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THE INFRARED SPECTRA OF SOME DIOXYGEN AND CARBON MONOXIDE METALLOPORPHYRIN COMPLEXES *

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Summary

The infrared stretching values for O_2 bound to Co, Fe, and Mn porphyrins are reported. It is noted that for similar complexes, $\nu(O_2)$ is insensitive to variations in the metal center or axial base. The value of $\nu(O_2)$ for O_2 adducts of tetraphenylporphyrinatomanganese(II) confirms earlier work that the O_2 moiety is bound in a peroxo-like manner. Also $\nu(CO)$ values are reported for the iron(II) porphyrin complexes.

Introduction

The manner in which dioxygen is bound in metal—dioxygen complexes has proven to be a matter of considerable interest and controversy [1]. Considerable attention has been given to model complexes in an attempt to better understand the bonding and reactivity of the dioxygen ligand in biological systems, in particular, dioxygen complexes of Fe [2], Co [3], Cr [4], and Mn [5] which relate to biological oxygen carriers have been obtained. The values of $\nu(O_2)$ are known for the Fe [6], Co [7], and Cr [4] systems. Surprisingly, $\nu(O_2)$ values all fall within a narrow range, although major differences occur in the porphyrins and the metal centers. The $\nu(O_2)$ appears to be insensitive to the amount of electron transfer, contrary to other experimental and theoretical work [1c]. However the value of $\nu(O_2)$ can be used as a guide to determine the manner in which the dioxygen molecule is bound to the metal center. Thus, the dioxygen complexes with $\nu(O_2)$ values between 1100 and 1200 cm^{-1} have dioxygen bonded in an end-on bent configuration (I), whereas those with stretches between 800 and 950 cm^{-1} have the dioxygen bonded in a side-on triangular symmetric manner (II).

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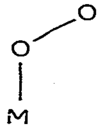
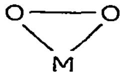
* Dedicated to Joseph Chatt on the occasion of his 65th birthday.



(I)



(II)

The infrared stretching frequencies of bound CO in hemes and hemoproteins appear to depend on steric interactions with the surrounding protein [6]. The greater the steric influences, the lower the frequency. For example, in natural proteins where the CO is reported [8] in a bent conformation, the ν(CO) value is 1951 cm^{-1} compound with values of 1969 cm^{-1} and larger for model compounds.

In this paper we report on the infrared $\nu(O_2)$ values for the O_2 adducts of Fe(Cap)(py), Fe(Cap)(1-MeIm), Fe(HmCap)1-MeIm)$_2$ [10], Co(Cap)(1-MeIm), and Co(TTP)(1-MeIm) systems *. The values obtained strongly support the M^{III}—O_2^- formalism. In addition comparisons are made among the Fe and Co systems as a probe for the effects of environmental and metal variations on the values of $\nu(O_2)$ and ν(CO). Also presented is the first report of $\nu(O_2)$ for the Mn(TPP)(O_2) systems. This value supports the chemical and EPR interpretations that the dioxygen molecule is bonded in a side-on symmetrical triangular configuration (II) [5a—c].

Experimental

Benzene and toluene were refluxed over sodium benzophenone ketyl, while pyridine (BaO), 1-methylimidazole (KOH) and CH_2Cl_2 (P_4O_{10}) were refluxed with the appropriate drying agent. All liquids were distilled under an atmosphere of N_2 prior to use. The free base porphyrin CapH_2 and Fe^{III}(Cap)Cl were synthesized according to published procedures [2c,9]. Their purity was checked by comparison of the visible spectra to the corresponding published spectra. The analogous compounds, HmCapH_2 and Fe^{III}(HmCap)Cl, were synthesized in a similar manner and checked by visible spectroscopy and molecular weight determinations [10].

Reductions were carried out by a two phase $Na_2S_2O_4$ process, with the rigorous exclusion of oxygen. Typically 3 mg of Fe^{III}(Cap)(Cl) was dissolved in 20 ml of toluene and purged with N_2 to remove O_2. An equal volume of a deoxygenated 0.3 *M* $Na_2S_2O_4$ solution was added to the flask containing the Fe^{III}-(Cap)Cl solution. This was followed by vigorous shaking for 5 min. Reduction was accompanied by a color change from brown to an orange-red. The aqueous layer was separated and discarded. If a mixed solvent system was to be used, the additional solvent was then added to the toluene solution followed by immediate transfer to the infrared cell. The iron base complexes were formed immediately upon addition of base to the reduced solutions. Their complete for-

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* Abbreviations used, Cap and CapH_2, dianion and neutral "capped" porphyrin [2a]; Hb and HbCO, hemoglobin and its carbon monoxide adduct; His, histidine residue; HmCap, homologous "capped" porphyrin [12]; 1-MeIm, 1-methylimidazole; $P_{1/2}$, pressure of O_2 necessary to oxygenate $\frac{1}{2}$of available sites, 1/KO_2; py, pyridine; TPP, dianion of tetraphenylporphyrin; TTP, dianion of tetra-*p*-methylphenylporphyrin; Tyr, tyrosine.

mation was checked by visible spectroscopy [2c,10]. Both Mn(TPP) [5a] and Co(TTP) [11] were synthesized by previously reported preparations.

