Synthesis and Spectroscopic Properties of Co(salen) Derivatives Containing Pendant Thioether Groups and their Dioxygen Adducts

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Abstract

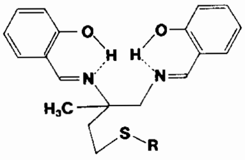
Two Co(salen) derivatives, Co(sal-ipsen) and Co(sal-bsen), containing pendant $(CH_2)_2-S-(i-C_3H_7)$ and $(CH_2)_2-S-C_6H_5$ groups were synthesized. Electronic and ESR spectra in methylene chloride show that the former is five-coordinate with pendant thioether coordination at 198 K or below whereas the latter is four-coordinate at 198 K and becomes a mixture of the four- and five-coordinate species at liquid nitrogen temperature. Upon oxygenation at low temperatures, both complexes form dioxygen adducts in which the pendant thioether groups are coordinated to the *trans* position to dioxygen. Resonance Raman spectra show that Co(sal-ipsen) yields an equilibrium mixture of the 1:1 and $1{:}2(O_2/Co)$ adducts at 190 K while Co(sal-bsen) forms only the 1:1 adduct under similar conditions. These differences between Co(sal-ipsen) and Co(sal-bsen) can be attributed to the variance in basicity of their pendant sulfur atoms.

Introduction

Reversible dioxygen-carrying functions of N,N′-disalicylideneethylenediaminatocobalt(II)(Co(salen)) and its congeners are well known and are regarded as models for natural oxygen carriers such as hemoglobin and myoglobin [1]. These cobalt(II) complexes generally need a base as the fifth ligand to bind molecular oxygen. Such a pentacoordination consisting of a planar tetradentate ligand and an axial base is indeed the coordination environment at the active site of hemoglobin [2] and myoglobin [3], where an imidazole group on globin protein coordinates to heme iron affording a square-pyramidal geometry around the metal. It is worthwhile, therefore, to design salen analogs possessing a pendant group capable of axial coordination.

Several quinquedentate salen analogs possessing the pyridyl [4], phenol [5], ether [5] or thioether [6] group as the axial tail group have been synthesized. Coordination of the pendant pyridyl group in N,N′-[2-(2′-pyridyl)ethyl]ethylenebis(salicylideneaminato)cobalt(II) [4, 7] and its dioxygen adduct [8] has been confirmed by X-ray analysis. Previously, we investigated the structures of the dioxygen adducts of N,N′-disalicylidene-2-methyl-4-(2-methoxy-5-methylphenyl)-1,2-butanediaminatocobalt(II) and N,N′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediaminatocobalt(II) by means of resonance Raman (RR) spectroscopy and found that the pendant group coordinates to the Co atom in the former but not in the latter [9]. Although a salen analog with a pendant thioether group, (S)-N,N′-[(2-(methylthio)ethyl)ethylene]bis(salicylideneamine), was prepared by Amundsen *et al.* [6], they found no evidence of thioether coordination in its Cu(II), Ni(II) and Fe(III) complexes.

In order to study the effect of the pendant thioether group on the configuration and oxygenation of Co(II) complexes, we have prepared two new quinquedentate salen analogs containing pendant thioether groups; N,N′-disalicylidene-2-methyl-4-(1-methylethylthio)-1,2-butanediamine (abbreviated as H_2(sal-ipsen), Fig. 1,a) and N,N′-disalicylidene-2-methyl-4-phenylthio-1,2-butanediamine (abbreviated as H_2(sal-bsen), Fig. 1,b), and measured the electronic, ESR and RR spectra of their Co(II) complexes in methylene chloride in the absence and presence of dioxygen.



H_2(sal-ipsen), $R = i\text{-}C_3H_7$ (Ia)

H_2(sal-bsen), $R = C_6H_5$ (Ib)

Fig. 1. Structures of H_2(sal-ipsen) and H_2(sal-bsen).

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Experimental

Syntheses

The synthetic scheme for the Schiff bases is shown in Fig. 2. 4-(Methylethylthio)butane-2-one (**IIa**) and 4-phenylthiobutane-2-one (**IIb**) were prepared by the literature method [10].

