Synthesis and Spectra of Co(Salen) Derivatives Containing Pendant Groups and their Dioxygen Adducts. Pendant Chain Length and Coordinating Ability

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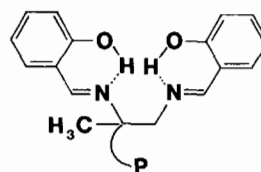
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Abstract

Five Co(salen) derivatives, Co(sal-moen), Co(sal-motn), Co(sal-ipstn), Co(sal-eatn) and Co(sal-batn) containing the $(CH_2)_2-O-CH_3$, $(CH_2)_3-O-CH_3$, $(CH_2)_3-S-CH(CH_3)_2$, $(CH_2)_3-N(C_2H_5)_2$ and $(CH_2)_3-N(n\text{-}C_4H_9)_2$ as the pendant groups, respectively, were newly synthesized. Electronic spectra obtained at room temperature show that all the complexes are free from pendant coordination. On the other hand, ESR spectra in frozen CH_2Cl_2 at liquid nitrogen temperature indicate that Co(sal-motn) and Co(sal-batn) retain the four-coordinate structure while Co(sal-moen), Co(sal-ipstn) and Co(sal-eatn) exist as a mixture of the four- and five-coordinate species. Upon oxygenation at $-90\ °C$, all the complexes form dioxygen adducts in which the pendant group occupies the axial position *trans* to the dioxygen. Resonance Raman spectra exhibit the $\nu(O_2)$ and $\nu(Co-O_2)$ at 1150–1142 and 538–522 cm^{-1}, respectively, which are typical of six-coordinate, 'base-bound' dioxygen adducts. These results suggest that pendant coordination is possible regardless of the nature of the donor atom as long as the latter is bonded to the Co(salen) core via two or three methylene bridges.

Introduction

Previously, we have prepared a number of salen analogs (H$_2$salen: *N,N'*-disalicylideneethylenediamine) containing pendant groups, P, capable of axial coordination (Fig. 1), and examined the effect of axial coordination on the structure and property of their metal complexes [1–5]. In particular, we focused our attention on dioxygen adducts of their

Co(II) complexes [2, 4] since they serve as model compounds of heme proteins such as myoglobin and cytochrome P-450. It is well known that Co(II) complexes of salen-like Schiff base ligands form dioxygen adducts with or without an axial base ligand and that the electronic structure and property of these 'base-free' and 'base-bound' dioxygen adducts are markedly different [6–8]. As we demonstrated previously [2, 4, 9, 10], the distinction of these two types of dioxygen adducts can be made most conveniently by measuring resonance Raman (RR) spectra in solution; base-bound, six-coordinate adducts exhibit the $\nu(O_2)$ in the 1148–1142 cm^{-1} region whereas base-free, five-coordinate adducts exhibit the $\nu(O_2)$ in the 1097–1095 cm^{-1} region. The former are Co(salen) derivatives containing pendant groups (P) such as $-(CH_2)_2-$(2-methoxy-5-methylphenyl) (mpen) [2], $-(CH_2)_2-S-($i-$C_3H_7)$ (ipsen) [4] and $-(CH_2)_2-S-$(phenyl) (bsen) [4], and the latter is that containing the pendant group, $-(CH_2)_2-$(2-hydroxy-5-methylphenyl) (Hpen) [2].

In order to obtain more information about the relationship between the coordinating ability and the pendant chain structure, we have synthesized five new salen analogs containing ether oxygen, thioether sulfur or aliphatic amino nitrogen in the pendant group. Figure 1 shows the structures of these pendant groups and their abbreviations. This paper deals with the syntheses, spectra and structures

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a) P=CH$_2$CH$_2$-O-CH$_3$ moen
b)   =CH$_2$CH$_2$CH$_2$-O-CH$_3$ motn
c)   =CH$_2$CH$_2$CH$_2$-S-CH(CH$_3$)$_2$ ipstn
d)   =CH$_2$CH$_2$CH$_2$-N(C$_2$H$_5$)$_2$ eatn
e)   =CH$_2$CH$_2$CH$_2$-N(n-C$_4$H$_9$)$_2$ batn

Fig. 1. Chemical structure of Schiff bases.

of the Co(salen) analogs containing these five pendant groups and their dioxygen adducts in solution at low temperature.