All manipulations of solids were performed under an atmosphere of nitrogen. Transfer of solutions were performed using gas-tight syringes. Concentrations of the metalloporphyrin solutions were approximately 1×10^{-3} *M*. Samples of these solutions were then exposed to an atmosphere of CO, O_2, or $^{18}O_2$ (90% enriched). Sample spectra were obtained at room temperature for the CO adducts. Spectra of the dioxygen adducts were obtained at room temperature or at —78° C, depending on the oxygen affinity of the metalloporphyrin.

Infrared spectral data of all solutions were collected between 4000 and 400 cm^{-1} on a Nicolet 7199 Fourier transform spectrometer, at 1 cm^{-1} resolution. An RIC VL-2 low temperature cell fitted with AgCl plates with a pathlength of 0.05 mm was used for low temperature runs. A standard solution IR cell equipped with NaCl plates with a pathlength of 0.5 mm was used for room temperature work. Difference spectra were computed using the standard software of the spectrometer. The coefficients in the difference spectra were chosen to reduce to baseline the porphyrin bands in the region studied (either 1250 to 1050 cm^{-1}, or 900 to 750 cm^{-1}). In addition small amounts of the solvent systems were subtracted or added to account for small changes in concentrations. Samples of Mn(TPP) in toluene at room temperature were exposed to $^{16}O_2$ and $^{18}O_2$, with the resulting solid oxidized products being prepared as Nujol mulls between NaCl plates. These spectra were obtained at a resolution of 2 cm^{-1} on a Perkin—Elmer 283 spectrometer.

Results

The difference spectrum of Co(Cap)(1-MeIm)(O_2) in CH_2Cl_2 versus Co(Cap)-(1-MeIm) shows that the absorbance due to the O_2 stretch appears at 1176 cm^{-1} for $^{16}O_2$ and 1084 cm^{-1} for $^{18}O_2$. The band due to $^{18}O_2$ is shifted to a considerably lower frequency than the harmonic oscillator prediction. This lowering along with an unassigned feature at 1108 cm^{-1} indicates the presence of Fermi coupling [12]. Fermi coupling occurs when there is an accidental degeneracy between the strong porphyrin bands in this region and some of the $^{18}O_2$ stretches. For comparative purposes, the $\nu(O_2)$ values for Co(TTP)-(1-MeIm)(O_2) were also obtained. Because cobalt complexes have extremely low oxygen affinities [11,13] at room temperature ($P_{1/2} \approx 15000$ Torr), it was necessary to lower the temperature to —78°C. The values for $\nu(O_2)$ of Co(TTP)-(1-MeIm)(O_2) are 1142 and 1071 cm^{-1} for $\nu(^{16}O_2)$ and $\nu(^{18}O_2)$, respectively.

The values for $\nu(O_2)$ are in Table 1. All values were obtained by subtracting the spectrum of the unoxygenated complex from the oxygenated compound, making use of the same sample solution. This minimized problems due to concentration differences. The values for Fe(Cap) systems (Table 1) were obtained at room temperature, since their oxygen affinity [14] was great enough to ensure better than 95% oxygenation at 1 atm of oxygen. The absorption bands for $\nu(^{16}O_2)$ of 1175 and 1172 cm^{-1} disappear upon the use of $^{18}O_2$ (90% enriched) and these solutions absorb at 1096 and 1097 cm^{-1}, respectively. The absorption bands for $^{16}O_2$ also vanished when CO was bubbled through the