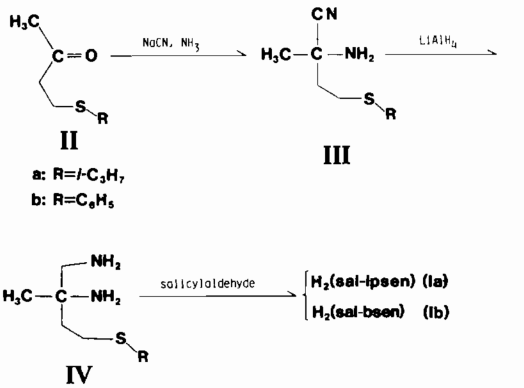

Fig. 2. Synthetic scheme of H_2(sal-ipsen) and H_2(sal-bsen).

2-Amino-2-methyl-4-(1-methylethylthio)butylonitrile (IIIa)

A mixture of 4-(1-methylethylthio)butane-2-one (10 g), ammonia (28%, 38 ml), sodium cyanide (6.7 g), and ammonium chloride (7.3 g) were placed in a 300 ml flask. The flask was sealed with a stopper and heated at 70–75 ℃ under stirring for 20 h. The reaction mixture was shaken with five 100 ml portions of ether, and the combined ether extract was dried over sodium sulfate. On evaporating the solvent the crude aminonitrile was obtained as a pale-yellow oily substance.

2-Amino-2-methyl-4-phenylthiobutylonitrile (IIIb)

This was obtained as a pale-yellow oily substance in nearly the same way as mentioned above using 4-phenylthiobutane-2-one instead of 4-(1-methylethylthio)butane-2-one.

2-Methyl-4-(1-methylethylthio)-1,2-butanediamine (IVa)

To a stirred mixture of $LiAlH_4$ (15 g) in absolute ether (300 ml) was added dropwise a solution of the aminonitrile, **IIIa** (*ca.* 12 g) in ether (50 ml). After the addition was completed, the mixture was stirred under reflux for 40 h and then decomposed with water. The ether layer was separated and the residue was extracted with ten 100 ml portions of ether. To the combined ether extract was bubbled a stream of hydrogen chloride. The solvent was evaporated and the residue was dried over P_2O_5 in a vacuum desiccator. The crude diamine dihydrochloride formed a pale yellow semisolid. It was used for the preparation of the Schiff base H_2(sal-ipsen) without further purification.

2-Methyl-4-phenylthio-1,2-butanediamine (IVb)

This was obtained in nearly the same way as mentioned above by the reduction of the aminonitrile (**IIIb**).

H_2(sal-ipsen) (Ia)

2-Methyl-4-(1-methylethylthio)-1,2-butanediamine dihydrochloride (2.5 g) and salicylaldehyde (2.5 g) were dissolved in methanol (20 ml). The mixture was neutralized by the addition of triethylamine (2 g). The solvent was evaporated on a water bath, and the Schiff base was extracted with chloroform and submitted to an alumina column (15 X 70 mm) for purification. The Schiff base was obtained as a yellow viscous substance on evaporating the solvent.

H_2(sal-bsen) (Ib)

This was obtained as a yellow viscous substance by the reaction of 2-methyl-4-phenylthio-1,2-butanediamine dihydrochloride (2.8 g) and salicylaldehyde (2.5 g) in the presence of triethylamine (2 g).

Co(sal-ipsen)

A mixture of crude H_2(sal-ipsen) (390 mg) and cobalt(II) acetate tetrahydrate (250 mg) in ethanol (50 ml) was stirred for 10 h under reflux in an atmosphere of nitrogen. Red crystals thus formed were filtered and dried *in vacuo*. *Anal.* Found: C, 59.41; H, 5.92; N, 6.53. Calc. for $C_{22}H_{26}N_2O_2SCo$: C, 59.84; H, 5.94; N, 6.35%.

Co(sal-bsen)

This complex was obtained as red crystals by the reaction of H_2(sal-bsen) (420 mg) and cobalt(II) acetate tetrahydrate (250 mg) in ethanol. *Anal.* Found: C, 61.79; H, 5.22; N, 5.65. Calc. for $C_{25}H_{24}N_2O_2SCo\cdot\frac{1}{2}H_2O$: C, 61.98; H, 5.20; N, 5.78%.

