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Catalytic Function of Cobalt(III) Complexes with *N,N'*-Disalicylideneethylenediamine on Oxygenation of *t*-Butylphenols

Yūko Aimoto, Wakako Kanda, Sadatoshi Meguro,[†] Yūji Miyahara,
Hisashi Ōkawa,[*] and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812
[†]*Department of Forest Products, Faculty of Agriculture, Kyushu University 46-08, Hakozaki, Higashiku, Fukuoka 812*
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Catalytic oxygenation of *t*-butylphenols has been examined with the cobalt(III) complexes with *N,N'*-disalicylideneethylenediamine (H_2salen), K[Co(salen)CO_3], Na[Co(salen)$(N_3)_2$], K[Co(salen)$(CN)_2$], [Co(salen)(py)$_2$]PF_6, and [Co(salen)$(NH_3)_2$]PF_6. The CO_3-complex showed a high catalytic activity while the other complexes a low or no catalytic activity. Based on electronic and ESR spectral investigations, it has been shown that the reaction is initiated by the direct oxidation of *t*-butylphenols by the CO_3-complex through a phenolatocobalt(III) intermediate.

Reversible oxygen-carrying functions of cobalt(II) complexes with Schiff base ligands are well known.[1,2] Recently, catalytic oxidations of *t*-butylphenols[3–11] and indoles[12,13] by the use of such cobalt(II) complexes have become of interest as models for biological oxidations, since the catalysis in biological systems is considered to involve the activation of molecular oxygen by metalloenzymes. In the oxygenation of *t*-butylphenols with [Co(salpr)] (salpr^{2-}=bis(3-salicylideneaminopropyl)amine anion), it has been shown that the reaction is initiated by the hydrogen abstraction from the phenol by the superoxocobalt(III) complex [Co(salpr)O_2] initially formed.[9–11] On the other hand, the catalytic function of [Co(salen)](salen^{2-}=*N,N'*-disalicylideneethylenediamine anion) in oxygenations of *t*-butylphenols is less known, though it is generally thought that its oxygen complex takes part in the initiation of the reactions.[3]

It is also shown that [Co(salen)] acts as a good catalyst for oxygen delignification.[14] In the oxidative degradation of guaiacol as a model for the oxygen delignification, the catalytic activity of [Co(salen)] decreases in the order of additives in aqueous solution: $NaHCO_3 > Na_2CO_3 > NaOH$.[15] Under these conditions [Co(salen)] must be oxidized to a cobalt(III) complex. However, the species formed in alkaline aqueous media have not been characterized as yet.

The objects of this study are (1) to isolate and characterize the cobalt(III) complex derived from [Co(salen)] in aqueous solution containing hydrogencarbonate ion and (2) to examine catalytic activities of this cobalt(III) complex and its related complexes on the oxygenations of *t*-butylphenols, in the hope of obtaining an insight into the catalytic function of [Co(salen)] in the oxygenation reaction.

Experimental

Isolation of the Cobalt(III) Complex Formed in Aqueous Potassium Hydrogencarbonate Solution. [Co(salen)] (5 g) was suspended in a solution of $KHCO_3$ (10 g) in water (300 cm^3). Then chloroform (30 cm^3) was added, and the mixture was stirred for a week at room temperature. The deep green aqueous layer was separated and evaporated to dryness at a temperature lower than 40 °C. The crude product thus obtained was recrystallized from cold water containing potassium hydrogencarbonate (5%) to form green prisms.

Found: C, 43.45; H, 3.81; N, 6.06%. Calcd for $C_{17}H_{14}N_2O_5CoK\cdot 5/2H_2O$: C, 43.50; H, 4.08; N, 5.97%.

Syntheses of Other Cobalt(III) Complexes. *Na[Co(salen)$(N_3)_2$]*: An aqueous solution of NaN_3 (1 g) was added to a solution of K[Co(salen)CO_3]$\cdot$5/2H_2O (hereafter denoted as CO_3-complex, 450 mg) in water (10 cm^3). Soon the $(N_3)_2$-complex separated as brown crystals.

Found: C, 43.34; H, 3.29; N, 25.51%. Calcd for $C_{16}H_{14}N_8O_2CoNa\cdot 1/2H_2O$: C, 43.55; H, 3.43; N, 25.39%.

[Co(salen)N_3]: The $(N_3)_2$-complex (30 mg) was dissolved in water (40 cm^3) to form a reddish brown solution, from which brown crystals separated. They were collected, washed with water, and dried *in vacuo*.

