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Resonance Raman Spectra of Molecular Oxygen Adducts of Co(salen) and Its Derivatives in Solution

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Resonance Raman spectra of the molecular oxygen adducts of six Co(salen) derivatives have been measured in CH_2Cl_2 or $CHCl_3$ containing pyridine using the mini-bulb method (~−80 °C, ~4 atm O_2 pressure). These adducts exhibit the O_2 and Co–O stretching bands at 1146–1143 and 530–515 cm^{-1}, respectively. Although the former is insensitive to the nature of the in-plane ligand, the latter is sensitive to the geometry of the CoN_2O_2 core (steric effect) and the degree of π-conjugation over the entire chelate ring (electronic effect).

Introduction

N, N′-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), has been known for many years as a synthetic oxygen carrier [1]. This compound reacts with molecular oxygen reversibly in the solid state to form the 1:2 (O_2/Co) adduct, $[Co(salen)]_2O_2$. Previously, Suzuki *et al.* [2] and Nour and Hester [3] have measured the resonance Raman (RR) spectra of this compound and assigned its $\nu(O_2)$ and $\nu(CoO)$ vibrations by $^{16}O_2$–$^{18}O_2$ substitution (ν: stretching).

Both 1:1 and 1:2 adducts are in equilibrium when Co(salen) dissolved in organic solvents containing a base ligand (B) is saturated with molecular oxygen:

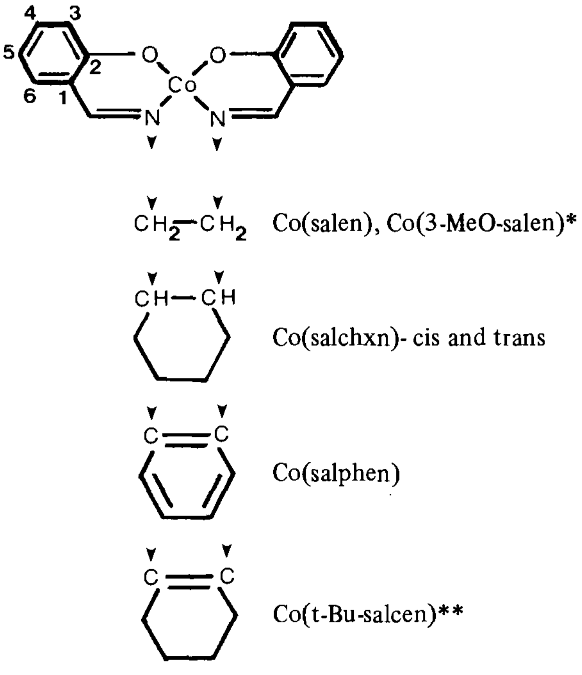
$$Co(salen)B + O_2 \rightleftharpoons Co(salen)BO_2$$

$$Co(salen)BO_2 + Co(salen)B \rightleftharpoons [Co(salen)B]_2O_2$$

Nour and Hester [4] and Nakamoto *et al.* [5] also isolated some of these 'base-bound' 1:2 adducts and measured their RR spectra and excitation profiles.

In general, it is difficult to isolate 1:1 adducts of Co(II) Schiff base complexes from the solution except for a few compounds such as Co(3-methoxysalen) [6], Co(salen) [7] and Co(bzacen:N,N′-ethylenebis(benzoylacetoniminato)anion) [8]. In the former case, it is necessary to measure the RR spectra of 1:1 adducts in solution equilibria. The concentration of the 1:1 adduct in the above equilibria increases as the temperature is lowered and as the O_2 pressure is increased [9, 10]. The mini-bulb method reported previously [10] enables us to measure the RR spectra under these conditions. This paper reports the RR spectra of a series of molecular oxygen adducts of Co(salen) derivatives obtained by using this method. Our main interest has been focused on the effect of changing the in-plane chelating ligand on the $\nu(O_2)$ and $\nu(CoO)$ vibrations of their 1:1 adducts.

The following six Co(salen) derivatives have been studied:



Co(salen), Co(3-MeO-salen)*

Co(salchxn)- cis and trans

Co(salphen)

Co(t-Bu-salcen)**

Co(salphen) and Co(t-Bu-salcen) are different from the remaining four compounds in that their π-conjugation extends over the entire ligand *via* the central C=C bond. It was, therefore, of particular interest to examine the effect of this conjugation on the $\nu(O_2)$ and $\nu(CoO)$ vibrations.

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*The MeO group at the 3 position of the salen ring.

