

an inert atmosphere. Spectra of KBr pellet samples were comparable to the spectra of Nujol mull samples prepared under a helium atmosphere in a Vacuum Atmospheres Dri-Lab glovebox.

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## Resonance Raman Spectra, Excitation Profiles, and Infrared Spectra of $[\text{Co}(\text{salen})]_2\text{O}_2$ in the Solid State

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Resonance Raman (RR) spectra of the dioxygen adduct of  $[N,N'$ -ethylenebis(salicylideneiminato)]cobalt(II),  $[\text{Co}(\text{salen})]_2\text{O}_2$ , have been measured in the crystalline state. The  $\text{O}_2$  stretching and symmetric and antisymmetric CoO stretching vibrations have been located at 1011, 533, and  $\sim 370$   $\text{cm}^{-1}$ , respectively, on the basis of  $^{16}\text{O}_2$ - $^{18}\text{O}_2$  substitution experiments. The structure of the Co-O<sub>2</sub>-Co bridge has been concluded to be approximately trans planar on the basis of the intensities of these vibrations in the IR and RR spectra. The Co-O<sub>2</sub> charge-transfer transition has been located at ca. 570 nm via the excitation profiles of the 1011- and 533- $\text{cm}^{-1}$  bands.

### Introduction

Since Tsumaki<sup>1</sup> discovered the reversible oxygenation of  $[N,N'$ -ethylenebis(salicylideneiminato)]cobalt(II),  $\text{Co}(\text{salen})$ , in the solid state, extensive investigations have been carried out on molecular oxygen adducts of Schiff base complexes, metalloporphyrins, and  $\text{N}_4$ -macrocyclic complexes.<sup>2</sup> The techniques used in these investigations include X-ray analysis, MO treatments, and electronic, ESR, and vibrational spectroscopy together with kinetic, thermodynamic, and electrochemical measurements. As to vibrational spectroscopy, the  $\text{O}_2$  stretching frequencies,  $\nu(\text{O}_2)$ , determined by infrared (IR) and resonance Raman (RR) studies have played a significant role in elucidating the nature of the metal-O<sub>2</sub> bonding.

In general,  $\nu(\text{O}_2)$  of molecular oxygen adducts fall in two ranges: the superoxo ( $\text{O}_2^-$ ) type which exhibits  $\nu(\text{O}_2)$  in the 1200-1070- $\text{cm}^{-1}$  region, and the peroxo ( $\text{O}_2^{2-}$ ) type which exhibits  $\nu(\text{O}_2)$  in the 930-740- $\text{cm}^{-1}$  region<sup>2</sup> (see Figure 1). However, the cocondensation products of metal atoms such as Pd,<sup>3</sup> Ni,<sup>3</sup> and Fe<sup>4</sup> with  $\text{O}_2$  in inert-gas matrices exhibit their  $\nu(\text{O}_2)$  between these two regions. Recently, we have located the  $\nu(\text{O}_2)$  of  $\text{Co}(\text{TPP})(\text{O}_2)$  in an argon matrix at 1278  $\text{cm}^{-1}$  that is substantially higher than the normal range for superoxo adducts.<sup>5</sup> Since the  $\nu(\text{O}_2)$  of  $\text{Co}(\text{TPP})(1\text{-MeIm})\text{O}_2$  is known to be 1142  $\text{cm}^{-1}$ ,<sup>6</sup> we have attributed this large high-frequency shift of  $\nu(\text{O}_2)$  (136  $\text{cm}^{-1}$ ) to the absence of the axial base ligand in  $\text{Co}(\text{TPP})(\text{O}_2)$ . That is, a base such as 1-MeIm increases the negative charge on the  $\text{O}_2$  via  $\sigma$  and  $\pi$  donation, thus causing the low-frequency shift of  $\nu(\text{O}_2)$ .

