

Infrared Spectra of Dioxygen Adducts of Iron(II)(salen): Observation of Two O–O Stretching Bands

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Abstract

The infrared (IR) spectra of Fe(salen) cocondensed with O₂ and O₂/Ar at 25 K exhibit two $\nu(\text{O}–\text{O})$ bands at 1104 and 1001 cm⁻¹ which are shifted to 1041 and 943 cm⁻¹, respectively, by ¹⁶O₂–¹⁸O₂ substitution. Previously, the band at 1104 cm⁻¹ has been assigned to the ‘side-on’ dioxygen adduct, Fe(salen)O₂. We assign the newly observed band at 1001 cm⁻¹ to the $\nu(\text{O}–\text{O})$ of the dimeric complex [Fe(salen)]₂O₂ based on the following observations. (1) This band becomes stronger as the concentration of Fe(salen) relative to dioxygen is increased. (2) Fe(salen) film exposed to O₂ at 15 K exhibits one $\nu(\text{O}–\text{O})$ at 1102 cm⁻¹ but an additional $\nu(\text{O}–\text{O})$ at ~1000 cm⁻¹ when the film is warmed to 40 K. Apparently, increased diffusion of dioxygen into Fe(salen) layers promotes the formation of the dimeric complex at 40 K. In both matrix and film states, the infrared intensity of the $\nu(\text{O}–\text{O})$ near 1000 cm⁻¹ is low, suggesting that the Fe–O–O–Fe bridge is approximately centrosymmetric.

Introduction

Ferrous porphyrins and related compounds are highly important as models of heme proteins. In contrast to heme proteins, however, ‘unprotected’ Fe(II) chelates such as Fe(TPP) (TPP = 5,10,15,20-tetraphenylporphyrinato dianion) or Fe(salen) (salen = *N,N'*-ethylenebis(salicylideniminato) dianion) are highly air-sensitive under normal conditions and bind molecular oxygen rapidly and irreversibly to form μ -oxo dimers. This oxidation can be prevented by using protected porphyrins such as

‘picket-fence’, ‘capped’, ‘strapped’ or ‘basket-handle’ porphyrins [1] or by lowering the temperature in the case of ‘unprotected’ porphyrins. Previously we have utilized the matrix cocondensation technique to elucidate the structures of dioxygen adducts of Fe(TPP), Fe(OEP) (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion), Fe(Pc) (Pc = phthalocyanato dianion) and Fe(salen) by infrared (IR) and resonance Raman (RR) spectroscopies [2–6], and found [2, 3] that Fe(TPP) and Fe(OEP) cocondensed with dioxygen at 15 K form two isomeric adducts having the ‘end-on’ and ‘side-on’ structures which exhibit $\nu(\text{O}–\text{O})$ at ~1190 and ~1105 cm⁻¹, respectively. We have also found that Fe(Pc) forms only the ‘end-on’ adduct (1207 cm⁻¹) while Fe(salen) forms only the ‘side-on’ adduct (1106 cm⁻¹) under similar conditions [3]. In this work we observed two $\nu(\text{O}–\text{O})$ at 1104 and 1001 cm⁻¹ in the IR spectrum of Fe(salen) cocondensed with dioxygen at 25 K, and present evidence to show that the newly reported band at 1001 cm⁻¹ is due to the $\nu(\text{O}–\text{O})$ of dimeric [Fe(salen)]₂O₂.

Experimental

Fe(salen)py (py = pyridine) was prepared by modification of the method used by Niswander and Martell [7]. H₂(salen) was isolated from the reaction mixture and dried prior to the addition of an iron salt. Then, 1 × 10⁻² mol of H₂(salen) was dissolved in 25 ml of propanol mixed with 12.5 ml of freshly distilled pyridine and the solution was refluxed under nitrogen atmosphere for 45 min. After refluxing, FeSO₄·7H₂O (1 × 10⁻² mol) was dissolved in deaerated water (60 ml) and added dropwise (~60 min) to the hot H₂(salen) solution. Use of more water than that specified in the original procedure [7] avoids coprecipitation of pyridine sulfate with Fe(salen)py. After cooling the reaction mixture to room temperature, brown–purple precipitates were collected by filtration, washed with deaerated water under nitrogen atmosphere and dried in a vacuum desiccator overnight. The product was stable in air.

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The gases were obtained from Matheson ($^{16}\text{O}_2$, 99.99% and Ar, 99.9995%) and Monsanto Research ($^{18}\text{O}_2$, 98.15%) and were used without further purification. A mixture of $^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ = 1:2:1 was prepared by electrical discharge of an equimolar mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$. Ozone produced during this process was decomposed on activated 4A molecular sieves. The mixing ratio of these isotopic molecules was determined by Raman spectroscopy.