TABLE 1

DIOXYGEN STRETCHING FREQUENCIES

Compound	$\nu(O_2)$ [a] (cm^{-1})	Ref.
Fe(Cap)(py) [b]	1175 (1096)	c
Fe(Cap)(1-MeIm) [d]	1172 (1097)	c
Fe(HmCap) [d, e]	1160 (1085, 1080) [f]	c
Co(Cap)(1-MeIm) [d, g]	1176 (1084)	c
Co(TTP)(1-MeIm) [d, g]	1142 (1071)	c
Fe(TpivPP)(N-IrIm) [h]	1163 (1080)	6
Fe(TpivPP)(1-MeIm) [i]	1159 (1075)	6
MbO_2	1103 (1065)	17
HbO_2	1107 (1065)	17
Hb(deut Fe)	1106 (1065)	18
Hb(deut Co)	1105 (1065)	18
Cr(TPP)(py)	1142	4
Co(TpivPP)(N-IrIm) [h]	1155, 1150 [f], (1079, 1074) [f]	6
Co(TpivPP)(1-MeIm) [i]	1150 (1065)	6

[a] Value in parenthesis for $^{18}O_2$, obtained at room temperature unless otherwise noted. [b] Solvent vs. neat py. [c] This paper. [d] Solvent is 3% 1-MeIm/toluene. [e] Values obtained at —78°C. [f] $\nu(^{18}O_2)$ occurs as a doublet. [g] Solvent is 5% 1-MeIm/Ch_2Cl_2. [h] Solvent is benzene. [i] Nujol mull.

oxygenated solution and the corresponding CO adducts were formed.

The value of $\nu(^{16}O_2)$ for Fe(HmCap)(1-MeIm)(O_2) occurs at 1160 cm^{-1}. The difference spectrum resulting from the use of $^{18}O_2$ shows the $^{18}O_2$ stretch to be a doublet. The splitting due to $\nu(^{18}O_2)$ was not observed for $\nu(^{16}O_2)$. The Fe(HmCap)(1-MeIm) complex was studied at —78° C because of its low oxygen affinity [10,14] at 25°C. In order to confirm the identity of the $\nu(O_2)$ bands, CO was bubbled slowly through the chilled solutions. This resulted in the disappearance of the 1160 cm^{-1} ($\nu(^{16}O_2)$) band and of the 1085, 1080 cm^{-1} doublet ($\nu(^{18}O_2)$). Concomitant with the disappearance of the $\nu(O_2)$ bands was the growth of a new band at 1979 cm^{-1}. This band is assigned to ν(CO) of the CO adduct.

The O_2 stretches show little dependence on the metal centers or the axial bases. Changing the axial base in the Fe(Cap) system from py to 1-MeIm results in only a 4 cm^{-1} difference. Also surprising is the observation that the $\Delta\nu(O_2)$ for analogous Fe versus Co complexes is only 1 cm^{-1}.

For the Mn(TPP) system, experiments were again performed at —78° C. This was necessary in order to prevent irreversible oxidation [5a,b]. The difference spectrum resulting from the addition of $^{16}O_2$ shows no new additional bands in the superoxide region (1100 to 1200 cm^{-1}) or in the peroxide region (900 to 800 cm^{-1}) (Fig. 1A, C). However, an additional band at 797 cm^{-1} arises from oxygenation. This band is also present in the final irreversibly oxidized species. However the use of $^{18}O_2$ results in the appearance of a new band at 803 cm^{-1}, along with the band at 797 cm^{-1} (Fig. 1B). That oxygenation had occurred was confirmed by obtaining the visible spectrum of the sample. The visible spectra agreed with those previously published [5a,b]. After the addition of $^{18}O_2$ and the initial IR spectrum was taken, the solution was warmed to room temperature to allow irreversible oxidation. This was followed by cooling the solution to the original temperature of —78°C. The cold solution no longer had a band