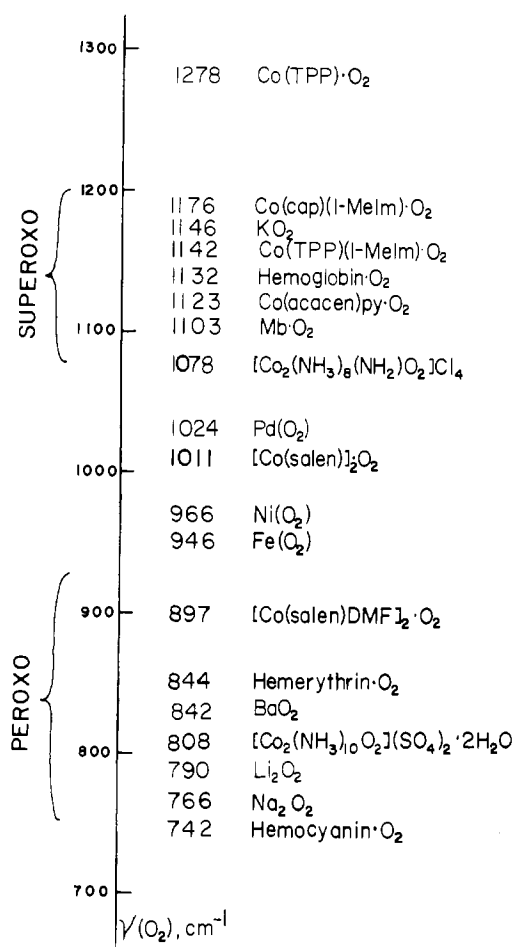
The  $\nu(\text{O}_2)$  frequency is moderately sensitive to the change in the base ligand. For example, the  $\nu(\text{O}_2)$  of the  $[\text{Co}(\text{sal-}$

en)]<sub>2</sub> $\text{O}_2$ -type complexes are at 910, 897, and 888  $\text{cm}^{-1}$  for  $\text{B} = \text{pyO}$ , DMF, and py, respectively.<sup>7</sup> However, these frequencies are much higher than the  $\nu(\text{O}_2)$  of the  $[(\text{Co}(\text{NH}_3)_3)_2\text{O}_2]^{4+}$  ion (808  $\text{cm}^{-1}$ )<sup>8</sup> since both axial and equatorial ligands in the latter are more electron donating than those in the  $[\text{Co}(\text{salen})\text{B}]_2\text{O}_2$ -type complexes. Several examples cited above clearly demonstrate that the  $\nu(\text{O}_2)$  can be varied in a wide range depending upon the electron density on the Co atom which is governed by its surrounding groups.

As stated above,  $\text{Co}(\text{salen})$  is the first synthetic reversible Co(II) oxygen carrier; 2 mol of crystalline  $\text{Co}(\text{salen})$  bind 1 mol of molecular oxygen to form a unique 1:2 adduct,  $[\text{Co}(\text{salen})]_2\text{O}_2$ , in the absence of a base ligand.  $\text{Co}(\text{salen})$  exists in several crystalline modifications, some of which are oxygen active while others are not.<sup>18</sup> Different modifications are obtained depending upon the method of preparation, and the interconversion among them is caused by heating or grinding. According to X-ray analysis,<sup>18</sup> oxygen-inactive  $\text{Co}(\text{salen})$  consists of discrete five-coordinate dimers without open structures (holes) which allow the passage of oxygen molecules in the crystal. Previously, Martell and Calvin<sup>19</sup> suggested the

