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Synthesis and Characterization of Co(III)–salen Complexes with a Substituted Phenolato Ion as Apical Ligand

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Abstract

Cobalt(III) complexes, [Co(sal-pen)] with N,N′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediaminate trianion (sal-pen^{3-}) and [Co(salen)(R-phO)] with N,N′-disalicylideneethylenediaminate dianion (salen^{2-}) and a series of substituted phenolate ions (R-phO$^-$), were sysnthesized. The complexes were characterized as an essentially square-pyramidal structure with a phenolate ion at the apex. The intense absorption in the visible region of the complexes was assigned to a charge transfer band from the apical phenolate oxygen to the cobalt(III) ion, based on a linear correlation between the band frequency and the pK_a value of the phenol. The properties of the present cobalt(III) complexes were discussed in comparison with those of [Fe(salen)(R-phO)].

Introduction

Metal complexes of pentadentate Schiff bases, consisting of a planar tetradentate system and a pendant group capable of acting as an apical donor, are of current interest [1–6] because of the relevance to metallo-enzymes such as natural oxygen carriers [7, 8] and coenzyme vitamin B_{12} [9]. As one of these Schiff bases we have synthesized N,N′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (abbreviated as H_2(sal-Hpen), Fig. 1) [5], which is a salen analog containing a phenolic pendant group. In the cases of [Cu(sal-Hpen)], [Ni(sal-Hpen)], and [Co(sal-Hpen)], each metal adopts a planar configuration free from the coordination of the pendant phenolic group [5]. On the other hand, the ligand functions as a quinquedentate chelating agent toward the iron(III) ion to form Fe(sal-pen), in which the deprotonated phenolic oxygen coordinates at the fifth position [5, 10].

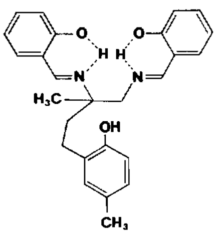

Fig. 1. The chemical structure of H_2(sal-Hpen).

Previously we have shown that [Co(sal-Hpen)] forms black-purple prismatic crystals when air-oxidized in dichloromethane [6]. This was presumed to be a dioxygen adduct of a composition [Co(sal-pen)O_2], on the basis of elemental analysis, resonance Raman (RR) spectra, and the reactivity toward 2,2,6,6-tetramethyl-4-piperidinol. However, subsequent investigations have revealed that our preliminary conclusion is not correct, since there is no difference in the RR spectra between the products oxidized by $^{16}O_2$ and $^{18}O_2$.

In order to obtain the correct conclusion for the oxidation product of [Co(sal-Hpen)], we prepared a series of cobalt(III) complexes [Co(salen)(R-phO)] with N,N′-disalicylideneethylenediaminate ion (salen^{2-}) and a phenolate ion (R-phO$^-$; R is a substituent on the ring), because these complexes are expected to take a structure similar to that of the oxidation product of [Co(sal-Hpen)] and thence serve for the characterization of the oxidation product.

Experimental

Syntheses

The method of synthesizing [Co(sal-Hpen)] was given earlier [5]. [Co(salen)] was obtained by the literature method [11].

Oxidation of [Co(sal-Hpen)]

To a dichloromethane solution of [Co(sal-Hpen)] was bubbled oxygen for 2 h. The purple solution

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thus formed was concentrated to a small volume to give purple prismatic crystals. They were collected and dried in a vacuum desiccator. The experiments were carried out three times, and the samples from each run were submitted to elemental analysis. *Anal.* Found: C, 62.32, 62.91, 62.60; H, 5.46, 5.45, 5.43; N, 5.55, 5.78, 5.54%. Calcd. for Co(sal-pen)·3/2H_2O: C, 62.52; H, 5.65; N, 5.61%.

Syntheses of [Co(salen)(R-phO)]

The complexes with *m*-cresolate (R = *m*-CH_3), *p*-chlorophenolate (*p*-Cl), *p*-bromophenolate (*p*-Br), *p*-nitrophenolate (*p*-NO_2), and 2,4-dinitrophenolate (2,4-$(NO_2)_2$) were synthesized. The synthesis of [Co(salen)(*p*-NO_2-phO)] is shown as an example.

To a dichloromethane solution (50 cm^3) of [Co(salen)] (325 mg) was added *p*-nitrophenol (150 mg) in an open atmosphere. The color of the solution soon changed from red to reddish-black. The mixture was allowed to stand overnight. The solvent was evaporated to dryness at room temperature, and the residue was thoroughly washed with dichloromethane to give almost black crystals.

Elemental analyses of the complexes are given in Table I.

Measurements

Infrared spectra were recorded on a Hitachi Infrared Spectrometer Model 215 on KBr disks and in nujol mulls. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000, in dichloromethane or by the reflection on powder samples.