Measurements

Electronic spectra in CH_2Cl_2 at room temperature were recorded on a Shimadzu Multipurpose Spectrometer Model MPS-5000. Spectra at low temperature were recorded on a Perkin-Elmer Model 320 spectrophotometer with a cryocell designed at Marquette University. Dry ice–ethanol mixture was used to cool the solution to 198 K. X-band ESR spectra were recorded on a JES-FE3X Spectrometer in frozen CH_2Cl_2 by the use of liquid nitrogen as the cryogenic material. RR spectra were measured in CH_2Cl_2 under high dioxygen pressure (~4 atom) by using the mini-bulb method reported previously [11]. The bulb was attached to the front edge of the cold tip cooled by a CTI Model 21 closed cycle helium refrigerator. The spectra was recorded on a Spex Model 1401 double monochromator with a Spex digital photometer system. Excitation at 568.2 nm was made by a Spectra-Physics Model 164-01 Kr-ion laser. Calibration of frequency reading was made by using the solvent bands.

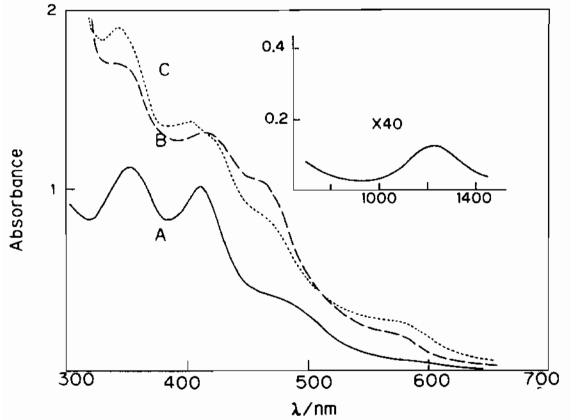

Fig. 3. Electronic spectra of Co(sal-ipsen) in methylene chloride: (A) room temperature (9.84×10^{-5} M/L); (B) 198 K; (C) 198 K under oxygen. Traces (B) and (C) were obtained with a solution of undetermined concentration, and their absorbance scales are shifted relative to trace (A).

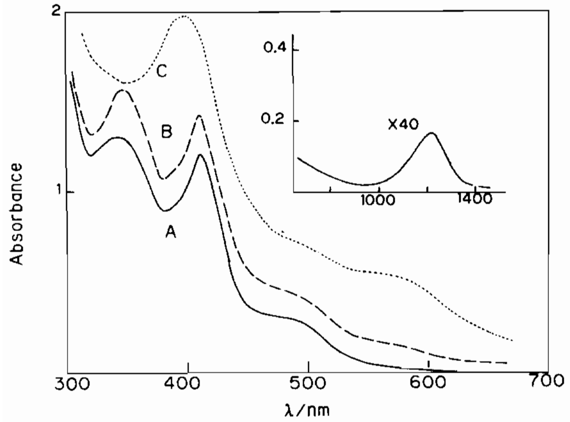

Fig. 4. Electronic spectra of Co(sal-bsen) in methylene chloride: (A) room temperature (1.145×10^{-4} M/L); (B) 198 K; (C) 198 K under oxygen. Traces (B) and (C) were obtained with a solution of undetermined concentration, and their absorbance scales are shifted relative to trace (A).

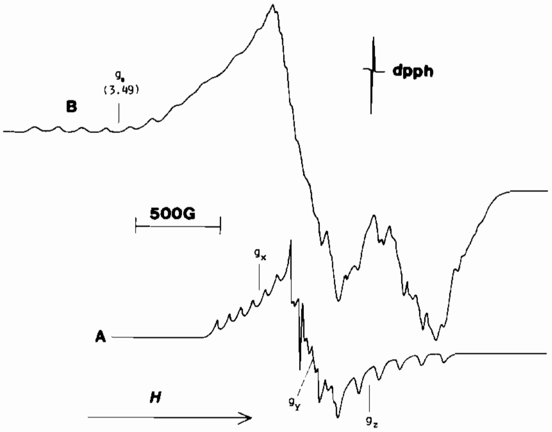

Fig. 5. ESR spectra of Co(sal-ipsen) (trace A) and Co(sal-bsen) (trace B) in frozen methylene chloride at liquid nitrogen temperature.

Results and Discussion

Figures 3,A and 4,A show the electronic spectra of Co(sal-ipsen) and Co(sal-bsen), respectively, in methylene chloride at room temperature. Both spectra are similar to that of Co(salen) [12] and characterized by a band near 1200 nm (shown in insets) which is typical of planar Co(II) complexes of salen-like Schiff-base ligands [13].