Cocondensation reactions were carried out as previously described [2, 3]. Very slow codeposition (about 8 h) of Fe(salen) with O_2 or O_2/Ar was carried out at 25 K to obtain high quality matrices on a CsI window. The IR spectra were measured on a Beckman Model 4260 IR spectrophotometer. Polystyrene film was used for frequency calibration. Accuracy of the frequency readings was $\pm 1\text{ cm}^{-1}$.

Results and Discussion

Trace A of Fig. 1 shows the IR spectrum of Fe(salen) in an Ar matrix. This spectrum is identical with that published previously [3]. When Fe(salen) vapor was cocondensed with $^{16}\text{O}_2$ two new bands appeared at 1104 and 1001 cm^{-1} as are seen in trace B. These bands were shifted to 1041 and 943 cm^{-1} , respectively, when Fe(salen) was cocondensed with $^{18}\text{O}_2$ (trace C). The observed isotopic shifts of these bands (63 and 58 cm^{-1} , respectively) are in

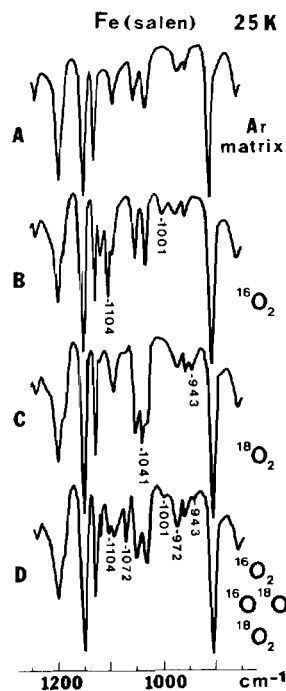


Fig. 1. IR spectra of Fe(salen) cocondensed at 25 K with: (A) Ar, (B) $^{16}\text{O}_2$, (C) $^{18}\text{O}_2$, (D) $^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ = 1:2:1.

good agreement with those expected from the diatomic harmonic oscillator. Thus, we assign these bands to the $\nu(\text{O}-\text{O})$ of two different dioxygen adducts of Fe(salen). The bands at 1104 (trace B) and 1041 cm^{-1} (trace C) have already been assigned to the 'side-on' isomers of Fe(salen) $^{16}\text{O}_2$ and Fe(salen) $^{18}\text{O}_2$, respectively [3]. However, the nature of the newly observed $\nu(\text{O}-\text{O})$ at 1001 and 943 cm^{-1} is not clear. As shown in trace D, the cocondensation product with isotopically scrambled oxygen ($^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ = 1:2:1) shows five $\nu(\text{O}-\text{O})$ bands at 1104, 1072, 1001, 972, and 943 cm^{-1} . The band at 1041 cm^{-1} in trace C is not seen in trace D due to its expected low intensity and overlap with the relatively strong band due to salen core vibration. The band at 1072 cm^{-1} is readily assignable to the $\nu(^{16}\text{O}-^{18}\text{O})$ of the 'side-on' adduct of Fe(salen)- $^{16}\text{O}^{18}\text{O}$ [3] since its frequency is close to the average of the two frequencies, 1104 ($^{16}\text{O}_2$) and 1041 ($^{18}\text{O}_2$) cm^{-1} . The band at 972 cm^{-1} must be assigned to the $\nu(^{16}\text{O}-^{18}\text{O})$ of a dioxygen adduct of the unknown structure since its frequency is exactly equal to the average of $\nu(^{16}\text{O}-^{16}\text{O})$ at 1001 cm^{-1} (trace B) and $\nu(^{18}\text{O}-^{18}\text{O})$ at 943 cm^{-1} (trace C).

In order to elucidate the structure of this dioxygen adduct, we studied the effects of dilution and temperature on the IR spectra of the Fe(salen)- O_2 system. Changing the O_2 :Ar ratio in a wide range from pure O_2 to 1:600 (O_2 :Ar) while maintaining the same vaporization conditions of Fe(salen), we observed that the band at 1001 cm^{-1} gained intensity (up to $\sim 20\%$) when O_2 was diluted to 1:600 with Ar. Under these conditions, the O_2 :Fe(salen) ratio decreases, thus favoring the formation of the 1:2 adduct, $[\text{Fe}(\text{salen})]_2\text{O}_2$.

