curve fitting. The copolymer with $f_{ph} = 0.19$ showed an apparently dynamic nature although some static contribution was noticeable. These results suggest that the nature of the amphiphilic copolymer would change rather critically between $f_{ph} = 0.19$ and 0.41. The

data obtained in the equilibrium dialysis and surface tension experiments evidenced that the extent of the intramolecular hydrophobic association of the phenanthryl groups is significantly changed between $f_{\rm ph} = 0.19$ and 0.41.

Matrix Isolation Infrared Spectra of Carbonyl Complexes of Iron(II) Tetraphenyiporphyrin

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The IR spectra of cocondensation products of Fe(TPP) with CO/Ar exhibit six ν (CO) bands which are assigned to CO-H₂O (2148/2100), monomeric CO (2135/2088), Fe(TPP)(CO)₂ (2036/1997), Fe(TPP)(CO)O₂ (2004/1961), Fe(TPP)(CO)(H₂O) (1988/1944), and Fe(TPP)(CO) (1974/1929). (The numbers in the parentheses are in cm⁻¹ and indicate ν ⁽¹²CO) and ν ⁽¹³CO), respectively.) Formation of $Fe(TPP)(CO)(H_2O)$ and $Fe(TPP)(CO)O_2$ results from the presence of trace H_2O and O_2 , respectively, in the system. In fact, the bands due to these species become the strongest when Fe(TPP) is cocondensed with $CO/H_2O/Ar$ and $CO/O_2/Ar$, respectively, at ~20 K and warmed to ~40 K. Upon forming Fe(TPP)(CO)O_2, the $\nu(O_2)$ of Fe(TPP)O₂ at 1195 cm⁻¹ is shifted to 1190 cm⁻¹ while the ν (CO) of Fe(TPP)(CO) at 1974 cm⁻¹ is shifted to 2004 cm⁻¹ These results indicate that σ donation occurs from CO to O₂ in Fe(TPP)(CO)O₂. The antisymmetric and symmetric δ (Fe-C-O) bands of Fe(TPP)(CO), are observed at 583 (IR) and 569 cm⁻¹ (Raman), respectively, while the δ (Fe-C-O) band of $Fe(TPP)(CO)O_2$ is at 552 cm⁻¹ (IR).

Introduction

Recently, a number of novel and transient complexes have been synthesized via matrix cocondensation reactions of metal atom vapors with ligands such as CO, NO, and O₂, and their structures determined by using IR and Raman spectroscopy.² We^{3,4} and other workers⁵ have extended this technique to the reactions of metal halide vapors with similar ligands. In 1981, we⁶ carried out matrix cocondensation reactions of bulky molecules such as Co(TPP) (TPP: tetraphenylporphyrin) with CO, NO, and O₂ diluted in inert gases (Ar or Kr) and obtained the IR and Raman spectra of Co(TPP)L and Co(TPP)LL' type complexes, where L and L' denote the axial ligands mentioned above. Since then, our work has been concentrated on IR and RR (resonance Raman) studies of dioxygen adducts of Co(II) Schiff base complexes⁷ and Fe(II) porphyrins⁸ which serve as model compounds of oxyhemoglobin and oxymyoglobin.

In this work, we have directed our attention to CO adducts of Fe(TPP) because CO binding with hemes has not been studied as extensively as O_2 binding. To our knowledge, the only report on Fe(TPP)(CO) and Fe(TPP)(CO)₂ is that of Wayland et al.,⁹ who measured the IR spectra of these compounds in the solid state. Here, we report the IR spectra of novel mixed-ligand complexes such as $Fe(TPP)(CO)O_2$ and $Fe(TPP)(CO)(H_2O)$ and discuss

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TABLE I: IR Spectra of CO Cocondensed with Fe(TPP) in Ar Matrices (cm⁻¹)

| designa- tion ^a | species | ν(¹² CO) | ν(¹³ CO) | ν(¹² CO)/ ν(¹³ CO) |
|-------------------------------|---------------------|----------------------|----------------------|---|
| а | CO-H ₂ O | 2148 | 2100 | 1.023 |
| b | monomeric CO | 2135 | 2088 | 1.023 |
| с | $Fe(TPP)(CO)_2$ | 2036 | 1997 | 1.020 |
| d | $Fe(TPP)(CO)O_2$ | 2004 | 1961 ⁶ | 1.022 |
| e | $Fe(TPP)(CO)(H_2O)$ | 1988 | 1944 ⁶ | 1.023 |
| f | Fe(TPP)(CO) | 1974 | 1929 | 1.023 |

^aSee Figure 1. ^bThese frequencies were obtained at \sim 35 K where the spectrum shows distinct maxima (see Figure 3B).

the nature of interactions between the two axial ligands in terms of vibrational frequencies.