**The t-Bu group at the 5 position of the salen ring.

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Experimental

Compounds

Co(salen) [11], Co(3-methoxy-salen) [12], cis and trans-Co(salchxn)[N,N′-cis(or trans)-1,2-cyclohexylenebis(salicylideneiminato)cobalt(II)] [12], Co(salphen) [N,N′-*o*-phenylenebis(salicylideneiminato(cobalt(II)] [11] and Co(t-Bu-salcen) [N,N′-1-cyclohexen-1,2-ylenebis(5-t-butylsalicylideneiminato)cobalt(II)] [13] were prepared by the literature methods cited herein. The gases, $^{16}O_2$ (99.99%) and $^{18}O_2$ (99.89%) were purchased from Matheson and Monsanto Research, respectively. All solvents were dried by refluxing over CaH_2 and then distilled prior to use. Pyridine (py) was dried over NaOH and distilled before use.

Spectral Measurements

RR spectra of solutions of Co(II) Schiff-base complexes ($\sim 10^{-2}$ *M*) containing 3% pyridine were measured under high oxygen pressure (~4 atm) by using the 'mini-bulb' method reported previously [10]. The bulb was attached to the front edge of the cold tip cooled by a CTI Model 21 closed cycle helium refrigerator. Approximate temperatures of the bulbs were estimated by the relative intensities of Stokes and Anti-Stokes lines of the solvent measured under the same experimental conditions. The spectra were recorded on a Spex Model 1401 double monochromator with a Spex digital photometer system. Excitation at 590 nm was made by a Spectra-Physics Model 365 dye-laser (Rhodamine 6G) pumped by a Spectra-Physics Model 164 Ar-ion laser. Calibration of frequency readings was made by using the solvent bands. Excitation at 514.5 nm was made with the above Ar-ion laser.

Results and Discussion

Co(salen) and Co(3-methoxysalen)

Trace A of Fig. 1 shows the RR spectrum (590 nm excitation) of Co(salen) in CH_2Cl_2 ($\sim 10^{-2}$ *M*) containing 2.5% pyridine at ~ −80 °C under ~4 atm O_2 pressure. The bands at 1144 and 527 cm^{-1} are assigned to the $\nu(O_2)$ and ν(CoO) of the 1:1 adduct, Co(salen)(py)O_2, because (1) they do not appear in the absence of O_2, (2) their frequencies are in the general ranges expected for the 1:1 adduct [11], and (3) they are shifted to 1082 and 511 cm^{-1}, respectively, by $^{16}O_2-^{18}O_2$ substitution (*vide infra*).

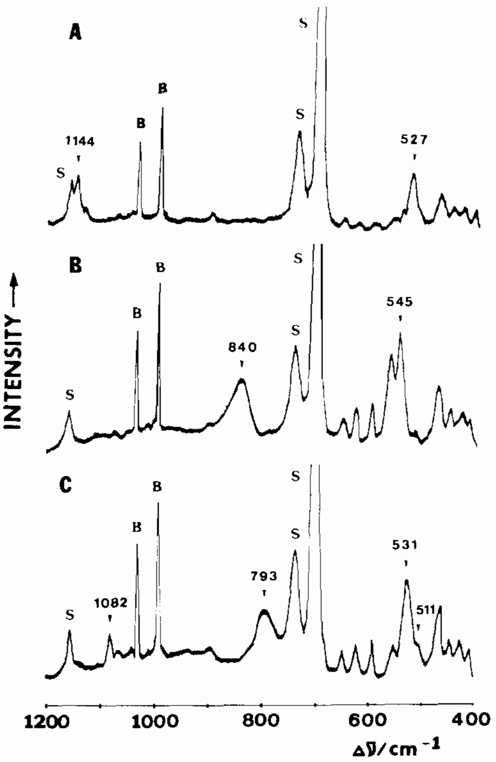

Fig. 1. RR spectra (590 nm excitation) of Co(salen) in CH_2Cl_2 containing 2.5% pyridine at ~ −80 °C. A) $\sim 10^{-2}$ *M*, saturated with ~4 atm $^{16}O_2$ gas, B) $\sim 2 \times 10^{-2}$ *M*, saturated with ~2 atm $^{18}O_2$ gas, C) $\sim 1.5 \times 10^{-2}$ *M*, saturated with ~3 atm $^{18}O_2$ gas. S denotes the solvent peak.

Trace B of Fig. 1 shows the RR spectrum obtained under similar experimental conditions except that the concentration of Co(salen) was higher ($\sim 2 \times 10^{-2}$ *M*) and the O_2 pressure was lower (~2 atm). As a result, the equilibrium was shifted to favor the formation of the 1:2 adduct; two new bands characteristic of the 1:2 adduct appear at 840 ($\nu(O_2)$) and 545 cm^{-1} (ν(CoO)) while the bands characteristic of the 1:1 adduct (1144 and 527 cm^{-1}) disappear completely. The former two bands are shifted to 793 and 531 cm^{-1}, respectively, by $^{16}O_2-^{18}O_2$ substitution (trace C).