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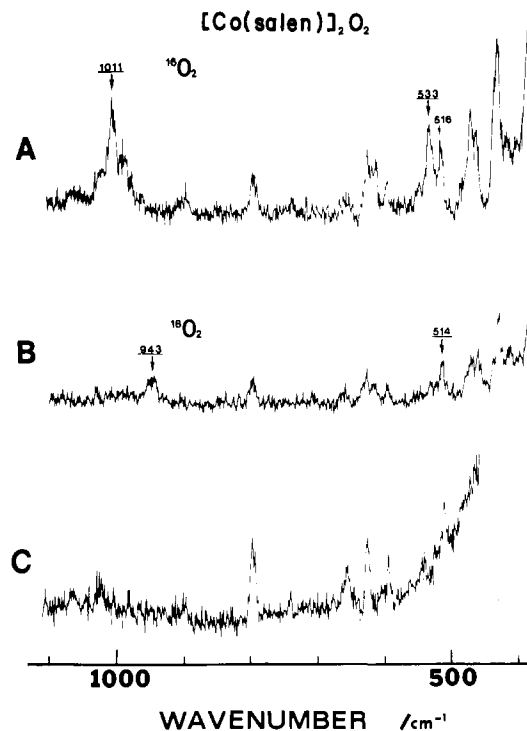
**Figure 1.** O<sub>2</sub> stretching frequencies (cm<sup>-1</sup>) of molecular oxygen adducts: Co(TPP)O<sub>2</sub>;<sup>5</sup> Co(Cap)(1-MeIm)O<sub>2</sub>;<sup>6</sup> KO<sub>2</sub>;<sup>9</sup> Co(TPP)(1-MeIm)O<sub>2</sub>;<sup>6</sup> Hb-O<sub>2</sub> (average frequency of two bands split by Fermi resonance; see ref 10); Co(acacen)(py)O<sub>2</sub>;<sup>11</sup> Mb-O<sub>2</sub>;<sup>12</sup> [Co<sub>2</sub>(NH<sub>3</sub>)<sub>8</sub>(NH<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub>];<sup>13</sup> PdO<sub>2</sub>;<sup>3</sup> [Co(salen)]<sub>2</sub>O<sub>2</sub> (present work); NiO<sub>2</sub>;<sup>3</sup> FeO<sub>2</sub>;<sup>4</sup> [Co(salen)DMF]<sub>2</sub>O<sub>2</sub>;<sup>7</sup> hemerythrin-O<sub>2</sub>;<sup>14</sup> BaO<sub>2</sub>;<sup>15</sup> [Co<sub>2</sub>(NH<sub>3</sub>)<sub>10</sub>O<sub>2</sub>](SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O;<sup>8</sup> Li<sub>2</sub>O<sub>2</sub>;<sup>15</sup> Na<sub>2</sub>O<sub>2</sub> (average frequency of two bands split by solid-state effect; see ref 16); hemocyanin-O<sub>2</sub>.<sup>17</sup>

presence of such an open structure in oxygen-active Co(salen). However, complete X-ray analysis has not been made on the active form because of the difficulty in growing single crystals.

The main objectives of our investigations are (1) to measure the RR and IR spectra of [Co(salen)]<sub>2</sub>O<sub>2</sub> and its <sup>18</sup>O<sub>2</sub> analogue, (2) to elucidate the structure of the Co-O<sub>2</sub>-Co bridge on the basis of these data, and (3) to locate the Co-O<sub>2</sub> charge-transfer (CT) band from the excitation profiles of the O<sub>2</sub> and CoO stretching vibrations. During the course of this work, Nour and Hester<sup>20</sup> published the RR spectra (514.5- or 568.2-nm excitation only) of [Co(salen)B]<sub>2</sub>O<sub>2</sub> (B = Me<sub>2</sub>SO, py, DMF, pyO, and none) and their <sup>18</sup>O<sub>2</sub> analogues. As for [Co(salen)]<sub>2</sub>O<sub>2</sub>, our results are not in complete agreement with theirs. Furthermore, we have newly provided the excitation profiles and IR spectra to discuss the origin of the Co-O<sub>2</sub> CT transition and the structure of the Co-O<sub>2</sub>-Co bridge, respectively.

