phenoxy signal was higher than that obtained with [Co(babp)]. According to the proposed mechanism of the reaction,[4] attack of another $O_2{}^-$ adduct on the phenoxy radical leads to the formation of quinone, while the diphenoquinone by-product is formed by coupling of the phenoxy radicals (Scheme 2). Therefore, the results are nicely explained by the high selectivity of the [Co(babp)] towards the quinone. The lower phenoxy radical concentration might be due in part to the higher reactivity of the $O_2{}^-$ adduct which is evidenced by the greater electron transfer.

Among the present complexes, those having electron-donating groups show better catalyst performance. This was particularly evident when the reaction was carried out at 60 °C. The ESR spectrum of the reaction mixture catalysed by [Co(babp)] shows signals due to phenoxy radicals and the bis(pyridine) complex, and a negligibly small $O_2{}^-$ adduct signal, indicating the low concentration of the latter. The higher ability of the Me- and Bu^t-substituted complexes to form $O_2{}^-$



Scheme 2 (*i*) Co^{III}(O$_2{}^-$)adduct; (*ii*) dimerization; (*iii*) −Co^{III}L(OH)

adducts (Table 4) might contribute to their better catalyst performance.

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