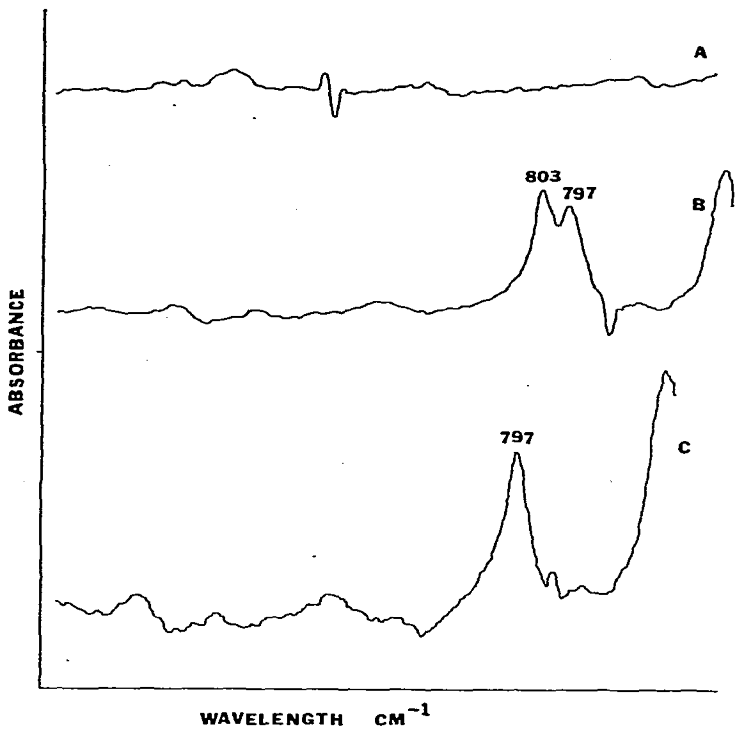

Fig. 1. All spectra are of the same MnTPP concentration and conditions. (A) Spectrum of Mn(TPP)($^{16}O_2$) minus Mn(TPP) in the region of 1240 to 1090 cm^{-1}. (B) Spectrum of Mn(TPP)($^{18}O_2$) minus Mn(TPP) in the region of 940 to 750 cm^{-1}. (C) Spectrum of Mn(TPP)($^{16}O_2$) minus Mn(TPP) in the region of 930 to 740 cm^{-1}.

at 803 cm^{-1}, but the band at 797 cm^{-1} remained. That oxidation had occurred was further confirmed by visible spectroscopy [5a,b]. Results from Nujol mulls of the oxidized solids ($^{16}O_2$ and $^{18}O_2$) also agree with the low temperature toluene solution infrared spectra. In both cases there was no band at 803 cm^{-1}, yet the band at 797 cm^{-1} was present.

TABLE 2

CARBONYL STRETCHING FREQUENCIES

Compound	ν(CO) (cm^{-1})	Ref.
Fe(Cap)(py) [a]	2003	*b*
Fe(Cap)(1-MeIm) [c]	2002	*b*
Fe(Cap) [d]	2020, 1997 [e]	*b*
Fe(HmCap)(1-MeIm) [f]	1979	*b*
Fe(TpivPP)(1-MeIm) [g]	1969	6
Fe(OEP)(1-MeIm) [g]	1970	21
MbCO	1945	22 [a, b]
HbCO	1951	22

[a] Solvent is neat py. [b] This paper. [c] Solvent is 5% 1-MeIm/Toluene. [d] Solvent is toluene. [e] Values are for the bis adduct. [f] Solution is 1.8 *M* 1-MeIm in toluene. [g] Solvent is benzene.

The carbonyl adducts of the Fe complexes were formed either from the five-coordinated species, or from replacement of the coordinated oxygen of the dioxygen complex. In both cases when the spectra of the five-coordinated base compounds or six-coordinated oxygen adducts were subtracted from that of the carbonyl adduct, the same values for ν(CO) were obtained. Values of 2003 and 2002 cm^{-1} were obtained for Fe(Cap)(py)(CO) and Fe(Cap)(1-MeIm)(CO), respectively. For Fe(HmCap)(1-MeIm)(CO) the observed ν(CO) was 1979 cm^{-1}. The values for ν(CO) are reported in Table 2.

Discussion

Dioxygen metal complexes. Earlier chemical and EPR experiments [5a—c] indicate that the Mn(TPP) complex binds dioxygen in a side-on symmetrical trigonal configuration (II). This premise is consistent with the observed value of 803 cm^{-1} for $\nu(^{18}O_2)$. That the value for $\nu(^{16}O_2)$ was not obtained may be due to the unfortunate coincidence that the $^{16}O_2$ stretch coincides with the toluene solvent absorption at 844 cm^{-1}. This is the region of the spectrum where $\nu(^{16}O_2)$ is estimated to occur on the basis of the position of $\nu(^{18}O_2)$. It is quite apparent that the stretch at 803 cm^{-1} is due to $\nu(^{18}O_2)$. This stretch appears only when $^{18}O_2$ is used and only when the dioxygen adduct is present, as confirmed by optical spectroscopy. In addition, upon warming the solution to allow complete conversion of the dioxygen adduct to the irreversibly oxidized species, the 803 cm^{-1} stretch disappears. Nujol mulls of the solid oxidized by both $^{16}O_2$ and $^{18}O_2$, show the absence of a 803 cm^{-1} band. It is also significant that there are no new absorption bands in the superoxide region (1100 to 1200 cm^{-1}) upon oxygenation. The additional presence of a band at 797 cm^{-1} may be due to the splitting of a porphyrin band due to the loss of symmetry brought about by oxygenation. This is supported by the EPR analysis [5b,c] which indicates a large rhombic distortion present upon adduct formation.