Experimental

Preparations

The general synthetic scheme for H$_2$(sal-P) is shown in Fig. 2. Ketones containing the P group at the carbonyl carbon (**Ia–Id**) or P$'$ group as the precursor of P(**Ie$'$**) were used as the starting materials. They were converted into aminonitriles (**IIa–IId, e$'$**), which were then reduced to diamines (**IIIa–IIIe**). In the case of reduction of **IIe$'$**, the amide group was also reduced. The Schiff bases H$_2$(sal-P) were obtained by condensing these diamines with salicylaldehyde in the 1:2 molar ratio.

4-Methoxy-2-butanone (**Ia**) was obtained by the literature method [11]. Other ketones (**Ib–Ie**) were obtained as described below.

5-Methoxy-2-pentanone (Ib)

5-Chloro-2-pentanone [12] was converted to the ethylene ketal by the standard method. The ketal (50 g) was added dropwise to anhydrous sodium methoxide, which was prepared by dissolving sodium (7.0 g) in absolute methanol (100 ml) and then evaporating the solvent to dryness. The mixture was heated at 100 °C for 10 h, and the reaction mixture was decomposed with water (100 ml). The organic layer was separated and the aqueous layer was extracted with three 50 ml portions of ether. The extracts were combined with the organic layer and dried over anhydrous sodium sulfate. On evaporating the solvent, a pale colored oily substance was obtained. It was dissolved in a methanol/water (3/7) mixture containing 0.2 ml of conc. sulfuric acid, and the solution was refluxed for 6 h. The solution was neutralized with sodium carbonate and concentrated until the organic layer separated out. It was shaken with ether (200 ml), and the ether extract was dried over anhydrous sodium sulfate. On evaporating the solvent, 5-methoxy-2-pentanone was obtained as pale yellow oil.
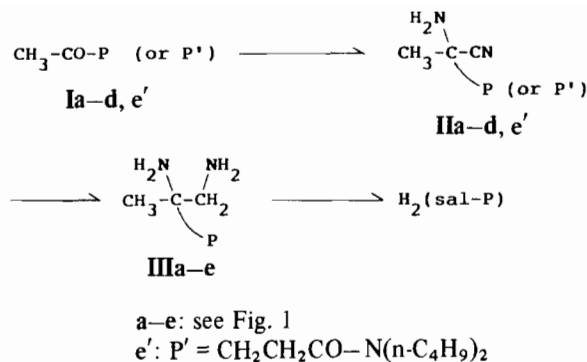

a–e: see Fig. 1
e$'$: P$'$ = CH$_2$CH$_2$CO–N(n-C$_4$H$_9$)$_2$

Fig. 2. Synthetic scheme for H$_2$(sal-P).

5-(1-Methylethylthio)-2-pentanone (Ic)

This was obtained by the reaction of sodium 1-methylethylmercaptide and 5-bromo-2-pentanone, in nearly the same way as that for 5-methoxy-2-pentanone.

5-(Diethylamino)-2-pentanone (Id)

This was obtained in a way similar to that of 4-(2-methoxy-5-methylphenyl)-2-butanone [1] except for the use of 2-(diethylamino)ethylchloride instead of 2-methoxy-5-methylbenzylchloride.

1-Di(n-butyl)amino-1,4-pentanedione (Ie$'$)

A solution of di-n-butylamine (41 g) in absolute dioxane (50 ml) was dropwise added to α-ketovaleryl chloride with stirring. After stirring at room temperature for one day, the reaction mixture was poured into water (500 ml) and **Ie$'$** thus formed was extracted with ether.

The detailed procedures for the synthesis of H$_2$(sal-P) from the ketones (**Ia–Ie$'$**) are not described here because they are practically the same as those described previously [1, 2]. The Schiff bases were obtained as yellow paste. They were partially purified by silica-gel chromatography and used for the synthesis of [Co(sal-P)].