Experimental Section

Compounds. $Fe(TPP)(pip)_2$ (pip: piperidine) was prepared by the literature method.¹⁰ The gases, Ar (99.9995%, Matheson), ¹⁶O₂ (99.5%, Airco), ¹⁸O₂ (95.91%, Monsanto Research), ¹²CO (99.995%, MG Scientific), and ¹³CO (90.5%, Merck), were used without further purification. Mixed gases of various ratios of CO and O_2 were prepared in our vacuum system equipped with a Mcleod type gauge and diluted by adding argon. The accuracy of pressure reading was ± 0.1 torr at pressures below 5 torr. Red-violet crystals of Fe(TPP)(CO)₂ were obtained by saturating a toluene solution of Fe(TPP) with CO.

Spectral Measurements. Since Fe(TPP) is highly air sensitive, a stable, "base-bound" complex, Fe(TPP)(pip)2, was placed inside the Knudsen cell of our matrix isolation system, and heated in a vacuum of 10^{-6} torr at ~370 K for 4 h or longer until the vacuum gauge indicated complete dissociation of the base ligand from the complex. Heating was continued at ~ 400 K for 2 h

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Fe(TPP) + CO in Ar at 20 K



Figure 1. IR spectra (ν (CO) region) of Fe(TPP) cocondensed with ¹²CO/Ar (A) and ¹³CO/Ar (B) at ~20 K.



Figure 2. Effect of warming the matrix on relative intensity: (A) Fe-(TPP) + ${}^{12}CO/Ar$ (3.0/600), (B) Fe(TPP) + ${}^{12}CO/O_2/Ar$ (1.0/50/ 600), and (C) Fe(TPP) + CO/H₂O/Ar (1.0/~15/600).

or longer to ensure complete dissociation. The resulting "base-free" complex was vaporized from the Knudsen cell at 430–550 K and codeposited with pure argon or gases diluted by argon on a CsI window which was cooled to ~ 20 K by a CTI Model 21 closed-cycle helium refrigerator. The temperature of the matrix was controlled by a nichrome wire heater wrapped on the cold finger.



Fe(TPP) + CO + U in Ar

2036

198

2135



Figure 3. IR spectra (ν (CO) and ν (O₂) regions) of Fe(TPP) cocondensed with ¹²CO/O₂/Ar (A) and ¹³CO/O₂/Ar (B).

IR spectra were recorded on a Beckman Model 4260 infrared spectrophotometer with a 25 cm⁻¹/in. chart expansion and a 25 cm⁻¹/min chart speed. Rotation-vibration bands of standard molecules and polystyrene film bands were used for frequency calibration. The resonance Raman spectra of crystalline Fe(T-PP)(CO)₂ were measured on our Spex Model 1401 double monochromator equipped with a Spex digital photometer system. The 406.7-nm line of a Spectra-Physics Model 164-01 Kr ion laser was used for excitation.

Results and Discussion

Fe(TPP) + CO. Figure 1, A and B, show the IR spectra of Fe(TPP) cocondensed with ¹²CO/Ar (3.0/600) and ¹³CO/Ar (5.0/600), respectively, on a CsI window cooled to ~20 K. As is shown in Table I, all the six bands (a to f) listed must be assigned to the ν (CO) of free and complexed CO since these bands are shifted by a factor of 1.020–1.023 by ¹²CO–¹³CO substitution. Previous workers¹¹ have shown that the bands at 2148 (a) and 2135 cm⁻¹ (b) are due to CO complexed to trace water and monomeric CO, respectively. It is also known that Fe(TPP)(CO)₂ and Fe(TPP)(CO) exhibit IR-active ν (CO at 2042 and 1973 cm⁻¹, respectively, in the crystalline state.⁹ Thus, it is reasonable to assign the bands at 2036 (c) and 1974 cm⁻¹ (f) of Figure 1A to Fe(T-PP)(CO)₂ and Fe(TPP)(CO), respectively, which are formed in Ar matrices. However, the nature of the remaining two bands at 2004 (d) and 1988 (e) cm⁻¹ is not obvious.