Found: C, 49.75; H, 4.31; N, 17.76%. Calcd for $C_{16}H_{14}N_5O_2Co\cdot H_2O$: C, 49.88; H, 4.19; N, 18.18%.

K[Co(salen)$(CN)_2$]: This complex ($(CN)_2$-complex) was obtained as yellowish orange crystals by the reaction of the CO_3-complex and an excess amount of KCN in water.

Found: C, 51.20; H, 3.49; N, 13.23%. Calcd for $C_{18}H_{14}N_4O_2CoK\cdot 1/2H_2O$: C, 50.82; H, 3.55; N, 13.17%.

[Co(salen)(py)$_2$]PF_6: The CO_3-complex (460 mg) was dissolved in water (15 cm^3) containing pyridine (10 cm^3). To the resulted red solution was added an aqueous solution of KPF_6 to give the (py)$_2$-complex as orange prisms.

Found: C, 49.69; H, 3.85; N, 8.92%. Calcd for $C_{26}H_{24}N_4O_2CoF_6P\cdot 1/2H_2O$: C, 49.70; H, 3.85; N, 8.92%.

[Co(salen)py]PF_6: The (py)$_2$-complex was left standing in a vacuum desiccator over P_2O_5 for a week to give the monopyridine adduct.

Found: C, 45.24; H, 3.58; N, 7.84%. Calcd for $C_{21}H_{19}N_3O_2CoF_6P\cdot 1/2H_2O$: C, 45.18; H, 3.61; N, 7.53%.

[Co(salen)$(NH_3)_2$]PF_6: This complex ($(NH_3)_2$-complex) was obtained in a way similar to that for the (py)$_2$-complex.

Found: C, 37.40; H, 4.07; N, 10.98%. Cacd for $C_{16}H_{20}N_4O_2CoF_6P\cdot 1/2H_2O$: C, 37.44; H, 4.12; N, 10.92%.

Oxygenation Reactions of t*-Butylphenols.* Oxygenation reactions of 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-methylphenol were examined by the use of the CO_3-, $(N_3)_2$-, $(CN)_2$-, (py)$_2$-, and $(NH_3)_2$-complexes as catalysts. The reactions were carried out by stirring an ethanolic solution containing a substrate and a catalyst for 12 h at room temperature, where the concentration of the substrate was 1×10^{-1} M (1 M=1 mol dm^{-3}) and the [substrate]/[catalyst] ratio was 50. Oxygenation products were separated by preparative thinlayer chromatography with alumina as an adsorbent or by high-speed liquid chromatography (column; Zorbax-ODS, 15 cm: eluent; acetonitrile-water (4:1)). Identifications of the products were performed by comparing the NMR and IR spectra and melting points of the products with those of authentic samples.

Physical Measurements. Infrared spectra were measured on a Hitachi Infrared Spectrometer Model 215 on KBr disks. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000. ESR spectra (X-band) were recorded on a JES-FE3X Spectrometer. Conductivity measurements were carried out with a Yanagimoto Conductivity Output Model MY-8 in ethanol, the cell constant being determined by the use of tetraethylammonium chloride.

Results and Discussion

The CO_3-complex exhibits the IR bands at 1590 and 1290 cm^{-1}, which are assigned to the vibration of bidentate carbonate group.[16] Absorption spectrum of this complex in water containing excess potassium hydrogencarbonate shows a d-d band at $16.3\times10^3\,cm^{-1}$ and an intraligand transition band at $26.6\times10^3\,cm^{-1}$ (Fig. 1). The spectrum resembles the spectra of *cis*-β-[Co(salen)(acac)][17] and its homologs.[18–21] All these facts indicate that the CO_3-complex adopts a *cis*-β octahedral configuration with nonplanar $salen^{2-}$ and bidentate carbonate ion (Fig. 2a).

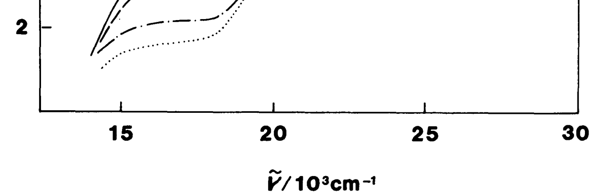


Fig. 1. Absorption spectra of the CO_3-complex: (——) in 10% $KHCO_3$ (1×10^{-3} M), (– – –) in 1% $KHCO_3$ (1×10^{-3} M), (—·—) in water (1×10^{-2} M), and (······) in water (1×10^{-3} M).