Next of importance in this study is the effect of the environment of the dioxygen on its $\nu(O_2)$ in metal complexes with similar structure and bonding, e.g. Co and Fe complexes. The results show (Table 1) that the metal has little effect on the value of $\nu(O_2)$ for model compounds. In the cap systems there is only a 4 cm^{-1} difference, and in the "picket fence" complexes a 10 cm^{-1} difference [6]. Not suprisingly, Maxwell and Caughey [18] report that for the deuteroporphyrin Fe and Co reconstituted oxyHbs there was only a 1 cm^{-1} difference in $\nu(O_2)$ values. This is unexpected, because it was believed tha the greater the electron transfer from metal to dioxygen, the lower the values of $\nu(O_2)$. Although EPR [15] and theoretical calculations [16] indicate there is significant variation in the amount of electron transfer with changes in metal centers and porphyrins, the values of $\nu(O_2)$ do not reflect this. Thus the O_2 stretching frequencies should be used primarily for the determination of the mode of bonding of the dioxygen ligand, e.g. 1150 cm^{-1} region for superoxide like end-on bonding (I) and 850 cm^{-1} region for peroxide-like side-on bonding (II). However, it should be noted that the values of $\nu(O_2)$ for the natural oxyproteins are 50—70 cm^{-1} lower than for the model compounds. This may be caused by interaction of the protein residues with the dioxygen moiety, or it may reflect the larger oxygen affinity of the natural proteins relative to the models.

The $\nu(O_2)$ values for the Fe and Co "capped" porphyrin models are similar to those reported earlier for other Fe [2] and Co [3] systems (Table 1). The presence of the doublet for $^{18}O_2$ for Fe(HmCap)(1-MeIm)(O_2) may be due to the two different conformers of O_2 and 1-MeIm orientations [6]. The dioxygen "capped" complexes have $\nu(O_2)$ values only about 10 cm^{-1} higher than the "picket fence" compounds which should be expected since both are tetraarylporphyrins that affor a nonpolar pocket free from solvent interactions for the dioxygen ligand. Consistent with this behavior is the observation that there is only a 3 cm^{-1} shift in $\nu(O_2)$ for Fe(Cap)(py)(O_2) versus Fe(Cap)(1-MeIm)(O_2). Where the dioxygen moiety has a chance to interact with solvent we note a decrease in $\nu(O_2)$. The Co(TTP)(1-MeIm) system has a $\nu(O_2)$ of 1142 cm^{-1} which is 34 cm^{-1} lower than Co(Cap)(1-MeIm)(O_2).

Carbon monoxide metal complexes. The values for ν(CO) in the Fe(Cap) complexes are higher than those found in other model ferrous porphyrins and in the natural proteins (Table 2). For the simple model systems, the carbonyl group is bound normal to the porphyrin plane and is relatively free of steric constraints. It has been suggested [6] that the lowering of ν(CO) in the natural system is due to distortion of the normally linear Fe—CO group to a bent structure, reported for three different hemoproteins. In addition, it has been observed that in mutant Hbs where the binding site is more open, ν(CO) increases [19]. These results appear to be in contrast with our present data. In the Fe(Cap) system, the CO binding site is less open than in the Fe(HmCap) complex, yet ν(CO) is higher in the Fe(Cap) complex. This may cast some doubt on the validity of the above theory. However, there does exist an alternative explanation for the exceptionally high ν(CO) for Fe(Cap) compounds. Preliminary data [20] on the X-ray structure of the free base porphyrin CapH_2 indicate that the distance from the center of the porphyrin plane to the benzene ring in the cap is 3.84 Å. This value indicates there would be interaction between a linear bound CO and the cap. This interaction between the oxygen atom of the carbonyl group and the π system of the cap benzene may account for the higher value of ν(CO). Should this be the case, then it follows that the larger cap size of Fe(HmCap) would result in less interaction and a lower ν(CO). The value of ν(CO) for Fe(HmCap), 1979 cm^{-1}, is similar to the values for other simple model ferrous porphyrin complexes.

Conclusions

The value of $\nu(O_2)$ can be used to determine the geometry of the bound dioxygen, differentiating between end-on bent and symmetrical side-on binding. In the case of Mn(TPP)(O_2), the dioxygen is bound symmetrically, while in the cobalt and iron systems it is bound end-on in a bent fashion. For end-on bent bonding, the value of $\nu(O_2)$ is relatively insensitive to the metal center and porphyrin. The values of ν(CO) disagree with arguments that steric constraints lower ν(CO), since in comparing ν(CO) values for Fe(HmCap)(1-MeIm)(CO) and Fe(Cap)(1-MeIm)(CO) we found that the system, Fe(HmCap)(1-MeIm)(CO) has fewer steric constraints, but a lower ν(CO).

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