# Resonance Raman Spectra of Dioxygen Adducts of Co(salen) Derivatives Containing Pendant Oxygen Donors

K. BAJDOR, H. OSHIO, K. NAKAMOTO
*Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wis. 53233, U.S.A.*
W. KANDA, H. ŌKAWA and S. KIDA
*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812, Japan*

Received November 29, 1984

## Abstract

The resonance Raman spectra of dioxygen adducts of Co(sal-Hpen) and its methoxy derivative, Co(sal-mpen) were measured in methylene chloride solution at ~ −90 °C. Co(sal-mpen)$O_2$ exhibits the $\nu(O_2)$ at 1148 $cm^{-1}$, typical of six-coordinate Co(salen)(base)-$O_2$ type complexes, whereas Co(sal-Hpen)$O_2$ shows the $\nu(O_2)$ at 1095 $cm^{-1}$, which is close to that of 'base-free' Co(salen)-$O_2$ (1097 $cm^{-1}$). These results indicate that the pendant methoxyphenyl group of Co(sal-mpen)$O_2$ is coordinated to the axial position whereas the pendant hydroxyphenyl group of Co(sal-Hpen)$O_2$ is free from such interaction. When anisole is added to a solution of Co(salen)-$O_2$, a new $\nu(O_2)$ band due to Co(salen)(anisole)$O_2$ appears at 1145 $cm^{-1}$. No such band is observed, however, when phenol is added to the same solution. The phenolate ion ($OR^-$) tends to form Co(III) complexes Co(III)-(salen)($OR^-$) which yield peroxo dimers, $[\{Co(III)(salen)(OR^-)\}_2O_2]^{2-}$ ($\nu(O_2)$, ~805 $cm^{-1}$) upon oxygenation.

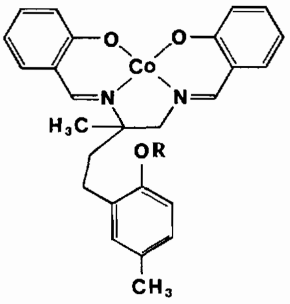
## Introduction

Co(salen)(N,N′-ethylenebis(salicyclideniminato)-cobalt(II)) is the first synthetic cobalt-oxygen carrier, discovered by Tsumaki [1] in 1938. It absorbs dioxygen at room temperature in the solid state to form a 'base-free' adduct, $[Co(salen)]_2O_2$ in which two Co atoms are linked by the Co–O–O–Co bridge. We have previously shown that its $\nu(O_2)$(1011 $cm^{-1}$) [2] is higher (by 123 $cm^{-1}$) than that of the corresponding 'base-bound' crystalline adduct, $[Co(salen)(py)]_2O_2$ (888 $cm^{-1}$) [3]. Similar observations have been made for a pair of Co(TPP)$O_2$(1278 $cm^{-1}$ in an Ar matrix) [4] and Co(TPP)(py)$O_2$ (1144 $cm^{-1}$ in $CH_2Cl_2$ solution) [5]. These results demonstrate that the coordination of a base ligand at the axial position increases the negative charge on the $O_2$ *via* σ- and/or π-donation, thus stabilizing the Co–$O_2$ bond and shifting the $\nu(O_2)$ to lower frequency.

In biological oxygen carriers such as hemoglobin [6] and myoglobin [7], dioxygen binds to the axial position of iron-protoporphyrin which is *trans* to the proximal imidazole(F8 His) of the peptide chain. To mimic these hemoproteins, iron–porphyrins [8, 9] and Co(salen) derivatives [10] containing pendant N-base ligands have been prepared. Cytochrome P-450 (in the D-state) [11] binds dioxygen or carbon monoxide at the axial position of iron-protoporphyrin which is *trans* to the mercaptide sulfur of a cysteinyl residue. This state was modeled by iron–porphyrins having pendant thiolate groups [12, 13].