Figure 2 shows an IR spectrum of a thin film of Fe(salen) (trace A) which was exposed to O_2 at 15 K (trace B). This spectrum is similar to that reported previously [3], *i.e.* only one $\nu(\text{O}-\text{O})$ band is observed at 1102 cm^{-1} (2 cm^{-1} lower than that in the O_2 matrix). We interpret this as indicating that O_2 cannot penetrate Fe(salen) layers at 15 K, thus only the 1:1 dioxygen adduct is formed. When this film was warmed to 40 K, a band with very low intensity appeared at $\sim 1000\text{ cm}^{-1}$ (trace C). This result suggests that at higher temperatures, dioxygen can diffuse slowly into Fe(salen) layers to form the 1:2 dioxygen adduct, $[\text{Fe}(\text{salen})]_2\text{O}_2$. Both 1:1 and 1:2 adducts are stable in the film up to $\sim 100\text{ K}$ but the intensities of their $\nu(\text{O}-\text{O})$ bands decrease substantially (trace D). The observed temperature behavior of these dioxygen adducts was different from that reported for Fe(TPP) O_2 [3]. In the latter case, the higher frequency band at 1195 cm^{-1} gained intensity at the expense of the lower frequency band at 1106 cm^{-1} upon warming the thin film, and both bands regained their original intensity when the film was recooled to 15 K.

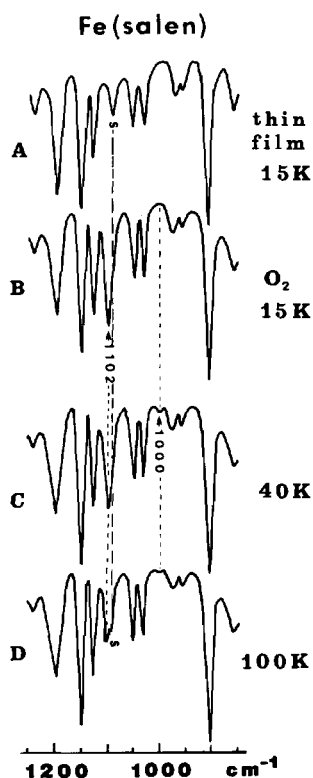
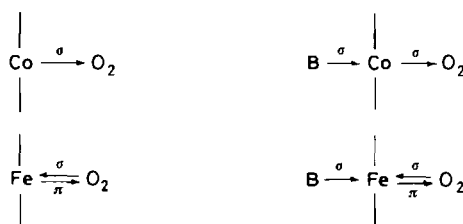


Fig. 2. IR spectra of a thin film of Fe(salen) (A) reacted with $^{16}\text{O}_2$ at 15 K (B), 40 K (C) and 100 K (D). 's' denotes a salen vibration at 1096 cm^{-1} .

We interpret these results as indicating that the band at $\sim 1000\text{ cm}^{-1}$ is due to the $\nu(\text{O}-\text{O})$ vibration of $[\text{Fe}(\text{salen})]_2\text{O}_2$ and that only the 'side-on' Fe(salen) O_2 ($\nu(\text{O}-\text{O})$, 1102 cm^{-1}) is formed at 15 K. It was not possible, however, to confirm our IR results by RR spectroscopy since the dioxygen adducts are converted immediately to (salen)Fe(IV)O by laser irradiation [6]. In the case of ferrylporphyrins, the cleavage reaction of the O-O bond follows the first order kinetics and the reaction is completed after about 20 min. In the case of Fe(salen), both 1:1 and

1:2 adducts may yield the ferryl species via the cleavage of the 'side-on' and bridging O-O bonds, respectively. Similar cleavage reactions of the bridging O-O bond have been observed in toluene solution of (TPP)Fe-O-O-Fe(TPP) and its analogues by using ^1H NMR [8] and RR [9] spectroscopy.

It is important to note that the $\nu(\text{O}-\text{O})$ of the 1:2 adduct ($\sim 1000\text{ cm}^{-1}$) is 10 cm^{-1} lower than that reported for a similar adduct, $[\text{Co}(\text{salen})]_2\text{O}_2$ [10]. As shown in Table 1, this trend is seen for many pairs of 'base-free' O_2 adducts in which only the central metal is changed from Co(II) to Fe(II). The opposite trend ($\nu(\text{O}-\text{O})$, $\text{Fe} > \text{Co}$) holds, however, when the O_2 adducts are 'base-bound'. For example, the $\nu(\text{O}-\text{O})$ of Fe(TPP)(piperidine) O_2 (1157 cm^{-1}) is higher than that of its Co(II) analog (1142 cm^{-1}) [14]. This difference between 'base-free' and 'base-bound' adducts may be explained qualitatively by using the bonding schemes such as shown below.