Results and Discussion

Elemental analyses for the samples from three independent oxidations of [Co(sal-Hpen)] coincided within analytical error (±0.4%) to the composition [Co(sal-pen)]·3/2H_2O, rather than [Co(sal-pen)O_2] as supposed previously. Magnetic measurements revealed the oxidation product to be diamagnetic. However, a very low solubility of the product in appropriate solvents precluded the measurements of its NMR spectrum. The IR spectrum shows a broad band near 3400 cm^{-1} attributable to the O–H stretch of hydrated water in the crystal lattice [12]. The absence of O–H vibration in the region 3300–3200 cm^{-1} suggests that the deprotonated phenolate group coordinates at the apical site. In contrast, [Co(sal-Hpen)] shows the O–H vibration at 3250 cm^{-1}. Thus, we presume that the oxidized product is a simple cobalt(III) complex with the salen moiety in the equatorial plane and the pendant phenolate oxygen at the apical site (Fig. 2a). Any water coordination must be weak, if it occurs at all. This complex is represented hereafter by [Co(sal-pen)].

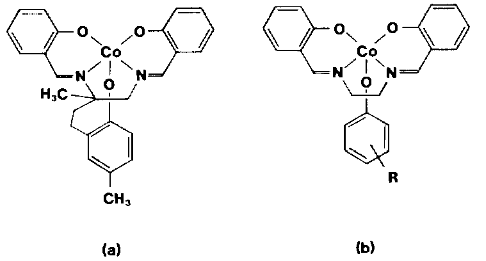

Fig. 2. The chemical structures of: (a) [Co(sal-pen)] and (b) [Co(salen)(R-phO)].

Cobalt(III) complexes with $salen^{2-}$ and a phenolate ion, [Co(salen)(R-phO)] (Fig. 2b), have not been synthesized so far. In this study we obtained the complexes via the reaction of [Co(salen)] with a phenol in dichloromethane in the presence of molecular oxygen. The complexes were readily obtained when a phenol with an electron-withdrawing group (or groups) was employed. However, pure complex could not be obtained with *p*-aminophenol and *p*-methoxyphenol. All the complexes obtained are diamagnetic. The complexes except [Co(salen)(2,4-$(NO_2)_2$-phO)] show an IR band around 3400 cm^{-1}, attributable to the lattice water. The coordination of the phenolate ion and non-coordination of water molecule to the metal are inferred from the absence of the O–H vibration in the region 3300–3200 cm^{-1}.

[Co(sal-pen)] and [Co(salen)(R-phO)] are sparingly soluble in non-donating solvents, and they are decomposed in polar, donating solvents. Thus, the

TABLE I. Elemental Analyses of [Co(salen)(R-phO)].

	Found (%)			Calculated (%)		
	C	H	N	C	H	N
[Co(salen)(*m*-CH_3-phO)]·1/2H_2O	62.39	5.16	6.30	62.59	5.02	6.35
[Co(salen)(*p*-Br-phO)]·1/2H_2O	52.31	3.71	5.50	52.50	3.78	5.53
[Co(salen)(*p*-Cl-phO)]·3/2H_2O	55.37	3.91	6.15	55.07	4.41	5.84
[Co(salen)(*p*-NO_2-phO)]·1/2H_2O	55.85	3.89	8.94	55.94	4.05	8.90
[Co(salen)(2,4-$(NO_2)_2$-phO)]	51.77	3.37	10.96	51.98	3.37	11.02

powder reflectance spectra of [Co(sal-pen)] and [Co(salen)(R-phO)] were compared. As shown in Fig. 3 each complex exhibits an intense absorption band in the visible region. The band frequency depends markedly upon the substitutent on the phenolic benzene ring and shifts to higher frequency when a more electron-withdrawing group is introduced into the ring. This implies that the band is attributable to a charge-transfer rather than a d–d transition in origin. Indeed, as is seen in Table II and Fig. 4, the frequency of the band can be correlated with the pK_a value of the phenol (the pK_a value for the pendant phenolic group of H_2(sal-Hpen) is assumed to be identical with that (10.55) of 2,4-dimethylphenol).

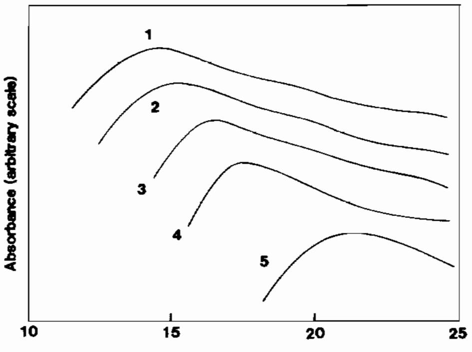

Fig. 3. Reflectance spectra of complexes: 1, [Co(sal-pen)]; 2, [Co(salen)(m-CH_3-phO)]; 3, [Co(salen)(p-Br-phO)]; 4, [Co(salen)(p-NO_2-phO)]; 5, [Co(salen)(2,4-$(NO_2)_2$-phO)].