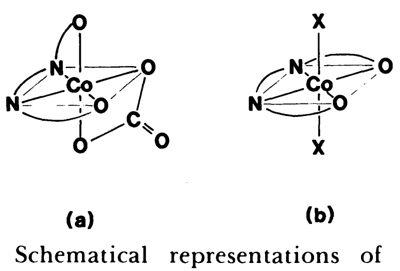
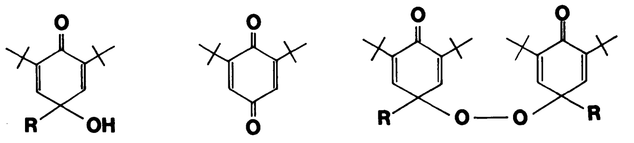


Fig. 2. Schematical representations of (a) *cis*-β-$[Co(salen)CO_3]^-$ and (b) *trans*-$[Co(salen)X_2]^-$ ($^-O^\frown N^\frown N^\frown O^- = N,N'$-disalicylideneethylenediaminate ion).

As is seen in Fig. 1, the $16.3\times10^3\,cm^{-1}$ band diminishes its extinction coefficient with lowering of the hydrogencarbonate concentration or diluting the solution with water. This spectral behavior suggests the ligand substitution and/or the configurational change of the complex in aqueous solution. Since the electronic spectrum of a dilute aqueous solution is very similar to that of *trans*-$[Co(salen)(H_2O)_2]^+$,[22] the following equilibrium is supposed for the complex: *cis*-β-$[Co(salen)CO_3]^- + 2H_2O \rightleftharpoons$ *trans*-$[Co(salen)(H_2O)_2]^+ + CO_3^{2-}$. Therefore, we presume that either *cis*-β-$[Co(salen)CO_3]^-$ or *trans*-$[Co(salen)(H_2O)_2]^+$ functions as a catalyst in the oxidative degradation of guaiacol.[15] In oxygen delignification in a dilute sodium hydroxide solution, *trans*-$[Co(salen)(H_2O)_2]^+$ must be the active species. However, this does not rule out the possibility of the catalytic function of *cis*-β-$[Co(salen)CO_3]^-$ in oxygen delignification in the presence of bicarbonate or carbonate ion.

It is also noted in this study that the CO_3-complex can be used as a starting material for the preparation of *trans*-$[Co(salen)X_2]^-$ ($X=N_3$, CN) and $[Co(salen)B_2]^+$ (B=py, NH_3) (Fig. 2b).

The oxygenation reactions of 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-methylphenol have been examined by the use of the CO_3-, $(N_3)_2$-, $(CN)_2$-, $(py)_2$-, and $(NH_3)_2$-complexes as catalysts, and the results are given in Table 1. The characterized major products are quinol (**1**), quinone (**2**), and peroxide (**3**) (Fig. 3). In the case with 2,4,6-tri-*t*-butylphenol as the substrate, the CO_3-



1 **2** **3**

Fig. 3. Oxygenation products from *t*-butylphenols: (1) quinol, (2) quinone, and (3) peroxide.

TABLE 1. OXYGENATION OF *t*-BUTYLPHENOLS[a)]

Catalyst	Substrate[b)]	Conv/%	Products[c)]/%		
			1	**2**	**3**
$K[Co(salen)CO_3]$	TBP	100	11	38	42
$Na[Co(salen)(N_3)_2]$	TBP	29	2	13	11
$K[Co(salen)(CN)_2]$	TBP	0			
$[Co(salen)(py)_2]PF_6$	TBP	0			
$[Co(salen)(NH_3)_2]PF_6$	TBP	0			
$K[Co(salen)CO_3]$	DBMP	45	30	15	0
$Na[Co(salen)(N_3)_2]$	DBMP	0			
$K[Co(salen)(CN)_2]$	DBMP	0			
$[Co(salen)(py)_2]PF_6$	DBMP	0			
$[Co(salen)(NH_3)_2]PF_6$	DBMP	0			

a) Reaction condition: [catalyst]=2×10^{-3} M, [substrate]/[catalyst]=50, 12 h in ethanol at room temperature. b) TBP=2, 4, 6-tri-*t*-butylphenol and DBMP=2, 6-di-*t*-butyl-4-methylphenol. c) **1**: quinol, **2**: quinone, and **3**: peroxide (*cf.* Fig. 3).