According to X-ray analysis [14] the ferric heme of the abnormal α subunit of Hemoglobin M Boston is bonded to the phenolate oxygen of the tyrosine residue (E7 Tyr), and not to the proximal histidine. The resonance Raman (RR) band observed at 603 $cm^{-1}$ was assigned to the $\nu$(Fe–O(tyr)) of this compound [15]. Recent X-ray analysis on beef liver catalase [16] indicates that the phenolate oxygen of the tyrosine residue (357 Tyr) occupies the axial position of the heme with the estimated Fe–O distance of 1.5 A. It has been suggested that the ligand *trans* to the mercaptide sulfur in the resting (A-) state of cytochrome P-450 is an oxygen donor and not a N-base ligand, as generally assumed [17]. All these reports point to the importance of axial oxygen coordination in hemoprotein chemistry.

We [18] have previously synthesized Co(sal-Hpen)-(N,N′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-butane-1,2-diamine, Fig. 1a) and its derivative, Co(sal-mpen) (Fig. 1b) which contain a pendant hydroxyphenyl and a methoxyphenyl group, respec-



R = H (a) or $CH_3$ (b)

Fig. 1. Structures of Co(sal-Hpen) (a) and Co(sal-mpen) (b).

0020-1693/85/$3.30

tively. The main purpose of this investigation is to determine by RR spectroscopy whether these pendant groups are coordinated to the axial position *trans* to dioxygen.

## Experimental

### *Compounds*

Co(sal-Hpen) and Co(sal-mpen) were synthesized by the methods reported previously [18]. Dichloromethane was distilled from $CaH_2$. Phenol and anisole were purchased from Aldrich Chemicals, and were purified respectively by sublimation and distillation before use. The $^{16}O_2$ (pre-purified, Matheson Gas Co.) and $^{18}O_2$ (~99% pure, Monsanto Research) gases were used as received.

### *Spectral Measurements*

The RR spectra were recorded on a Spex model 1401 double monochromator equipped with a Spex DPC-2 digital photometer system. Excitations at 568.2 and 514.5 nm were made by a Spectra-Physics Model 164-01 Kr-ion laser and a Spectra-Physics Model 164-08 Ar-ion laser, respectively. In general, the former gave better results since the Co–$O_2$ CT bands of $O_2$ adducts of Co(salen) derivatives are located near 550 nm [19]. Preparation of the sample for spectral measurement was made by using the mini-bulb method described previously [19]. All the spectra were obtained in $CH_2Cl_2$ solution at ~−90 °C under ~4 atm $O_2$ pressure. The concentrations of the Co complexes were $\sim 5 \times 10^{-3}$ M/L except for Co(sal-mpen) ($2 \times 10^{-2}$ M/L). About 3% of phenol or anisol was added to the methylene chloride solution of Co(salen). Calibration of the frequency reading was made by using the solvent bands. The accuracy of frequency reading was ±1 $cm^{-1}$.

## Results and Discussion

Figure 2 shows the RR spectra of Co(sal-mpen) and Co(sal-Hpen) in methylene chloride at ~−90 °C, saturated by $^{16}O_2$ and $^{18}O_2$ respectively. As seen in traces A and B, Co(sal-mpen) exhibits a new band at 1148 $cm^{-1}$ upon oxygenation, and this band is shifted to 1087 $cm^{-1}$ by $^{16}O_2$–$^{18}O_2$ substitution. Since these frequencies are very close to the $\nu(O_2)$ of six-coordinate Co(salen)(py)$O_2$ (1144 $cm^{-1}$) and its $^{18}O_2$ analog (1082 $cm^{-1}$) [20], these bands can be assigned to similar vibrations of the six-coordinate species, Co(sal-mpen)$O_2$, in which the pendant methoxy oxygen is coordinated to the axial position ***trans*** to dioxygen. In contrast, Co(sal-Hpen)$O_2$ exhibits the $\nu(^{16}O_2)$ and $\nu(^{18}O_2)$ bands at 1095 and 1033 $cm^{-1}$, respectively, under similar experimental conditions (traces C and D). Clearly, the nature of coordinated dioxygen is markedly different between these two compounds.