### Experimental Section

The active form of Co(salen) and its O<sub>2</sub> adduct, [Co(salen)]<sub>2</sub>O<sub>2</sub>, were prepared from Co(salen)(CHCl<sub>3</sub>) and Co(salen)(py) by the literature methods.<sup>21,22</sup> The <sup>18</sup>O<sub>2</sub> gas (93% enriched) was purchased from Monsanto Research Corp., Miamisburg, Ohio. The RR spectra



**Figure 2.** RR spectra of [Co(salen)]<sub>2</sub><sup>16</sup>O<sub>2</sub> (A), [Co(salen)]<sub>2</sub><sup>18</sup>O<sub>2</sub> (B), and Co(salen) (C) by the 579-nm excitation at ~100 K.

were recorded on a Spex Model 1401 double monochromator with a Spex digital photometer system. Excitations at 457.9, 476.5, 488.0, 496.5, and 514.5 nm were made by a Spectra-Physics Model 164 Ar ion laser. Excitations at 541.3, 551.6, 571.8, 578.9, and 588.0 nm were made by a Spectra-Physics Model 365 dye-laser (Rhodamine 6G and sodium fluorescein) pumped by the above argon ion laser. The spectra of the pellets were measured by using the rotating sample technique at room temperature. It was noted that the <sup>18</sup>O<sub>2</sub>-<sup>16</sup>O<sub>2</sub> conversion occurs rapidly when the <sup>18</sup>O<sub>2</sub> adduct is irradiated by the laser beam at room temperature. So that this conversion could be slowed down, the spectra of the <sup>18</sup>O<sub>2</sub> adduct were measured by attaching its pellet on the inclined surface of a cold tip cooled to ~100 K in vacuo by a CTI Model 21 cryocooler. All the experiments were repeated several times to ensure the results. So that the excitation profiles could be plotted, relative intensities of the  $\nu(\text{O}_2)$  and  $\nu(\text{CoO})$  were measured against the 983-cm<sup>-1</sup> band of K<sub>2</sub>SO<sub>4</sub> (internal standard) which was mixed homogeneously with the sample. The corrections for spectrometer sensitivity and the  $\nu^4$  law were made for each band.

The IR spectra were measured on a Beckman 4260 IR spectrophotometer with use of the KBr pellet technique. The electronic spectra were measured by using a Shimadzu multipurpose spectrophotometer Model MPS-5000.

### Results and Discussion

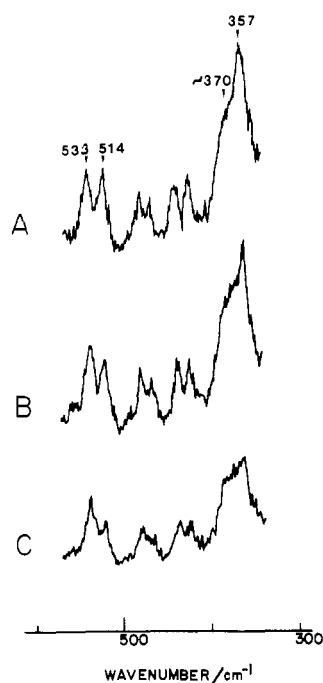
**RR Spectra.** Figure 2 shows the RR spectra of oxygen-active Co(salen) (trace C) and its <sup>16</sup>O<sub>2</sub> (trace A) and <sup>18</sup>O<sub>2</sub> adducts (trace B) obtained by using the 579-nm excitation. So that the <sup>18</sup>O<sub>2</sub>-<sup>16</sup>O<sub>2</sub> exchange by the laser irradiation could be minimized, the spectrum of the <sup>18</sup>O<sub>2</sub> adduct was measured at ~100 K in vacuo. The same condition was employed for the other compounds to facilitate the comparison of the spectra. The <sup>16</sup>O<sub>2</sub> adduct exhibits two strong bands at 1011 and 533 cm<sup>-1</sup> which are absent in the deoxygenated compound. Furthermore, these bands are sensitive to the <sup>16</sup>O<sub>2</sub>-<sup>18</sup>O<sub>2</sub> substitution; the former is shifted to 943 cm<sup>-1</sup> while the latter is probably shifted to the vicinity of the 514-cm<sup>-1</sup> band. Thus, it is most reasonable to assign the bands at 1011 and 533 cm<sup>-1</sup> to  $\nu(\text{O}_2)$  and  $\nu(\text{CoO})$ , respectively.