Figure 2A shows the effect of warming the matrix (${}^{12}CO/Ar = 3.0/600$) from ~20 to ~40 K on the relative intensities of the above six bands. It is seen that bands b and f become weaker and bands c, d, and e become stronger while the intensity of band a remains constant. Similar observations have been made for the ${}^{13}CO$ adducts; warming the matrix decreases the intensities of the bands at 2088 (b) and 1929 cm⁻¹ (f) and increases the intensities of the bands at 1997 (c), 1961 (d), and 1944 cm⁻¹ (e) without



Figure 4. Low-frequency IR spectra of Fe(TPP) cocondensed with ${}^{12}CO/Ar$ (A), ${}^{13}CO/Ar$ (B), ${}^{12}CO/O_2/Ar$ (C), and ${}^{13}CO/O_2/Ar$ (D) at ~35-40 K

causing appreciable change for band a (2100 cm^{-1}) . These observations suggest that the complexes responsible for bands d and e may involve the coordination of trace water and oxygen in the system which is accelerated by increasing diffusion in a matrix at higher temperature.

 $Fe(TPP) + CO + H_2O$. As is shown in Figure 2A, the intensity order is $f > b > a > c > d \approx e$ when Fe(TPP) is cocondensed with CO/Ar (3.0/600) at ~20 K. However, this order is changed to $f > a > b > e > c \approx d$ when Fe(TPP) is cocondensed with CO/H₂O/Ar (1.0/~15/600) at ~20 K (Figure 2C). The change in the order from $c > d \approx e$ to $e > c \approx d$ upon addition of water vapor suggests that band e involves water coordination. This is further confirmed by the warm-up experiment shown in Figure 2C; bands b and f become weaker, and bands e, c, and d become stronger while band a remains almost unchanged when the matrix is warmed. At ~40 K, band e is the strongest among the six bands. We can, therefore, safely assign band e to a six-coordinate complex, Fe(TPP)(CO)(H₂O). The very weak band observed at 1988 cm⁻¹ in Figure 1A must be due to this aquo complex which resulted from trace H₂O in the system.

Coordination of water molecules to iron porphyrins is of great interest in hemoprotein chemistry. X-ray analyses have been made on $Fe(II)(TPP)(CCl_2)(H_2O)^{12}$ and $[Fe(III)(TPP)(H_2O)_2]ClO_4$.¹³ Water coordination to the iron center of metmyoglobin has been suggested from electron spin-echo envelope spectroscopy.¹⁴ The present work provides the first vibrational data of aquo complexes of iron porphyrins.

Ligands such as CO and NO act as σ donors or as π acceptors or both.¹⁵ The σ donation tends to raise the ν (CO) since the

| TABLE II: | O ₂ Stretching | Frequencies | of Dioxygen | Adducts of |
|------------|---------------------------|-------------|-------------|------------|
| Fe(TPP) in | Argon Matric | es (cm⁻¹) | | |

| complex | $\nu({}^{16}O_2)$ | $\nu({}^{18}O_2)$ | |
|------------------------|---------------------|---------------------|--|
| Fe(TPP)O2 ^a | 1195 (I), 1106 (II) | 1127 (I), 1043 (II) | |
| $Fe(TPP)(^{12}CO)O_2$ | 1190 | 1118 | |
| $Fe(TPP)(^{13}CO)O_2$ | 1190 | 1118 | |

 a Fe(TPP)O₂ exists as a mixture of two isomers: isomer I with endon coordination of dioxygen and isomer II with side-on coordination of dioxygen (see ref 8).

electrons are removed from its weakly antibonding 5σ orbital while the π back-donation tends to lower the $\nu(CO)$ since the electrons from the metal enter into its antibonding π orbital. The increase of $\nu(CO)$ in going from Fe(TPP)(CO) to Fe(TPP)(CO)(H₂O) suggests that CO acts as a base by donating σ electrons to the water molecule in the trans position.