The cobalt(II) complexes were obtained as deep orange to red prisms through the reaction of cobalt(II) acetate tetrahydrate with H$_2$(sal-P) (in 1:1

TABLE I. Elemental Analyses for the Complexes

	Found (%)			Calculated (%)		
	C	H	N	C	H	N
[Co(sal-moen)]	60.46	5.64	7.09	60.46	5.58	7.05
[Co(sal-motn)]	61.11	5.94	6.73	61.32	5.88	6.81
[Co(sal-ipstn)]	60.54	6.12	6.12	60.65	6.20	6.15
[Co(sal-eatn)]$\frac{1}{2}$H$_2$O	62.61	6.52	8.79	62.47	6.77	9.11
[Co(sal-batn)]$\frac{1}{2}$H$_2$O	65.37	7.68	8.09	64.98	7.78	8.12

stoichiometry) in ethanol in an atmosphere of nitrogen. The results of elemental analyses for the complexes are given in Table I.

Measurements

Elemental analyses of carbon, hydrogen, and nitrogen were obtained at the Service Center of Elemental Analysis, Kyushu University. Electronic absorption spectra were recorded in dichloromethane on a Shimadzu Multipurpose Spectrometer Model MPS-5000 or a Shimadzu UV-240 Spectrometer. X-band ESR spectra were recorded on a JES-FE3X Spectrometer in frozen dichloromethane solutions. Resonance Raman (RR) spectra were obtained on a Spex Model 1403 double monochromator equipped with a Spex DM1B controller. All the spectra were obtained by using 568 nm excitation from a Spectra-Physics Model 154-01 Kr-ion laser. The mini-bulb techniques [13] were employed to measure the spectra of dioxygen adducts at ~ -90 °C.

Results and Discussion

All the Co(II) complexes obtained show a magnetic moment falling in the range 2.4–2.5 μ_B. Electronic spectra of the cobalt(II) complexes were measured in dichloromethane at room temperature, and typical examples are shown in Fig. 3. The spectra are similar to each other in the region $(7–35) \times 10^3$ cm^{-1} and also resemble that of Co(salen) [14]. The

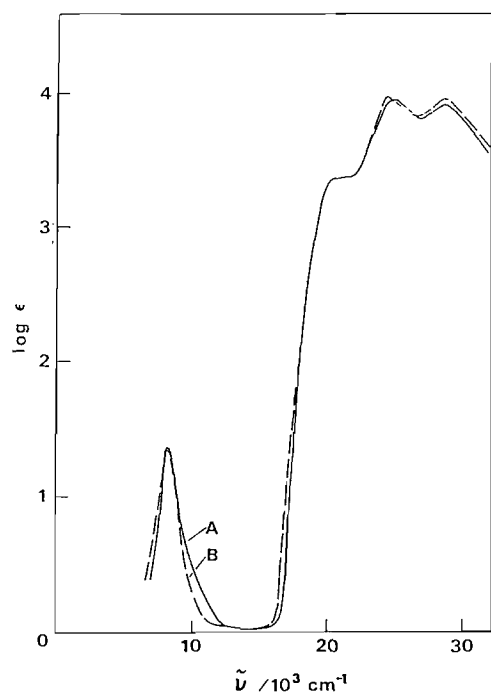most noticeable feature of the spectra is the absorption band near 8×10^3 cm^{-1} ($\epsilon \sim 20$ dm^3 mol^{-1} cm^{-1}) which is now known to be characteristic of low-spin planar Co(II) complexes with salen-like Schiff bases [15–17]. Evidently, all the complexes take a planar configuration in which the pendant group does not coordinate at the fifth position.

ESR spectra of the Co(II) complexes were measured in frozen dichloromethane at liquid nitrogen temperature. The results are shown in Figs. 4 and 5. The spectra of Co(sal-motn) and Co(sal-batn) resemble that of Co(salen) and show signals typical of planar Co(II) complexes with the $(d_{yz})^1$ ground state [17, 18]. It is presumed that these complexes retain a planar configuration even at liquid nitrogen temperature.