The RR spectra of these compounds were also measured at room temperature by using the 514.5-nm excitation. In this case, the <sup>18</sup>O<sub>2</sub> adduct was readily converted into its <sup>16</sup>O<sub>2</sub> adduct during the measurements. Thus, a pellet of the <sup>18</sup>O<sub>2</sub> adduct

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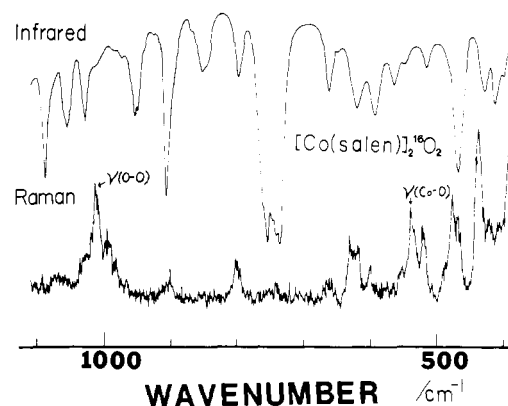


**Figure 3.** RR spectra of  $[\text{Co}(\text{salen})]_2^{16}\text{O}_2$  obtained as a function of exposure time to the laser beam (514.5 nm) under ambient condition: (A) 10 min; (B) 30 min; (C) 100 min.

gave a RR spectrum shown by trace A of Figure 3 where the band at  $533\text{ cm}^{-1}$  is clearly due to the  $\nu(\text{CoO})$  of the  $^{16}\text{O}_2$  adduct. The intensity of this band relative to that of the  $514\text{-cm}^{-1}$  band increases as a function of the time of exposure to the laser beam (30 min (trace B) and 100 min (trace C)). The use of the 514.5-nm excitation revealed the existence of another  $\nu(\text{CoO})$  near  $370\text{ cm}^{-1}$ . As is seen in Figure 3, the intensity of a shoulder band near  $370\text{ cm}^{-1}$  relative to the sharp band at  $357\text{ cm}^{-1}$  also increases as a function of the time. A similar band at  $376\text{ cm}^{-1}$  has been assigned to  $\nu(\text{CoO})$  by Nour and Hester.<sup>20</sup> Thus, we conclude that  $[\text{Co}(\text{salen})]_2\text{O}_2$  exhibits two  $\nu(\text{CoO})$  at  $533$  and  $\sim 370\text{ cm}^{-1}$  although the former was not reported by the previous workers.

The  $\nu(\text{O}_2)$  of  $[\text{Co}(\text{salen})]_2\text{O}_2$  at  $1011\text{ cm}^{-1}$  is unique in that it is between the superoxo and peroxo ranges. As stated before, an unusually high  $\nu(\text{O}_2)$  was found for  $\text{Co}(\text{TPP})(\text{O}_2)$  and has been attributed to the absence of an axial base ligand in this adduct. Exactly the same account is applicable to the present case; the lack of a base ligand in  $[\text{Co}(\text{salen})]_2\text{O}_2$  has shifted the  $\nu(\text{O}_2)$  by ca.  $120\text{--}100\text{ cm}^{-1}$  to a higher frequency relative to those of  $[\text{Co}(\text{salen})\text{B}]_2\text{O}_2$  ( $910\text{--}888\text{ cm}^{-1}$ ).<sup>7</sup> The deoxygenated  $\text{Co}(\text{salen})$  has a single unpaired electron whereas its oxygen adduct is diamagnetic.<sup>21</sup> This magnetic behavior is consistent with those of  $\mu$ -peroxo-dicobalt(III) complexes.<sup>2,20,21</sup> Our spectroscopic study suggests, however, that the  $\text{O}_2$  in  $[\text{Co}(\text{salen})]_2\text{O}_2$  should be regarded as an intermediate between those of superoxo and peroxo complexes.