Trace C was obtained with $^{18}O_2$ using an intermediate condition as those used for traces A and B. Thus, the $\nu(O_2)$ and ν(CoO) of both 1:1 and 1:2 adducts appear simultaneously. A RR spectrum similar to trace C was obtained when the solution used for trace A experiment was warmed to ~ −10 °C. In this case, the bands characteristic of the $^{16}O_2$ species of both adducts were observed at the frequencies shown in traces A and B.

It is to be noted that the $\nu(O_2)$ of the 1:2 adduct (840 cm^{-1}) obtained above is much lower than that found in the solid state (888 cm^{-1}) [5]. As discussed in our previous paper [10], this result may suggest an increase of the Co–O–O–Co torsional angle in going from the solid state (110° for [Co(salen)(DMF)$]_2O_2$) [14] to solution.

Since the results obtained for Co(3-methoxysalen) are similar to those of Co(salen), only the observed $\nu(O_2)$ and ν(CoO) of its 1:1 adduct are listed in Table I. Previously, Floriani and Calderazzo [6] tentatively assigned the $\nu(O_2)$ of Co(3-methoxysalen)–

TABLE I. $\nu(O_2)$ and $\nu(CoO)$ Frequencies (cm^{-1}) of 1:1 (O_2/Co) Adducts of Co(salen) Derivatives.[a]

Schiff-base complex	$\nu(^{16}O_2)$	$\nu(^{18}O_2)$	Shift	$\nu(Co-^{16}O)$	$\nu(Co-^{18}O)$	Shift
Co(salen)	1144	1082	62	527	~511	~16
Co(3-MeOsalen)	1143	1085	58	530	–	–
Co(salchxn)-trans	1145	1082	63	517	499	18
Co(salchxn)-cis	1146	1083	63	523	510	13
Co(salphen)	1145	1082	63	515	498	17
Co(t-Bu-salcen)	–*	1083	–	520	500	20

[a] In all cases, the base ligand was pyridine and the solvent was methylene chloride. The only exception was Co(salphen) for which chloroform was used as the solvent.

*Hidden under the strong Co(t-Bu-salcen) band at 1145 cm^{-1}.

(py)O_2 at 1140 cm^{-1} in its nujol mull IR spectrum. This frequency is very close to our value (1143 cm^{-1}) obtained from RR spectroscopy.

Other Co(salen) Derivatives

Traces A and B of Fig. 2 show the RR spectra (590 nm excitation) of Co(salchxn)-trans in CH_2Cl_2 containing 3% pyridine at ~ –80 °C saturated with ~3 atm $^{16}O_2$ and $^{18}O_2$ gases, respectively. The bands at 1145 and 517 cm^{-1} of trace A are assigned to the $\nu(O_2)$ and $\nu(CoO)$ of the 1:1 adduct since they are shifted to 1082 and 499 cm^{-1}, respectively, by $^{16}O_2$–$^{18}O_2$ substitution (trace B). The $\nu(^{16}O_2)$ was observed at 1143 cm^{-1} without nearby solvent bands when $CHCl_3$ was used as the solvent. As listed in Table I, the $\nu(O_2)$ was similar but the $\nu(CoO)$ was markedly different between the cis and trans complexes.

As stated earlier, Co(salphen) is different from others in that the whole chelate ring consists of one π-conjugated system. Traces C and D of Fig. 2 show the RR spectra of Co(salphen) in $CHCl_3$ containing 3% pyridine at ~ –80 °C saturated with ~3 atm $^{16}O_2$ and $^{18}O_2$ gases, respectively. The bands at 1145 and 515 cm^{-1} must be assigned to the $\nu(O^2)$ and $\nu(CoO)$ of the 1:1 adduct since they are shifted to 1082 and 498 cm^{-1}, respectively, by $^{16}O_2$–$^{18}O_2$ substitution. It should be noted that the $\nu(O_2)$ is the same but the $\nu(CoO)$ is markedly different for Co(salen) and Co(salphen). In the case of Co(t-Bu-salcen), the $\nu(^{16}O_2)$ band of the 1:1 adduct was not observed since it was hidden under the in-plane ligand band at 1145 cm^{-1}. It is safe to assume, however, that this frequency is close to that of Co(salphen) because the $\nu(^{18}O_2)$ of these two complexes are similar. On the other hand, their $\nu(CoO)$ are distinctly different; Co(t-Bu-salcen), 520 cm^{-1} *vs.* Co(salphen), 515 cm^{-1}.