The ESR spectra of Co(sal-moen), Co(sal-ipstn), and Co(sal-eatn), on the other hand, show complicated patterns with three main signals at $g \sim 3.5$ ($A = 130$ gauss [4]), $g \sim 2.0$, and $g \sim 1.9$. The signals at the lower and higher magnetic field ($g \sim 3.5$ and ~ 1.9, respectively) well correspond to those in Fig. 4. Previously, we have shown that Co(sal-ipsen), (P=CH$_2$CH$_2$–S–CH(CH$_3$)$_2$) takes a discrete five-coordinate structure with the pendant sulfur at the apical site and exhibits an ESR pattern typical of $(d_{z^2})^1$ electronic configuration: $g_x = 2.48$, $g_y = 2.20$, $g_z = 2.01$, $A_x = 66$, $A_y = 33$, $A_z = 115$ gauss [4]. In view of these facts, the spectra of Co(sal-moen), Co(sal-ipstn) and Co(sal-eatn) may be interpreted as the superposition of the spectra of four-coordinate and five-coordinate species which are coexisting in frozen solution. It is more reasonable to assume that at liquid nitrogen temperature these complexes prefer the five-coordinate structure
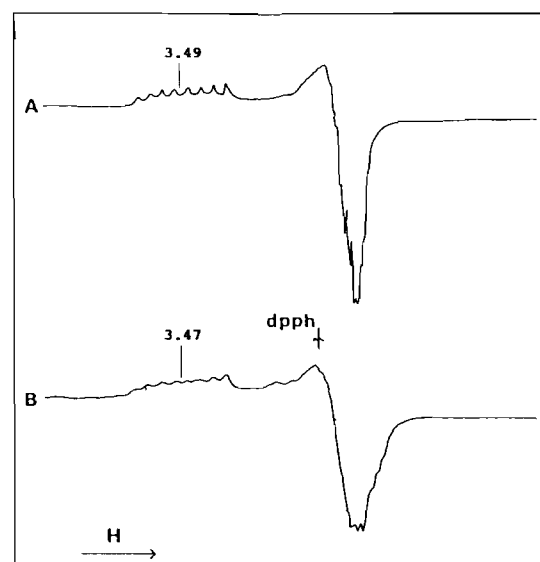

Fig. 3. Electronic spectra of (A) Co(sal-moen) and (B) Co(sal-eatn) in CH$_2$Cl$_2$.

Fig. 4. ESR (X-band) spectra of (A) Co(sal-motn) and (B) Co(sal-batn) in frozen CH$_2$Cl$_2$ at liquid nitrogen temperature.
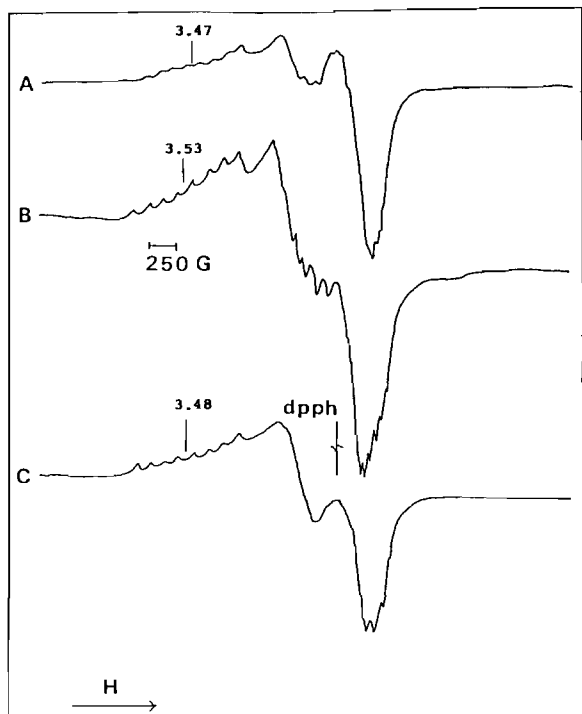
Fig. 5. ESR (X-band) spectra of (A) Co(sal-eatn), (B) Co(sal-moen), and (C) Co(sal-ipstn) in frozen CH_2Cl_2 at liquid nitrogen temperature.

Fig. 6. ESR spectrum of Co(sal-batn)O_2 in frozen CH_2Cl_2 at liquid nitrogen temperature.

with the axial coordination of the pendant group, although the axial coordination is not complete in the frozen solution.