**IR Spectra and Structure of the Co-O<sub>2</sub>-Co Bridge.** According to X-ray analysis, the Co-O<sub>2</sub>-Co' bridge in superoxo and peroxo amine (or ammine) dicobalt(III) complexes take a variety of structures depending upon the dihedral angle ( $\omega$ ) between the Co-O-O and O-O-Co' planes.<sup>23</sup> For example, the Co-O<sub>2</sub>-Co bridge in  $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  is trans planar ( $\omega = 180^\circ$ )<sup>24</sup> and its  $\nu(\text{O}_2)$  is completely forbidden in the IR although it appears strongly in the RR spectrum.<sup>13</sup> On the other hand, the Co-O<sub>2</sub>-Co bridge in



**Figure 4.** IR and RR spectra of  $[\text{Co}(\text{salen})]_2^{16}\text{O}_2$ . The latter was obtained by the 579-nm excitation at  $\sim 100\text{ K}$ .

$[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$  is cis planar ( $\omega = 0^\circ$ ),<sup>25</sup> and the  $\nu(\text{O}_2)$  of the analogous chloride appears strongly in both IR and RR spectra.<sup>13</sup> The Co-O<sub>2</sub>-Co bridge in  $[\text{Co}(\text{salen})\text{DMF}]_2\text{O}_2$  is intermediate between these two extremes ( $\omega = 110.1^\circ$ ).<sup>26</sup> In this case, we found that the  $\nu(\text{O}_2)$  of the analogous pyridine adduct appears weakly at ca.  $890\text{ cm}^{-1}$  ( $\nu(^{18}\text{O}_2)$  at  $833\text{ cm}^{-1}$ ) in the IR spectrum. These examples clearly demonstrate the utility of IR spectra in elucidating the structure of the Co-O<sub>2</sub>-Co bridge.

Figure 4 compares the IR spectrum of  $[\text{Co}(\text{salen})]_2\text{O}_2$  with the corresponding RR spectrum (trace A of Figure 2). It is seen that the IR spectrum shows a weak shoulder near  $1011\text{ cm}^{-1}$  where the RR spectrum exhibits a strong  $\nu(\text{O}_2)$ . This result suggests that the Co-O<sub>2</sub>-Co bridge in  $[\text{Co}(\text{salen})]_2\text{O}_2$  is approximately trans planar. According to normal coordinate calculations,<sup>13</sup> the trans-planar Co-O<sub>2</sub>-Co bridge in  $[(\text{N-H}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  exhibits the symmetric and antisymmetric ( $\nu_s$  and  $\nu_{as}$ ) CoO stretching vibrations at  $613$  and  $434\text{ cm}^{-1}$ , respectively. As stated in the preceding section, we have observed two  $\nu(\text{CoO})$  at  $533$  and  $370\text{ cm}^{-1}$  in the RR spectrum of  $[\text{Co}(\text{salen})]_2\text{O}_2$ . Then, it is most reasonable to assign them to the  $\nu_s(\text{CoO})$  and  $\nu_{as}(\text{CoO})$ , respectively. The fact that the latter was observed weakly as a shoulder on the  $357\text{-cm}^{-1}$  band also supports our conclusion that the Co-O<sub>2</sub>-Co bridge in this compound is approximately trans planar. The IR band at  $565\text{ cm}^{-1}$  which was previously<sup>27</sup> assigned to  $\nu(\text{CoO})$  is probably due to a  $\text{Co}(\text{salen})$  vibration since it is insensitive to the  $^{16}\text{O}_2\text{--}^{18}\text{O}_2$  substitution.