When the solution is cooled to 198 K, the spectrum of Co(sal-ipsen) changes markedly as shown in Fig. 3,B. This spectrum resembles that of Co(salen)-py [14]† except that the 413 nm band of the former is shifted to 380 nm in the latter. The penta-coordinate structure of Co(sal-ipsen) at low temperatures is also supported by the ESR spectrum in frozen methylene chloride shown in Fig. 5,A. It exhibits a well-defined rhombic pattern ($g_x = 2.48$, $g_y = 2.22$, $g_z = 2.01$; $A_x = 66$, $A_y = 33$, $A_z = 115$G). These ESR parameters are similar to those of Co(salen)py [14], and can be interpreted in terms of $(d_{z^2})^1$ electronic configuration typical of a five-coordinate Co(II) complex with a base at the apical site [14, 15]. Thus, we conclude that the thioether group of Co(sal-ipsen) occupies the axial position at low temperatures.

In contrast to Co(sal-ipsen), the electronic spectrum of Co(sal-bsen) at 198 K (Fig. 4,B) is essentially the same as that at room temperature. Figure 5,B shows the ESR spectrum of Co(sal-bsen) in frozen methylene chloride at liquid nitrogen temperature. Although the central part of the spectrum is very similar to that of Co(sal-ipsen) (Fig. 5,A), the signals at lower and higher magnetic fields (at $g = 3.49$ and $g < 2$) resemble those of planar Co(salen) and its analogs [15], and can be interpreted in terms of the $(d_{yz})^1$ electronic configuration. Thus, we conclude that Co(sal-bsen) is a mixture of a four-coordinate and a five-coordinate species even at liquid nitrogen temperature. This should be contrasted to the case of Co(sal-ipsen) where the coordination of the pendant group is complete at 198 K. These results may be attributed to the difference in basicities between the $(CH_2)_2$–S–$(i\text{-}C_3H_7)$ and $(CH_2)_2$–S–C_6H_5 groups; the former sulfur is more basic than that of the latter because the $i\text{-}C_3H_7$ group is electron-donating while the C_6H_5 group is rather electron-withdrawing [16]. In fact, the pK_a values of $i\text{-}C_3H_7SH$ and C_6H_5SH are 10.86 and 6.50, respectively [17].

The oxygenation of Co(sal-ipsen) and Co(sal-bsen) was examined by means of electronic, ESR and RR spectroscopy. Although both complexes are inert to

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†Previously, the electronic spectrum of Co(salen)py was measured in the 500–2000 nm region using the reflectance method [14]. In this study, we measured the absorption spectrum of Co(salen) in methylene chloride containing pyridine in the 300–700 nm region. The band maxima (nm) and their extinction coefficients (dm^3 mol^{-1} cm^{-1}) are: 342(4575), 380(4360), 465(2070) and 570(420).

oxygenation at room temperature, their methylene chloride solutions exhibit high sensitivity toward molecular oxygen at low temperatures. Figure 3,C shows the electronic spectrum of Co(sal-ipsen) in methylene chloride saturated with oxygen at 198 K. It is seen from Fig. 3,B and 3,C that the 415 nm band is shifted to 400 nm and the band near 570 nm becomes stronger upon oxygenation. The spectrum shown in Fig. 4, C was obtained by exposing a methylene chloride solution of Co(sal-bsen) to oxgyen at 198 K. It shows a broad intense absorption band at 398 nm, and is markedly different from those of Figs. 4,A and 4,B which are due to the planar complex with non-coordinating pendant thioether group. These spectral behaviors seem to suggest the formation of dioxygen adducts at 198 K. This is confirmed by the ESR spectra shown in Fig. 6 which were obtained in frozen methylene chloride at liquid nitrogen temperature. Both compounds exhibit ESR signals near $g \sim 2.02$ and their hyperfine structures due to the Co nucleus ($I = 7/2$) are almost indiscernible. These features are typical of 1:1 (O_2/Co) dioxygen adducts in which the unpaired electron is localized largely on the dioxygen [1]. It should be noted, however, that the ESR results do not rule out the possibility of forming 1:2 adducts in solution at low temperatures since the peroxo dimers are ESR-silent.