From ESR spectra at liquid nitrogen temperature, it was found that axial coordination of ether oxygen occurs in Co(sal-moen) but not in Co(sal-motn). Further, the axial coordination was complete in Co(sal-ipsen) [4] but not complete in Co(sal-ipstn). These results suggest that if the donor atom is the same, the pendant tail is sterically favorable for axial coordination when connected to the salen skeleton through two methylene groups. This is supported by the single-crystal X-ray analysis of [Co(sal-esen)(NH₃)]PF₆ (P = CH₂CH₂—S—C₂H₅) [19] in which the pendant thioether coordinates to the metal with the Co—S distance of 2.25 Å while maintaining the CoN_2O_2 moiety in the usual planar configuration. However, the axial coordination can occur in Co(sal-eatn) but not in Co(sal-batn). This suggests that the axial coordination of amine nitrogen is possible even when the amine nitrogen is bonded to the salen skeleton through three methylene groups, and that its coordinating ability is determined not only by the number of the methylene groups but also by the bulkiness of the substituents attached to it. In fact, model building studies show that a seven membered chelate ring structure involving three methylene groups can be constructed without severe strain.
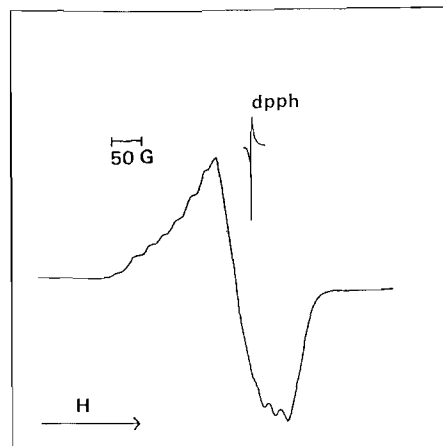
Although all the Co(II) complexes discussed above are inert towards dioxygen at room temperature, they show high oxygen affinity at low temperature. That is, when an orange dichloromethane solution of the Co(II) complex was frozen in an open atmosphere, the solution assumed an almost black color and showed an ESR signal near $g = 2.0$ with a half-bandwidth of 100 gauss. Figure 6 shows an ESR spectrum of Co(sal-batn)O_2 thus obtained. It is typical of the 1:1 Co—O_2 adduct in which the unpaired electron is localized largely on the dioxygen [6, 20]. It is not certain, however, from the ESR spectra if the axial coordination has occurred in these O_2-adducts. We have, therefore, studied the RR spectra of these dioxygen adducts since the $\nu(O_2)$ frequency is markedly different between 'base-free' and 'base-bound' complexes.

Figure 7 shows the RR spectra of methylene chloride solutions of Co(sal-moen) which were saturated with $^{16}O_2$ (A) and $^{18}O_2$ (B) at $-90\,°C$. The strong band at 1150 cm^{-1} of the former is shifted to 1088 cm^{-1} by $^{16}O_2-^{18}O_2$ substitution. The observed shift of 62 cm^{-1} is in good agreement with the theoretical isotope shift expected for a perturbed O_2 molecules. As discussed in our previous work [2, 4], this $\nu(O_2)$ frequency represents a typical 'base-bound', six-coordinate Co(II)—O_2 adduct. This is also supported by the observation of the $\nu(Co-O_2)$ band at 538 cm^{-1} which is shifted to 517 cm^{-1} by $^{16}O_2-^{18}O_2$ substitution [9]. It is interesting to note that the weak band at 1094 cm^{-1} is also shifted to 1034 cm^{-1} by $^{16}O_2-^{18}O_2$ substitution. Similar bands have already been observed for the O_2 adducts of Co(salen) (1097 cm^{-1}) and Co(sal-Hpen) (1095 cm^{-1}) [2]. These frequencies are characteristic of 'base-free' O_2 adducts of Co(salen) derivatives although their structures are still under investigation at this time. As stated earlier, the ESR spectrum of Co(sal-moen) indicates that
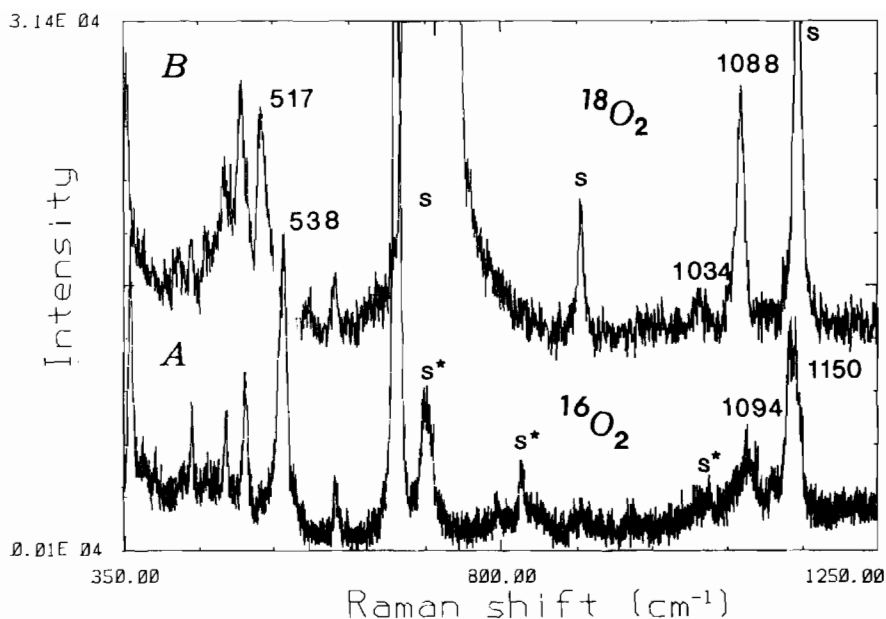
Fig. 7. RR spectra of Co(sal-moen)O$_2$ at −90 °C (568 nm excitation): (A) ^{16}O$_2$ (in CD$_2$Cl$_2$), (B) ^{18}O$_2$ (in CH$_2$Cl$_2$). S and S* indicate the bands due to CH$_2$Cl$_2$ and CD$_2$Cl$_2$, respectively.