 $Fe(TPP) + CO + O_2$. In order to determine the structure of the CO adduct responsible for band d, we have carried out matrix cocondensation reactions of Fe(TPP) with ${}^{12}CO/O_2/Ar$ (1.0/ 50/600) at ~20 K. As is seen in Figure 2B, the intensity order of the six bands is basically the same as that observed previously without adding extra dioxygen (Figure 2A). When the matrix is warmed to ~40 K however, band d becomes the strongest as seen in Figure 2B. This observation suggests that band d (2004 cm⁻¹) originates in Fe(TPP)(CO)O₂. Although the CO/O₂ ratio is 1/50, the concentration of Fe(TPP)(CO)O₂ is much less than that of Fe(TPP)(CO) at ~20 K since CO preferentially binds to Fe(TPP). Only after warming the matrix does its concentration increase because of accelerated diffusion of dioxygen in Ar matrices. Similar experiments with ${}^{13}CO$ have shown that the band at 1961 cm⁻¹ must be assigned to Fe(TPP)(${}^{13}CO)O_2$. Apparently,

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the weak band (d) at 2004 cm⁻¹ observed in Figure 1A is due to $Fe(TPP)(CO)O_2$ which was formed by trace O_2 contamination during long hours of matrix deposition (~12 h).

Figure 3A shows the IR spectrum of a matrix formed by cocondensation of Fe(TPP) with $CO/O_2/Ar$ (2.5/200/400) at ~20 K. In this experiment, the relative concentration of O_2 has been increased markedly compared to the previous experiment (Figure 2B) so that the $\nu(CO)$ as well as $\nu(O_2)$ near 1190 cm⁻¹ are observable. The left trace shows that the major product at ~20 K is Fe(TPP)(CO) (f). The right trace shows the presence of two new bands at 1195 and 1106 cm⁻¹ which are due to the $\nu(O_2)$ of the end-on isomer (I) and side-on isomer (II) of Fe(TPP) O_2 ,⁸ respectively. Thus, the major products at this temperature are Fe(TPP)(CO) and Fe(TPP) O_2 .

When this matrix is warmed to \sim 35 K (Figure 3A), bands c and d become stronger and a new shoulder band appears at 1190 cm^{-1} . At ~40 K, band d becomes much stronger than bands e and f, and the shoulder band at 1190 cm^{-1} is clearly discernible. These observations suggest that warming the matrix accelerates the reactions such as $Fe(TPP)O_2 + CO \rightarrow Fe(TPP)(CO)O_2$ (band d) and $Fe(TPP)(CO) + CO \rightarrow Fe(TPP)(CO)_2$ (band c). Figure 3B shows the IR spectrum of Fe(TPP) cocondensed with $^{13}CO/O_2/Ar$ (3.5/200/400). As expected, all the six bands in the $\nu(CO)$ region are shifted whereas the $\nu(O_2)$ at 1195, 1190, and 1106 cm⁻¹ are not shifted by ¹²CO-¹³CO substitution. If the concentrations of CO and O2 are comparable, the CO predominantly coordinates to Fe(TPP) because its affinity to iron porphyrin is much stronger than O_2 . Thus, the major products resulted from the cocondensation of Fe(TPP) with CO/O₂/Ar (25/25/600) are Fe(TPP)(CO)₂ and Fe(TPP)(CO).

It is interesting to note that the $\nu(CO)$ of Fe(TPP)(CO)O₂ (2004 cm⁻¹) is 30 cm⁻¹ higher than that of Fe(TPP)(CO) and the $\nu(O_2)$ of Fe(TPP)(CO)O₂ (1190 cm⁻¹) is 5 cm⁻¹ lower than that of Fe(TPP)O₂ (isomer I). As discussed earlier, these results indicate that σ donation from CO to O₂ increases $\nu(CO)$ and decreases $\nu(O_2)$ in a mixed-ligand complex such as Fe(TPP)(C-O)O₂.