complex exhibited a high catalytic activity while the $(N_3)_2$-complex a low activity. Other complexes showed practically no catalytic activity. In the case with 2,6-di-*t*-butyl-4-methylphenol, only the CO_3-complex showed a catalytic activity. The main oxygenation product in the former was the peroxide, while the product in the latter was the quinol. It should be noted that the same oxygenation products have been obtained by the use of Co(salen) as the catalyst.[6]

The catalytic activities of the cobalt(III) complexes evidently depend upon the fifth and sixth ligands. For obtaining an insight into the differences in catalytic activities of the complexes, the absorption spectra in ethanol were investigated. The CO_3-complex in ethanol shows bands at 14.2×10^3 and $\approx21\times10^3\,cm^{-1}$, attributable to d-d and intraligand transitions respectively (Fig. 4). This spectrum markedly differs from those of *cis*-β-$[Co(salen)CO_3]^-$ and *trans*-$[Co(salen)(H_2O)_2]^+$. Its molar conductivity has been determined to be 34 $\Omega^{-1}\,mol^{-1}\,cm$ in ethanol, which falls in the range for 1:1 electrolytes.[23] This indicates that carbonate ion is still bonded to the metal in this solvent. It is likely that the complex takes a configuration either of tetragonal pyramid with a unidentate carbonate ion at the apex or of an elongated octahedron with a carbonate ion and a solvent molecule at the apical positions.

The electronic spectra of the $(N_3)_2$-complex are shown in Fig. 4. The spectrum in ethanol differs from that in water containing excess of sodium azide. Further, $[Co(salen)N_3]$ shows the same spectrum as that of the $(N_3)_2$-complex in ethanol. These facts imply that the possible species of the $(N_3)_2$-complex in ethanol is $[Co(salen)N_3]$ or $[Co(salen)N_3(EtOH)]$.

A marked spectral change was also observed for the $(CN)_2$-complex when measured in water containing excess potassium cyanide and in ethanol (Fig. 5). Thus, the complex must have undergone some change in ethanol in more or less degree. The spectrum in ethanol is characterized by an absorption at $\approx18\times10^3\,cm^{-1}$. A similar absorption band was observed for the five-coordinate [RCo(salen)] (R=alkyl anion) and its homologs.[24–27] We have examined the electronic spectra of the ethanol solutions of the CO_3-complex containing potassium cyanide in various amounts, and found that the extinction coefficient at $\approx18\times10^3\,cm^{-1}$ becomes maximal when [Co]/[CN]=1. This suggests that [Co(salen)(CN)] or [Co(salen)(CN)(EtOH)] is formed in the solution.

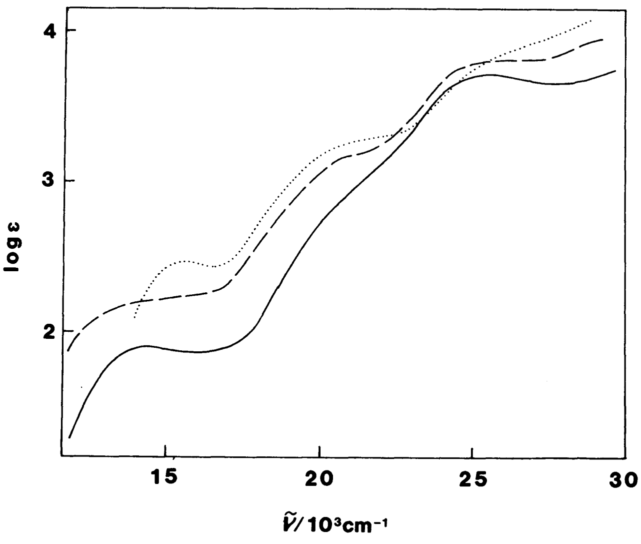


Fig. 4. Absorption spectra of the CO_3-complex in ethanol (——) and the $(N_3)_2$-complex in 2% NaN_3 solution (······) and in ethanol (– – –).