the four- and five-coordinate species coexist in frozen solution at liquid nitrogen temperature. Our RR studies show that the dioxygen adducts of these two species are in equilibrium in methylene chloride at −90 °C.

As stated earlier, the ESR spectrum of Co(sal-ipstn) in frozen CH$_2$Cl$_2$ indicated a mixing of the four- and five-coordinate species. The RR spectrum obtained at −90 °C shows that, in the presence of O$_2$, Co(sal-ipstn) is completely converted to the six-coordinate O$_2$ adduct in which the pendant sulfur atom is coordinated to the axial position *trans* to the dioxygen although it is bonded to the Co(salen) core via three CH$_2$ groups. These observations suggest that the coordinating ability of the pendant sulfur atom increases by lowering the temperature and/or by adding dioxygen.

As shown in Table II, the remaining three Co(II) complexes also exhibit the ν(O$_2$) and ν(Co−O$_2$) in the regions similar to those of Co(sal-ipstn)O$_2$ under similar experimental conditions. These results indicate that 'base-bound', six-coordinate Co(II)−O$_2$ adducts can be formed at −90 °C in methylene chloride regardless of the nature of the donor atom (ether oxygen, thioether sulfur or amine nitrogen) as long as the donor atom is connected to the Co(salen) structure via two or three methylene groups. It is noted, however, that the O$_2$ affinity is largest when the thioether sulfur atom coordinates to the axial position. This is consistent with the observation that Co(sal-ipsten) develops the darkest color upon oxygenation and that the ν(O$_2$) and ν(Co−O$_2$) are the lowest among the five complexes studied (Table II).

TABLE II. ν(O$_2$) and ν(Co−O$_2$) Frequencies (cm^{-1}) of O$_2$ Adducts of Co(salen) Derivatives Containing Pendant Groups in Methylene Chloride at −90 °C

Complex	ν(O$_2$)[a]	ν(Co−O$_2$)
Co(sal-moen)O$_2$	1150[b](1088)	538[b](517)
Co(sal-motn)O$_2$	1147[c](1089)	535[d]
Co(sal-ipstn)O$_2$	1142(1078)	522[d]
Co(sal-eatn)O$_2$	1149[c](1083)	534[d]
Co(sal-batn)O$_2$	1147[c](1085)	535[d]

[a]The numbers in brackets are those of the ^{18}O$_2$ adducts. [b]In CD$_2$Cl$_2$. [c]Partly overlapped with the solvent band. [d]The ν(Co−^{18}O$_2$) frequencies could not be determined unambiguously.

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