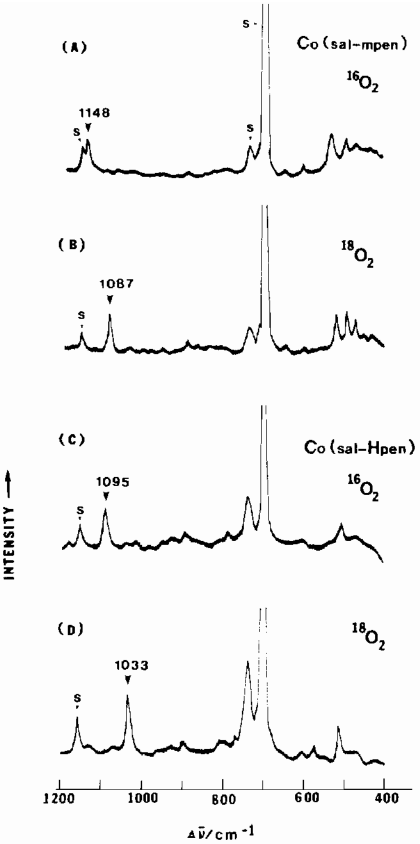


Fig. 2. RR spectra (568.2 nm excitation) of Co(sal-mpen) and Co(sal-Hpen) in methylene chloride which were saturated with $^{16}O_2$ or $^{18}O_2$ at ~−90 °C. S denotes the solvent band.

To gain more insight into the structures of these dioxygen adducts we measured the RR spectra of Co(salen) mixed with phenol and anisole in methylene chloride which were saturated with $^{16}O_2$ at ~−90 °C. As is seen in trace A of Fig. 3, Co(salen) without a base ligand exhibits the $\nu(O_2)$ at 1097 $cm^{-1}$, much lower than that of Co(salen)(py)$O_2$. When phenol is added to this solution, the $\nu(O_2)$ remains at 1097 $cm^{-1}$ indicating no coordination of phenol to Co(salen). When anisole is added instead of phenol, two $\nu(O_2)$ bands are observed at 1145 and 1096 $cm^{-1}$ (trace C). Since these frequencies are very close to those of Co(salen)(py)$O_2$(1144 $cm^{-1}$) and base-free Co(salen)-$O_2$(1097 $cm^{-1}$) respectively, we conclude that the 1145 $cm^{-1}$ band represents a six-coordinate species, Co(salen)(anisole)$O_2$ whereas the 1096 $cm^{-1}$ band originates in Co(salen)-$O_2$, which is free from anisole coordination. The former band is relatively weak immediately after the addition of anisole. However, it grows slowly at the expense of the latter band, and becomes stronger than the latter when the equilibrium state is reached after about one hour (trace C). These results provide further support for our conclusion that the pendant methoxy oxygen

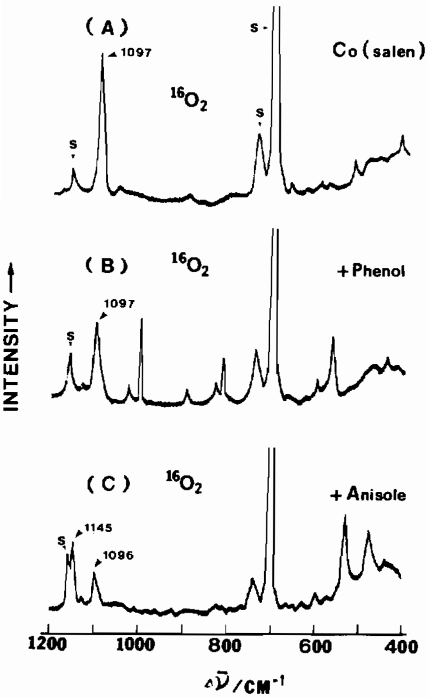


Fig. 3. RR spectra (568.2 nm excitation) of Co(salen), Co(salen) + phenol, and Co(salen) + anisole in methylene chloride which were saturated with $^{16}O_2$ at ~−90 °C. S denotes the solvent band. Extra bands between 1000 and 800 $cm^{-1}$ in trace B are due to free phenol.

of Co(sal-mpen)$O_2$ is coordinated to the axial position, whereas the pendant phenol oxygen of Co(sal-Hpen)$O_2$ is free from such bonding. The latter is contrary to our previous speculation [21] which must be retracted in view of the above finding. It should also be noted that there is no equilibrium between the coordinated and uncoordinated methoxy species in Co(sal-mpen)$O_2$, since coordination of the pendant group is thermodynamically favored by the entropy effect due to chelation.