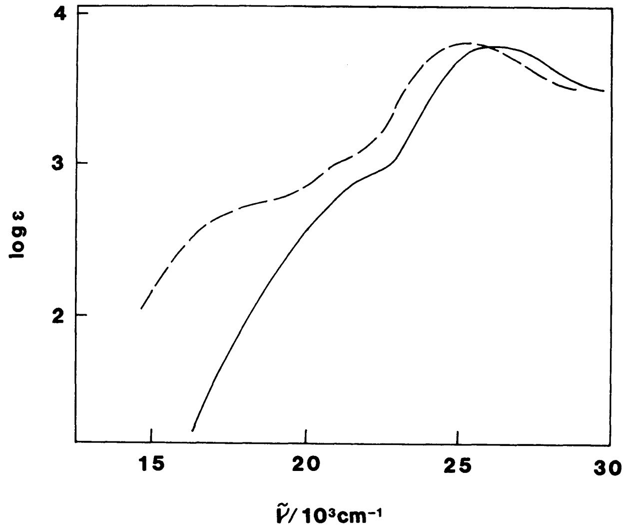


Fig. 5. Absorption spectra of the $(CN)_2$-complex in 2% KCN solution (——) and in ethanol (– – –).

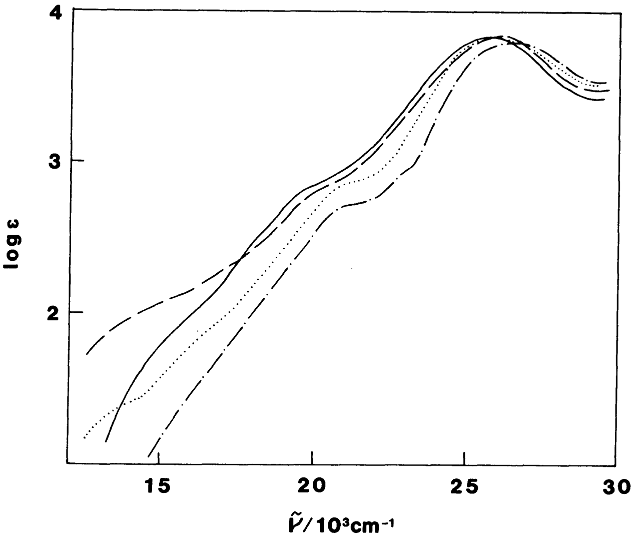


Fig. 6. Absorption spectra of the $(py)_2$-complex in pyridine (——) and in ethanol (– – –) and the $(NH_3)_2$-complex in 18% ammonia (—·—) and in ethanol (······).

Each spectrum of the $(py)_2$- and $(NH_3)_2$-complexes in ethanol differs from the spectrum in water containing the corresponding base (Fig. 6). Hence, the complex species in ethanol differs from $[Co(salen)B_2]^+$. Since the spectra of the $(py)_2$-complex and $[Co(salen)(py)]PF_6$ are practically the same in ethanol, the species in both solutions are likely to be $[Co(salen)(py)]^+$ or [Co(salen)-

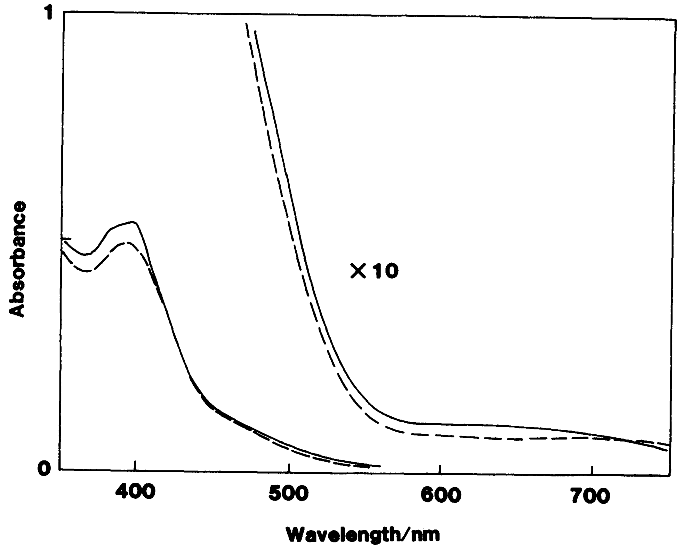


Fig. 7. Electronic spectral change on adding 2,4,6-tri-*t*-butylphenol to an ethanolic solution of the CO_3-complex: (-----) CO_3-complex (1×10^{-3} M) and (——) CO_3-complex (1×10^{-3} M)+2,4,6-tri-*t*-butylphenol (1×10^{-2} M).

(py)(EtOH)]$^+$. A similar feature is supposed for the $(NH_3)_2$-complex in ethanol.

Above spectral investigations suggest that all the complexes take an essentially identical configuration; a tetragonal pyramid or an elongated octahedron. Therefore, it is difficult to explain the catalytic activity of the CO_3-complex solely in terms of configurational aspect.