The  $\nu_s(\text{CoO})$  ( $533\text{ cm}^{-1}$ ) of  $[\text{Co}(\text{salen})]_2\text{O}_2$  assigned above is rather close to that of the  $[\text{Co}(\text{salen})\text{B}]_2\text{O}_2$  series ( $542\text{--}535\text{ cm}^{-1}$ ) in spite of the marked difference in their  $\nu(\text{O}_2)$ . Similar observations have been made previously for the pair  $[(\text{N-H}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  and  $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{N-H}_3)_5](\text{NO}_3)_4$ ; the former shows the  $\nu(\text{O}_2)$ ,  $\nu_s(\text{CoO})$ , and  $\nu_{as}(\text{CoO})$  at  $1123$ ,  $613$ , and  $434\text{ cm}^{-1}$ , respectively, whereas the latter shows them at  $805$ ,  $642$ , and  $547\text{ cm}^{-1}$ , respectively.<sup>13</sup> The corresponding Urey-Bradley force constants were calculated to be  $K(\text{O}_2) = 5.6$  and  $K(\text{CoO}) = 1.40$  for the former and  $K(\text{O}_2) = 2.7$  and  $K(\text{CoO}) = 2.15$  for the latter ( $H(\text{CoOO}) = 0.30$  and  $F(\text{Co}\cdots\text{O}) = 0.05$  were used for both; all in units of  $\text{mdyn}/\text{\AA}$ ).<sup>13</sup> These results clearly indicate that the  $\nu_{as}(\text{CoO})$  reflects the change in the Co-O bond order much better than the  $\nu_s(\text{CoO})$  in the trans-planar Co-O<sub>2</sub>-Co bridge.

**Excitation Profiles and Electronic Spectrum.** Molecular oxygen adducts of Co Schiff base complexes such as  $[\text{Co}(\text{salen})]_2\text{O}_2$  are expected to show the  $\pi\text{--}\pi^*$  transitions of salen,

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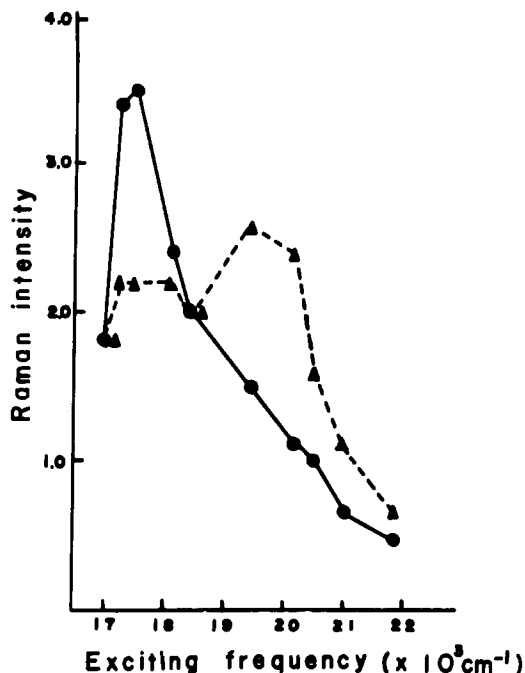


Figure 5. Excitation profiles of  $\nu(\text{O}_2)$  and  $\nu_s(\text{CoO})$  of  $[\text{Co}(\text{salen})]_2\text{O}_2$ : ●,  $\nu(\text{O}_2)$  at  $1011\text{ cm}^{-1}$ ; ▲,  $\nu_s(\text{CoO})$  at  $533\text{ cm}^{-1}$ .

$d-\pi^*$  transitions of  $\text{Co}(\text{salen})$ ,  $d-d$  transitions of the Co atom, and  $\text{Co}-\text{O}_2$  CT transitions of the  $\text{Co}-\text{O}_2$  moiety although such classifications are valid only for ideal cases where the mixing of these orbitals are minimal. However, they are sufficient for our qualitative discussion of the electronic transitions involved.

The electronic spectrum of crystalline  $[\text{Co}(\text{salen})]_2\text{O}_2$  yielded only a broad band in the 340–740-nm region without

any distinct maxima. Thus, it was almost impossible to obtain information about the individual transitions. In such cases, excitation profile studies of RR spectra have proved to be very useful in locating individual electronic transitions.<sup>28</sup> Previously, we<sup>7</sup> have located the  $\text{Co}-\text{O}_2$  CT transitions of the  $[\text{Co}(\text{salen})\text{B}]_2\text{O}_2$ -type compounds at ca. 500 nm on the basis of the excitation profiles of their  $\nu(\text{O}_2)$  and  $\nu(\text{CoO})$ .