In contrast, the phenolate ion readily coordinates to the Co(III) atom to form a series of five-coordinate complexes of the type Co(III)(salen)B where B denotes a substituted phenolate ion [22]. Co(sal-Hpen) also forms a Co(III) complex, Co(sal-pen)·(3/2)$H_2O$ where the deprotonated phenolate oxygen coordinates to the axial position [21]. When a mixture of Co(salen) and potassium phenolate in methylene chloride is reacted with dioxygen, the $\nu(O_2)$ is observed at 805 $cm^{-1}$ which is shifted to 759 $cm^{-1}$ by $^{16}O_2$–$^{18}O_2$ substitution. Since these frequencies are typical of peroxo complexes, we may formulate them as the $[\{Co(III)(salen)(OC_6H_5)\}_2O_2]^{2-}$ ion. As expected, these frequencies are lower by ~35 $cm^{-1}$ than those of $[Co(salen)(py)]_2O_2$(840 $cm^{-1}$) and its $^{18}O_2$ analog (793 $cm^{-1}$) [20], respectively. since the phenolate ion is much more electron-donating than is pyridine.

## Acknowledgement

The work performed at Marquette University was supported by the National Science Foundation Grants (PCM-8114676 and CHE-8205522).

## References

1 T. Tsumaki, *Bull. Chem. Soc. Jpn., 13,* 252 (1938).
2 M. Suzuki, T. Ishiguro, M. Kozuka and K. Nakamoto, *Inorg. Chem., 20,* 1993(1981).
3 K. Nakamoto, M. Suzuki, T. Ishiguro, M. Kozuka, Y. Nishida and S. Kida, *Inorg. Chem., 19,* 2822 (1980).
4 M. Kozuka and K. Nakamoto, *J. Am. Chem. Soc., 103,* 2162 (1981).
5 K. Bajdor, K. Nakamoto and J. Kincaid, *J. Am. Chem. Soc., 105,* 678 (1983).
6 S. E. V. Phillips, *Nature (London), 273,* 247 (1978).
7 B. Shaanan, *Nature (London) 296,* 683 (1982).
8 C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A., 70,* 2647 (1973).
9 J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert and K. Suslick, *Proc. Nat. Acad. Sci. U.S.A., 75,* 564 (1978).
10 J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley and W. T. Robinson, *J. Am. Chem. Soc., 95,* 1656 (1973).
11 L. S. Alexander and H. M. Goff, *J. Chem. Educ., 59,* 179 (1982).
12 T. G. Traylor, T. C. Mincey and A. P. Berzinis, *J. Am. Chem. Soc. 103,* 7084 (1981).
13 J. P. Collman and S. E. Groh, *J. Am. Chem. Soc., 104,* 1391 (1982).
14 D. D. Pulsinelli, M. F. Perutz and R. L. Nagel, *Proc. Nat. Acad. Sci. U.S.A., 70,* 3870 (1973).
15 K. Nagai, T. Kagimoto, A. Hayashi, F. Taketa and T. Kitagawa, *Biochem. 22,* 1305 (1983).
16 T. J. Reid III, M. R. N. Nurthy, A. Sicignano, N. Tanaka, W. D. L. Musick and M. G. Rossmann, *Proc. Nat. Acad. Sci. U.S.A., 78,* 4767 (1981).
17 J. H. Dawson, L. A. Andersson and M. Sono, *J. Biol. Chem., 257,* 3606 (1982).
18 W. Kanda, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn., 56,* 3268 (1983).
19 K. Nakamoto, Y. Nonaka, M. W. Urban, M. Suzuki, M. Kozuka, Y. Nishida and S. Kida, *J. Am. Chem. Soc., 104,* 3386 (1982).
20 K. Bajdor, K. Nakamoto, H. Kanatomi and I. Murase, *Inorg. Chim. Acta, 82,* 207 (1984).
21 W. Kanda, H. Ōkawa and S. Kida, *Chem. Comm., 973* (1983).
22 H. Ōkawa, W. Kanda, S. Kida and K. Nakamoto, *Bull. Chem. Soc. Jpn.,* submitted.