When O_2 binds to Co(II) (d^7), the Co- O_2 bond is formed by σ -donation from the $\text{Co}(d_{z^2})$ to the antibonding $\text{O}_2(\pi_g^*)$ orbital (viz. $\text{Co}(\text{III})-\text{O}_2^-$) [15]. In the case of Fe(II) (d^6) complexes, however, the Fe- O_2 bond is formed by σ -donation from $\text{O}_2(\pi_g^*)$ to $\text{Fe}(d_{z^2})$ which is counteracted by π -donation in the opposite direction [16]. This would strengthen the Fe- O_2 and weaken the O-O bond relative to the corresponding Co(II) complex. In fact, the $\nu(\text{Fe}-\text{O}_2)$ of Fe(TPP) O_2 at 509 cm^{-1} [17] is much higher than the $\nu(\text{Co}-\text{O}_2)$ of Co(TPP) O_2 at 345 cm^{-1} [11]. In 'base-bound' Co(II) complexes, σ -donation from the

TABLE 1. The $\nu(^{16}\text{O}_2)$ and $\nu(^{18}\text{O}_2)$ Frequencies in some Co(II) and Fe(II) 'Base-free' Dioxygen Adduct Complexes

| Species | $\nu(^{16}\text{O}_2)$ | $\nu(^{18}\text{O}_2)$ | $\nu(^{16}\text{O}_2) - \nu(^{18}\text{O}_2)$ | Reference |
|---|---------------------------------------|---------------------------------------|---|-----------|
| Co(TPP) O_2 | 1278 ^a | 1209 ^a | 69 | 11 |
| Fe(TPP) O_2 | 1195 ^a , 1106 ^b | 1127 ^a , 1043 ^b | 68, 63 | 2, 3 |
| Co(OEP) O_2 | 1275 ^a | 1202 ^a | 73 | 12 |
| Fe(OEP) O_2 | 1190 ^a , 1104 ^b | 1124 ^a , 1042 ^b | 66, 62 | 3 |
| Co(salen) O_2 | 1235 ^a | 1168 ^a | 67 | 13 |
| Fe(salen) O_2 | 1106 ^b | 1043 ^b | 63 | 3 |
| Fe(salen) O_2 | 1104 ^b | 1041 ^b | 63 | this work |
| $[\text{Co}(\text{salen})]_2\text{O}_2$ | 1011 ^c | 943 ^c | 68 | 10 |
| $[\text{Fe}(\text{salen})]_2\text{O}_2$ | 1001 ^c | 943 ^c | 58 | this work |

^a'End-on' adduct. ^b'Side-on' adduct. ^c'Bridging'.

base ligand causes a marked increase of the negative charge on the O₂, thus lowering the $\nu(\text{O}-\text{O})$ from 1278 [Co(TPP)O₂] to 1142 cm⁻¹ [Co(TPP)(piperidine)O₂]. However, this base ligand effect is much smaller in the Fe(II) complexes since σ -donation from the base is opposed by σ -donation from the O₂ to Fe. As a result, the $\nu(\text{O}-\text{O})$ of Fe(TPP)(piperidine)O₂ becomes higher than that of the corresponding Co(II) complex. In 'base-free' as well as 'base-bound' complexes, the $\nu(\text{Fe}-\text{O}_2)$ is higher than the $\nu(\text{Co}-\text{O}_2)$ because of the multiple bond character of the Fe-O₂ bond. Thus, the $\nu(\text{Fe}-\text{O}_2)$ of Fe(TPP)(piperidine)O₂ is at 575 cm⁻¹ while the $\nu(\text{Co}-\text{O}_2)$ of the corresponding complex is at 509 cm⁻¹ [14].

It should be noted that the $\nu(\text{O}-\text{O})$ of [Fe(salen)]₂O₂ and its Co analog are intermediate between those of typical superoxo (O₂⁻, 1200–1100 cm⁻¹) and peroxo (O₂²⁻, 930–780 cm⁻¹) complexes [10, 18]. Thus the negative charge on the O₂ of these 1:2 adducts must be between those of superoxo and peroxo complexes.

Finally, the results obtained above (Figs. 1 and 2) demonstrate the utility of the IR spectroscopy in elucidating the structure of the Fe-O₂-Fe bridge. If the O-O bridge in [Fe(salen)]₂O₂ is centrosymmetric its $\nu(\text{O}-\text{O})$ vibration is forbidden in IR. Similar to [Co(salen)₂O₂] [10], however, the $\nu(\text{O}-\text{O})$ of [Fe(salen)]₂O₂ appears weakly in the IR spectrum at 1001 cm⁻¹. This result indicates that the Fe-O₂-Fe bridge is only approximately centrosymmetric. These features have been already noted for some superoxo and peroxo dicobalt(III) ammine complexes containing the Co-O-O-Co bridges [19, 20].

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