It seems that the high catalytic activity of the CO_3-complex relative to the other complexes is attributable to the high lability of the carbonate ion. In order to verify this, the absorption spectrum of the CO_3-complex in the presence of ten times of 2,4,6-tri-*t*-butylphenol was examined under a nitrogen atmosphere. As seen in Fig. 7, the intensity around 390 nm increased and a new absorption appeared around 630 nm when the substrate was added, suggesting the generation of 2,4,6-tri-*t*-butylphenoxyl radical.[28] Further, this complex/substrate solution exhibited a three-lined ESR signal with a coupling constant of 1.7 gauss near $g\approx2.0$. This signal is very similar to that of 2,4,6-tri-*t*-butylphenoxyl radical,[29] though the hyperfine structures due to the tertiary butyl groups are absent probably because of the presence of the paramagnetic species ([Co(salen)]) in the solution. All these facts indicate that the CO_3-complex oxidizes the phenol to the phenoxyl radical. The preliminary electrochemical investigations have revealed that the Co^{III}/Co^{II} redox potential of the CO_3-complex (−1.2 V *vs.* SCE in ethanol, glassy carbon electrode) is much lower than that of the $(py)_2$-complex.[30,31] This fact suggests that the electron transfer between the CO_3-complex and a *t*-butylphenol is of inner-sphere rather than outer-sphere, through a five-coordinate intermediate with the phenolate group at the apical position. Thus, the mechanism of the catalytic oxygenation with the CO_3-complex may be represented as follows: (1) The substitution of the apical carbonate ion for the phenolate ion to form a phenolatocobalt(III) intermediate, (2) the intramolecular electron transfer to generate Co^{II} (salen) and the phenoxyl radical, and (3) the progression of radical reactions with molecular oxygen (Fig. 8).

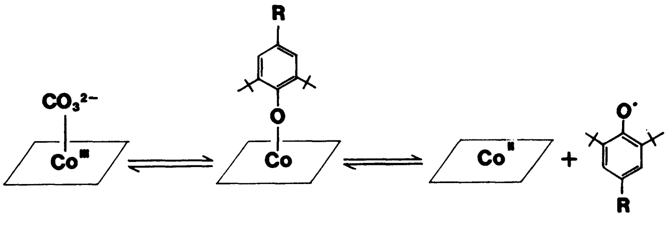


Fig. 8. Catalytic scheme for the oxygenation with the CO_3-complex.

TABLE 2. OXYGENATION OF 2,4,6-TRI-*t*-BUTYLPHENOL WITH [Co(salen)] IN THE PRESENCE OF ADDITIVES[a)]

Additive	Conv/%	Products[b)]/%		
		1	2	3
none[c)]	85	—	24	53
KCN	0			
py	0			

a) Reaction condition: [catalyst]=2×10^{-3} M, [substrate] [catalyst]=50, [additive]/[catalyst]=10, 12 hrs in ethanol at room temperature. b) *Cf.* Fig. 3. c) Results from Ref. 6, the solvent being methanol.

It is shown that the phenol/phenoxyl redox potential depends upon the substituent on the ring and becomes lower when a more electron donative substituent is introduced into the ring.[32] The ready oxidation of 2,4,6-tri-*t*-butylphenol relative to 2,6-di-*t*-butyl-4-methylphenol is probably due to the generation of the phenoxyl radical in a higher concentration in the former, since the *t*-butyl group is slightly more electron donative than the methyl group. Indeed, the electronic spectrum of the CO_3-complex (in ethanol under nitrogen atmosphere) showed a very little increase around 400 and 630 nm when 2,6-di-*t*-butyl-4-methylphenol (ten times) was added.

The low catalytic activities of the $(N_3)_2$-, $(CN)_2$-, $(py)_2$-, and $(NH_3)_2$-complexes may be due to the difficulties in forming the phenolatocobalt(III) intermediate with these complexes, because of the strong donating abilities of the apical ligands compared with the phenolate ion.

We have further examined the catalytic activity of [Co(salen)] on the oxygenation reactions of *t*-butylphenols in the presence of a donating additive. The results are given in Table 2. Contrary to a high catalytic activity in the absence of an additive,[6] the activity of [Co(salen)] for the oxygenation reaction was almost suppressed on adding cyanide ion or pyridine to the reaction system. This fact again demonstrates that the additives coordinate at the apical position of the air-oxidized Co^{III} (salen) and thence deactivate the catalytic function of [Co(salen)].

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