Table II lists $\nu(O_2)$ and $\nu(CoO)$ of typical Co(II) chelates determined recently. It is seen that both of these frequencies are sensitive to the change in the chelating ligand. In this respect, the results obtained here (Table I) are somewhat surprising since their $\nu(O_2)$ are insensitive to the change in the chelating ligand. In general, the Co(II)–O_2 bonding is regarded as an interaction between the Co $3d_{z^2}$ and the dioxygen $2p\pi^*$ orbitals [22], and the more electrons drifted from the Co atom to the dioxygen, the lower the $\nu(O_2)$ since the latter orbital is anti-bonding. We have shown previously [10] that such lowering in $\nu(O_2)$ is

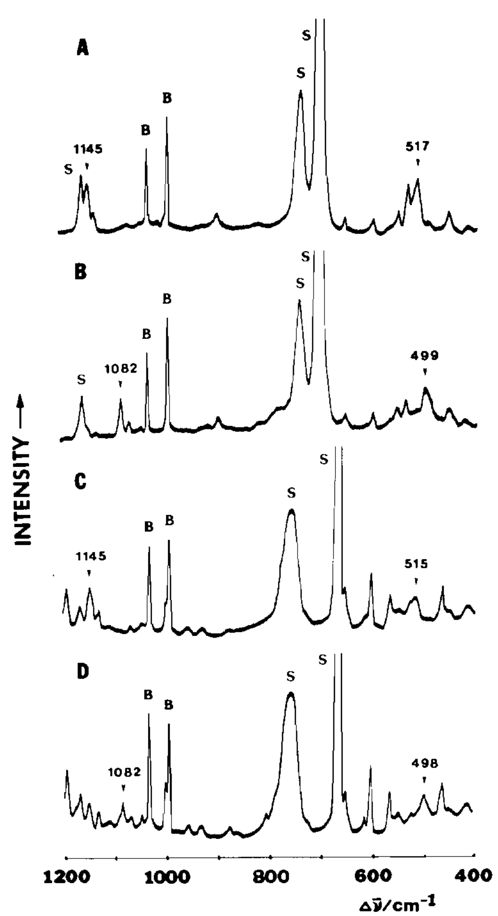

Fig. 2. RR spectra (590 nm excitation) of a Co-chelate (~10^{-2} *M*) in CH_2Cl_2 (A and B) or $CHCl_3$ (C and D) containing 3% pyridine at ~ –80 °C. A) Co(salchxn)-trans, saturated with ~3 atm $^{16}O_2$ gas, B) Co(salchxn)-trans, saturated with ~3 atm $^{18}O_2$ gas, C) Co(salphen), saturated with ~3 atm $^{16}O_2$ gas, D) Co(salphen), saturated with ~3 atm $^{18}O_2$ gas. S denotes the solvent peak.

TABLE II. $\nu(O_2)$ and ν(CoO) Frequencies (cm^{-1}) of O_2 Adducts of Co(II) Chelates.

Compound	$\nu(O_2)$	ν(CoO)	Ref.
Co(cap)(1-MeIm)	1172	–	15
Co(T_{piv}PP)(1-MeIm)	1153	516	16
Co-hemoglobin A	1152	537	17
	*1137 1107	537	17
Co-myoglobin	1153	539	17
	*1137 1103	539	
Co(J-en)(py)	1143	–	18
Co(TPP)(py)	1144	520	19
Co(PPDMEIX)(py)	1144	516	20
Co(acacen)(py)	1025	–	21

*Splitting due to Fermi resonance.

accompanied by raising in ν(CoO). Thus the present result does not seem to be accounted for on the basis of such electronic effect.

Table I shows that the ν(CoO) is sensitive to the chelating ligand; Co(salphen) which has the π-conjugation extended over the whole ligand shows the lowest ν(CoO) while Co(salen) and Co(3-methoxysalen) whose π-conjugation is interrupted at the central bridge show the highest ν(CoO). The remaining compounds exhibit their ν(CoO) between these two extremes.

According to X-ray analysis [23, 24], the N_2O_2 plane around the Co(II) atom is always distorted tetrahedrally in Co(II) Schiff base complexes. The substituents in the ethylene bridge play an important role in determining the extent of this distortion. It was also noted [23, 24] that substitution of the hydrogen atoms of the ethylene bridge by more bulky alkyl or aryl groups influences the oxygen uptake ability rather drastically. For example, the N_2O_2 plane of the cis(meso) form of the butanediamine derivative of Co(salen) is slightly closer to the planarity than that of the corresponding trans (optically active, +) form and this difference is responsible for the thousand time increase in oxygen uptake ability of the former relative to the latter [23]. Our RR study shows that the ν(CoO) decreases in the order, Co(salen)(527) > Co(salchxn), cis(523) > Co(salchxn), trans (517 cm^{-1}), which is probably the order of increasing distortion from the planarity of the N_2O_2 core.

The order of the ν(CoO) in the remaining compounds is Co(salen)(527) > Co(t-Bu-salcen)(520) > Co(salphen)(515). It is likely that this order represents the effect of π-conjugation on the Co–O bond since the N_2O_2 core is nearly planar in all these three compounds. Thus a combination of both steric and electronic effects is responsible for the observed order of the ν(CoO).

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