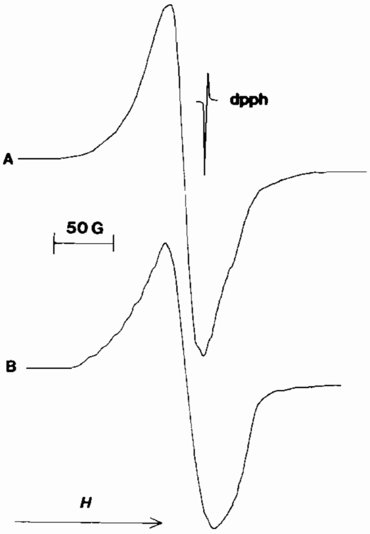

Fig. 6. ESR spectra of dioxygen adducts of Co(sal-ipsen) (trace A) and Co(sal-bsen) (trace B) in frozen methylene chloride at liquid nitrogen temperature.

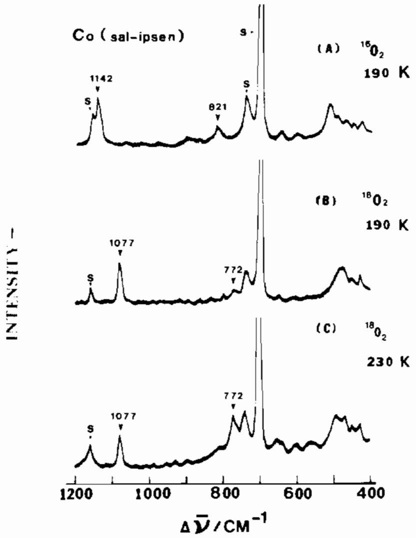

Fig. 7. RR spectra of dioxygen adducts of Co(sal-ipsen): (A) under $^{16}O_2$ at 190 K; (B) under $^{18}O_2$ at 190 K; (C) under $^{18}O_2$ at 230 K.

In order to gain further insight into the structure of the oxygenated species, the RR spectra of Co(sal-ipsen) and Co(sal-bsen) in methylene chloride were measured under ~4 atm O_2 pressure at ~190 K [11]. As is seen in Fig. 7, A, the RR spectrum of the former exhibits two bands at 1142 and 821 cm^{-1} which are shifted at 1077 and 772 cm^{-1}, respectively, by $^{16}O_2$–$^{18}O_2$ substitution (Fig. 7, B). These frequencies are close to those observed previously for the 1:1 and 1:2 dioxygen adducts of Co(salen)py measured under similar experimental conditions [18], and suggest the following equilibria in solution:

$$\text{Co(sal-ipsen)} + O_2 \rightleftharpoons \text{Co(sal-ipsen)}O_2\ (1142\ \text{cm}^{-1})$$

$$\text{Co(sal-ipsen)}O_2 + \text{Co(sal-ipsen)} \rightleftharpoons [\text{Co(sal-ipsen)}]_2O_2\ (821\ \text{cm}^{-1})$$

As shown in Figs. 7, B and 7, C, the $\nu(^{18}O_2)$ band of the 1:1 adduct becomes weaker and that of the 1:2 adduct becomes stronger when the solution is warmed to 230 K. This observation confirms our previous finding [11] that the formation of the 1:1 adduct is favored at lower temperatures.

In contrast, similar experiments with Co(sal-bsen) show only the $\nu(O_2)$ of the 1:1 adduct at 1145 cm^{-1} (1080 cm^{-1} for the $^{18}O_2$ adduct). No band corresponding to the 1:2 adduct was observed even at 230 K. This is also supported by the electronic spectrum of an oxygenated Co(sal-bsen) solution (Fig. 4, C) which is simpler than that of an oxygenated Co(sal-ipsen) solution (Fig. 3, C).

Finally, the $\nu(O_2)$ observed for these 1:1 and 1:2 adducts are typical of dioxygen adducts of Co(salen) derivatives in which dioxygen occupies the axial position *trans* to a base ligand [9, 11, 18]. Thus, our RR studies confirm the pendant sulfur coordination in the dioxygen adducts of both complexes. In the case of Co(sal-bsen), pendant sulfur coordination occurs only when the solution is oxygenated at 190 K. This seems to suggest that the formation of the polar $Co^{+\delta}$–$O_2^{-\delta}$ bond [19] stabilizes the Co–S bond in the *trans* position and vice versa. Apparently, this cooperative effect is not sufficient to stabilize the Co–O–O–Co bond for Co(sal-bsen).

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