TABLE II. Band Maximum of the Visible Band of Complexes and pK_a Values of Phenols[a].

	$\tilde{\nu}_{max}$ (10^3 cm^{-1})	pK_a
[Co(sal-pen)]	14.9	(10.55)[b]
[Co(salen)(m-CH_3-phO)]	15.2	10.09
[Co(salen)(p-Cl-phO)]	16.7	9.3
[Co(salen)(p-Cl-phO)]	16.7	9.38
[Co(salen)(p-NO_2-phO)]	17.6	7.15
[Co(salen)(2,4-$(NO_2)_2$-phO)]	21.3	4.11

[a] pK_a values are taken from ref. 19. [b] pK_a value for 2,4-dimethylphenol.

Based on these facts, the visible absorption may be assigned to the charge-transfer band from the phenolate oxygen at the apical position to the cobalt(III) ion.

The absorption spectrum of [Co(sal-pen)] in dichloromethane exhibits an intense absorption ($\epsilon \sim 7000$ dm^3 mol^{-1} cm^{-1}) at 17.8×10^3 cm^{-1}. It seems reasonable to assign this band to the charge-transfer from the phenolate oxygen to the cobalt(III), judging by its very high intensity. The spectrum obeys Beer's law in the concentration range 1×10^{-4}–1×10^{-5} M, suggesting that the pendant phenolate ion does not dissociate in this concentration range.

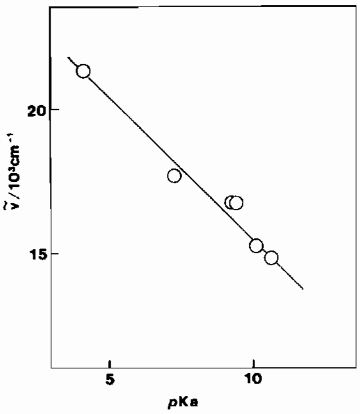

Fig. 4. Correlation between $\tilde{\nu}_{max}$ of CT band and pK_a of phenol.

It is interesting to compare the present cobal(III) complexes with the iron(III) complexes [Fe(salen)(R-phO)], which were synthesized by Heistand *et al.* as a model for dioxygenases [13]. The iron(III) complexes exhibit an absorption around 420 nm with a high extinction coefficient ($\epsilon \sim 7000$ dm^3 mol^{-1} cm^{-1}). The frequency of the band, however, shows little dependence on the substituent on the phenolic benzene ring. Therefore, this band seems to differ in origin from the visible band observed for [Co(sal-pen)] and [Co(salen)(R-phO)]; it may be assigned to a charge-transfer between the equatorial ligand $salen^{2-}$ and iron(III). It is known that phenolato–iron(III) complexes also show an intense absorption in the visible region, and such color phenomena are often used as a qualitative test for phenols [14]. On the other hand, such a color reaction is unknown for octahedral cobalt(III) complexes with phenolate ligands. For example, salicylato(quadridentate amine)cobalt(III) complexes [15] show a spectrum very similar to those [16] of $[Co(ox)(NH_3)_4]^+$, $[Co(CO_3)(NH_3)_4]^+$, and *cis*-$[(H_2O)_2(NH_3)_4]^{3+}$. It is noteworthy that [Co(sal-pen)] and [Co(salen)(R-phO)] exhibit a charge-transfer band from the apical phenolate oxygen to the metal in the visible region, while the [Fe(salen)(R-phO)] complexes do not.

The [Fe(salen)(R-phO)] complexes are considerably stable in solution, while the [Co(salen)(R-phO)] complexes readily undergo dissociation of the phenolate ion in polar solvents. This reflects a high affinity between the phenolate oxygen and iron(III); in high-spin iron(III) complexes the phenolate oxygen is bonded by π- as well as σ-donation, while in low-spin cobalt(III) complexes the phenolate oxygen is bonded by only σ-donation.

Based on the RR spectra, Pyrz and Que assigned the 568 cm^{-1} band of [Fe(salen)(p-CH$_3$-phO)] to the Fe–O(phenolate) stretching mode [17]. We have found that [Co(sal-pen)] exhibits RR bands at 1260 and 510 cm^{-1}, both of which are enhanced more by the excitation at 514.5 nm than by the excitation at 476.5 nm [6]. The 1260 cm^{-1} band is assigned to the C–O stretch of the coordinated phenolate ion [18]. The 510 cm^{-1} band may be assigned to the Co–O stretching vibration. The higher frequency of the Fe–O vibration relative to that of Co–O vibration is also in harmony with the general concept that the Fe^{III} ion forms a stronger bond with phenolate ions than with the Co^{III} ion.

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