Figure 5 shows the excitation profiles of the  $\nu(\text{O}_2)$  ( $1011\text{ cm}^{-1}$ ) and  $\nu_s(\text{CoO})$  ( $533\text{ cm}^{-1}$ ) of  $[\text{Co}(\text{salen})]_2\text{O}_2$ . The  $\nu(\text{O}_2)$  shows a single maximum near 570 nm, indicating the presence of a  $\text{Co}-\text{O}_2$  CT band near 570 nm. As discussed in our previous paper,<sup>7</sup> this is a transition from the  $\alpha d_{z^2} + \beta \pi^*(\text{O}_2)$  to the  $\beta d_{z^2} - \alpha \pi^*(\text{O}_2)$  orbital ( $\beta > \alpha$ ). If the energy gap between these two orbitals is largely determined by the energies of their original orbitals,<sup>7</sup> the red shift of the  $\text{Co}-\text{O}_2$  CT band in going from  $[\text{Co}(\text{salen})\text{B}]_2\text{O}_2$  to  $[\text{Co}(\text{salen})]_2\text{O}_2$  is understandable since the absence of a base ligand lowers the  $d_{z^2}$  orbital. The excitation profile of the  $\nu_s(\text{CoO})$  exhibits two maxima at ca. 570 and 500 nm. The presence of the maximum at 570 nm is expected since this vibration should be resonance enhanced by the  $\text{Co}-\text{O}_2$  CT transition. The presence of the second maximum near 500 nm may indicate that the  $d-\pi^*$  transition of  $\text{Co}(\text{salen})$  is in this vicinity.

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**Registry No.**  $[\text{Co}(\text{salen})]_2\text{O}_2$ , 23602-28-0;  $\text{Co}(\text{salen})$ , 14167-18-1;  $^{18}\text{O}$ , 14797-71-8.

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## Tungsten(V)-Oxo and Tungsten(VI)-Dioxo Complexes with Oxygen, Nitrogen, and Sulfur Ligands. Electrochemical, Infrared, and Electron Paramagnetic Resonance Studies

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Six new tungsten(V)- and -(VI)-oxo complexes have been synthesized ( $\text{WOCl}_3\text{L}$ ,  $\text{L} = \alpha, \alpha'$ -bipyridyl and *o*-phenanthroline;  $\text{WOCIL}_2$ ,  $\text{WO}_2\text{L}_2$ ,  $\text{L} = 8$ -hydroxyquinoline and 8-mercaptoquinoline) and their electrochemical properties, IR spectra, and EPR parameters determined. In addition, EPR and electrochemical data for five previously reported tungsten-oxo complexes ( $\text{WOCl}_3(\text{bpy})$ ;  $\text{WO}_2\text{X}_2\text{L}$ ,  $\text{X} = \text{Cl}, \text{Br}$ ,  $\text{L} = \alpha, \alpha'$ -bipyridyl, *o*-phenanthroline;  $\text{WO}_2(\text{acac})_2$ ) have also been obtained. Cyclic voltammograms of both tungsten(V) and -(VI) complexes show reduction peaks that are considerably more negative than those of the corresponding molybdenum complexes, and the reductions are less reversible. The tungsten(V) EPR signals are much broader and the  $g$  values are significantly lower than those of molybdenum(V) complexes. The results support the hypothesis that tungsten occupies the same binding site as molybdenum when substituted in the enzyme sulfite oxidase, with the lack of catalytic activity of the tungsten enzyme attributed to the lower reduction potential of tungsten as compared with that of molybdenum.

Among the elements of subgroup 6, chromium, molybdenum, and tungsten, only molybdenum has attracted great interest over the past two decades due to its important catalytic versatility in the fields of chemistry and biology. Recently tungsten has been incorporated into several molybdenum en-

zymes such as nitrogenase,<sup>2</sup> nitrate reductase,<sup>3</sup> and sulfite oxidase.<sup>4</sup> It substitutes for molybdenum, producing cata-

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