Matrix Isolation Infrared Spectra of Oxy(tetraphenylporphinato)iron(II)

K. Nakamoto,* T. Watanabe, T. Ama, and M. W. Urban

Todd Wehr Chemistry Building, Marquette University
Milwaukee, Wisconsin 53233
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Although ferrous porphyrins are highly important as models of hemoglobin and myoglobin, simple (unprotected) ferrous porphyrins such as Fe(TPP) (TPP: tetraphenylporphinato anion) cannot bind molecular oxygen reversibly under normal conditions since they are rapidly and irreversibly oxidized to form μ-oxo dimers. So that this oxidation could be prevented, "protected" porphyrins such as pикet-fence and cap porphyrins have been synthesized and their oxygenation reactions studied extensively. 1,2 We now present the first IR evidence for the formation of "base-free" O2 adducts of "unprotected" ferrous porphyrins with use of matrix cocondensation techniques. Since Fe(TPP) itself is highly air-sensitive, we have developed the following procedure to prevent its oxidation.

A stable, "base-bound" complex, Fe(TPP)(pip)2 (pip: piperidine),3 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 until the vacuum gauge indicated complete dissociation of the base from the complex. The "base-free" Fe(TPP) thus obtained was vaporized from the Knudsen cell at 430 K and cocondensed with pure Ar or O2 diluted in Ar on a CsI window that was cooled to ~15 K by a CTI Model 21 closed-cycle helium refrigerator. The IR spectra were measured on a Beckman Model 4260 IR spectrophotometer with a 25 cm−1/in. chart expansion and 5 cm−1/min chart speed.

Trace A of Figure 1 shows the IR spectrum of Fe(TPP) in an Ar matrix. As is expected, this spectrum is very similar to those of Co(TPP)4 and Mn(TPP)4 because the spectra in the 1600–1800 cm−1 region are dominated by the TPP vibrations. When Fe(TPP) vapor was cocondensed with 18O2/Ar (1/99), two new bands were observed at 1195 and 1106 cm−1, as is seen in trace B. Similar spectra were obtained in pure O3 and more diluted 18O2/Ar (1/50–1/100) matrices. These results suggest that the O2 adduct has the 1:1 (O2:Fe) stoichiometry. The bands at 1195 and 1106 cm−1 were shifted to 1127 and 1043 cm−1, respectively, by the 18O2→16O2 substitution (trace C). The observed isotopic shifts of these bands (68 and 63 cm−1, respectively) are in perfect agreement with that expected for a perturbed diamagnetic molecule. Thus, we assign both bands to the ν(O=O or O=O of "base-free" adduct, Fe(TPP)O2.

The appearance of two ν(O=O) bands for Fe(TPP)O2 is intriguing. The weaker band at 1106 cm−1 is not due to Fe(TPP)(pip)O2 since exactly the same spectrum was obtained when Fe(TPP)(pip) was used as the starting complex. The possibility of Fermi resonance with the first overtone of the ν(FeO)5 or a porphyrin mode is remote since both 16O2 and 18O2 adducts exhibit the same number of bands without any shifts of the TPP vibrations. The matrix site effect does not seem to be responsible since the intensity ratio of the two bands remains unchanged in a variety of matrix environments. In fact, a thin film of Fe(TPP) reacted with O2 exhibits spectra similar to those shown in Figure 1. If this film is warmed, the 1195-cm−1 band gains intensity at the expense of the 1106-cm−1 band. Although the latter disappears completely at ~100 K, recoiling to ~15 K recovers its original intensity. These observations suggest that there are two isomers of Fe(TPP)O2, and that isomer I (1195 cm−1) is stable up to 240 K (at which it decomposes), whereas isomer II (1106 cm−1) is converted to isomer I by raising the temperature up to ~100 K. These two isomers may differ in the spin state of Fe(II) or the Fe–O–O

gemetry or both. At present, a more detailed and thorough study is in progress to understand the nature of these isomers.

It should be noted that the order of ν(18O2) of "base-free" adducts is Co(TPP)O2 (1278 cm−1) > Fe(TPP)O2 (1195/1106 cm−1) > Mn(TPP)O2 (983 cm−1). The O2 in Mn(TPP)O2 is approximated by the peroxide (O2−) ion.7 The O2 of "base-free" Co(TPP)O2 is much more positive than that of "base-bound" Co(TPP)(N-MeIm)O2 (1142 cm−1)8 which is regarded as the superoxide (O2−) type.9 Thus, we conclude that the negative charge on the O2 of "base-free" Fe(TPP)O2 is between these two extremes and probably close to O2−. Although the nature of the Fe–O2 interaction in "base-bound" adducts is controversial,10 the present IR study seems to favor the superoxide(FeO−O)11,12 over the neutral O2(Fe=O2) model,13,14 since even the O2 in "base-free" Fe(TPP)O2 is close to O2−.

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Registry No. Fe(TPP)(pip)2, 17845-65-7; Fe(TPP), 16591-56-3; Fe(TPP)O2, 67887-55-2.