Fe(TPP) in an Ar matrix exhibits a strong TPP band at 1351 cm⁻¹. Upon oxygenation, this band splits into four peaks as shown in the top trace of Figure 3A. The pairs at higher (1355 and 1350 cm⁻¹) and lower frequencies (1345 and 1341 cm⁻¹) are assigned to isomer I (end-on type) and isomer II (side-on type) of Fe(T-PP)O₂,⁸ respectively, because the latter pair becomes weaker as the $\nu(O_2)$ band of isomer II at 1106 cm⁻¹ becomes weaker upon warming the matrix. The corresponding TPP band for Fe(TP-P)(CO)O₂ is probably hidden under the strong bands near 1352 cm⁻¹.

Low-Frequency Spectra. Figure 4A shows the low-frequency IR spectrum of Fe(TPP) cocondensed with ¹²CO/Ar (25/600) at ~20 K and then warmed at ~35 K. This reaction produced only one new band at 583 cm⁻¹ (c') which was shifted to 568 cm⁻¹ by ¹²CO-¹³CO substitution (Figure 4B). As already demonstrated

in Figure 2A, Fe(TPP)(CO)₂ is the predominant species produced under these conditions. Thus, these two bands must be attributed to the bis-CO adducts. To locate the corresponding Raman-active modes, we measured the resonance Raman (RR) spectra of crystalline Fe(TPP)(¹²CO)₂ and its ¹³CO analogue using 406.7-nm excitation. It was found that the band of the former at 569 cm⁻¹ is shifted to 550 cm⁻¹ by ¹²CO-¹³CO substitution.

In a linear Fe-C=O system, the ν (Fe-CO) mode shows only a small shift by ¹²CO-¹³CO substitution since the CO molecule behaves as a single dynamic unit. In contrast, the δ (Fe-C-O) (δ : bending) mode exhibits a large shift by the same substitution because the C atom is displaced moree than the O atom in the direction perpendicular to the molecular axis. Thus, Yu and co-workers¹⁶ assigned the 563-cm⁻¹ band of Hb-CO to the δ -(Fe-C-O) since it is shifted by -15 cm⁻¹ by ¹²CO-¹³CO substitution and the 503-cm⁻¹ band to the ν (Fe-CO) since it exhibits only a small shift of -4 cm^{-1} by the same substitution. As stated above, we observed a large ¹²CO-¹³CO shift for the IR band at 583 cm^{-1} (-15 cm⁻¹) and for the RR band at 569 cm⁻¹ (-19 cm⁻¹) of $Fe(TPP)(CO)_2$. Thus, it is most reasonable to assign these vibrations to the antisymmetric and symmetric δ (OC-Fe-CO) of $Fe(TPP)(CO)_2$, respectively. However, we have not been able to detect the corresponding stretching modes both in IR and RR spectra.

Figure 4C and D, show the low-frequency IR spectra of Fe-(TPP) cocondensed with $CO/O_2/Ar$, (2.5/200/400) and 13 CO/O₂/Ar (3.5/200/400), respectively, at ~20 K and then warmed to ~ 40 K. It is seen that two bands at 583 (c') and 552 cm^{-1} (d') of the former are shifted to 568 and 542 cm^{-1} , respectively, by ¹²CO-¹³CO substitution. The former band (c') has already been assigned to the antisymmetric δ (Fe-C-O) mode of Fe(TPP)(CO)₂. As stated earlier (Figure 3A), the spectra obtained under these conditions are dominated by $Fe(TPP)(CO)_2$ and $Fe(TPP)(CO)O_2$. Thus, it is most reasonable to assign the 552- and 542-cm⁻¹ bands to the δ (Fe–C–O) of Fe(TPP)(CO)O₂ (d) and its ¹³CO analogue, respectively. As expected, these bands show no shifts by ${}^{16}O_2 - {}^{18}O_2$ substitution. Finally, we conclude that $\nu(\text{Fe-O}_2)$ vibration must be below 400 cm⁻¹ since we could not detect any oxygen-isotope-sensitive band in the 600-400-cm⁻¹ region.

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