The infrared spectra of 'base-free' dioxygen adducts of ruthenium(II) and osmium(II) porphyrins

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Abstract

The IR spectrum of Ru(TPP) cocondensed with $^{16}O_2$ at ~30 K exhibits two O–O stretching bands at 1167 and 1114 cm^{-1} which are shifted to 1101 and 1057 cm^{-1}, respectively, by $^{16}O_2/^{18}O_2$ substitution. The former at 1167 (1101 cm^{-1} is assigned to the end-on type dioxygen adduct, Ru(TPP)O_2 whereas the latter at 1114 (1057) cm^{-1} is attributed to the O_2-bridging adduct, [Ru(TPP)]$_2O_2$. The IR spectrum of Os(TPP) cocondensed with $^{16}O_2$ under similar conditions exhibits only one O–O stretching band at 1090 cm^{-1} which is shifted to 1030 cm^{-1} by $^{16}O_2/^{18}O_2$ substitution. This band is also attributed to the bridging dioxygen adduct [Os(TPP)]$_2O_2$. These assignments are made based on the trends in frequencies and intensities of the O–O stretching bands in the Fe, Ru and Os series and the results of warm-up experiments on the IR spectrum of the Ru(TPP)–O_2 system.

Introduction

Ruthenium and osmium porphyrins are highly important as isoelectronic analogs of biologically important iron porphyrins. For example, Ru(II)-reconstituted myoglobin [1] has been prepared to examine the effect of changing the metal on the metal–O_2 binding. It is, therefore, of great interest to compare the vibrational spectra of a series of metallophorphyrins and their dioxygen adducts in which the central metal is changed from Fe to Ru to Os. We have previously compared the vibrational spectra of Fe(TPP)(pip)O_2 (TPP: tetraphenylporphyrinato dianion; pip: piperidine) and Ru(TPP)(py)O_2 (py: pyridine) where the dioxygen assumes end-on geometry; the former exhibits $\nu(O_2)$ and ν(Fe–O_2) at 1157 and 575 cm^{-1}, respectively [2] whereas the latter exhibits these bands at 1103 and 603 cm^{-1}, respectively [3, 4]. Thus, $\nu(O_2)$ is much lower and ν(M–O_2) is much higher in the latter than in the former. This result was interpreted as indicating that π-backbonding is stronger in the Ru(II)–O_2 bond than in the Fe(II)–O_2 bond due to the more extended 4d orbitals of Ru(II) relative to the 3d orbitals of Fe(II). A similar trend was noted for ν(CO) and ν(M–CO) of CO adducts of these porphyrins [5].

As to mono-oxo porphyrins, we assigned ν(Fe=O) of OFe(TPP) at 853 cm^{-1} for the first time [6]. The corresponding ν(Ru=O) of ORu(TMP) (TMP: tetramesitylporphyrinato dianion) was observed at 823 cm^{-1} in benzene (IR) [7] and at 812 cm^{-1} in toluene (resonance Raman) [4]. Although dioxo iron porphyrins are not known, those of Ru(VI) and Os(VI) have been prepared; ν_a(O=Ru=O) of Ru(TMP)(O)$_2$ [4, 7] and ν_a(O=Os=O) of Os (TMP)(O)$_2$ [8] are reported to be at 821 and 841 cm^{-1}, respectively. Thus far, no vibrational data are available on a series of 'base-free' dioxygen adducts of metalloporphyrins in which only the central metal is changed from Fe to Ru to Os. In this work, we prepared the dioxygen adducts of Ru(TPP) and Os(TPP) for the first time and compared their IR spectra with that of Fe(TPP)O_2 obtained previously [9].

It should be noted, however, that Ru(por) and Os(por) (por: OEP(octaethylporphyrinato dianion), TPP and TTP (tetra-*p*-tolylporphyrinato dianion)) are dimerized via the metal–metal bond in the solid state as well as in solution [10, 11]. Recently, Tait *et al.* [12] located the ν(MM) of $\{[Ru(OEP)]_2\}^{n+}$ and $\{[Os(OEP)]_2\}^{n+}$ ($n=0$, 1 and 2) in the 310–285 and 266–233 cm^{-1} regions, respectively. As will be shown later, we were able to produce monomeric

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vapor of Ru(TPP) and Os(TPP) and cocondense them with O_2 on a cold window.

Experimental

Compounds

Ru(TPP)CO(CH_3OH), Os(TPP)CO(CH_3OH) and Ru(TMP)CO(CH_3OH) were purchased from Midcentury, Posen, IL. The bis-pyridine complexes of these porphyrins were prepared by the literature method [13]. The gases, $^{16}O_2$ (99.9%, Amerigas) and $^{18}O_2$ (97%, Monsanto Research) were used without further purification.

Spectral measurements

The samples for IR measurements were prepared by using the laser-heated miniature oven technique which was developed originally for our matrix isolation Raman studies [14]. Figure 1 is a schematic representation of our apparatus which was modified for this work. The bis-pyridine complex of Ru or Os porphyrin (~ 2 mg) was placed in a Pyrex capillary tube which was fitted into a hole drilled at the center of a spectroscopic grade spark graphite rod (8) (6.25 mm in diammeter and 6 mm long). The rod was surrounded by an aluminum radiation shield to reduce heat loss and was placed in a Pyrex tubing (9) which was glued to an O-ring shape iron plate (10). As the first step, the laser beam was directed at the oven through a quartz window (11) to heat it up to ~200 °C under vacuum (~10^{-5} torr) for 30 min or less to remove adsorbed water and to dissociate coordinated pyridine from the porphyrin. During this procedure, the oven was oriented in a direction which projected the dissociating pyridine vapor away from the CsI window (7). After pyridine was completely removed, the CsI window was cooled down to ~30 K by an Airproduct model CS-202 closed cycle helium cryocooler (2). Then, the graphite oven (8) was turned around to face the CsI window (7) by using a magnet externally (this orientation is shown in Fig. 1). Then the oven temperature was raised quickly (within ~ 10 min) to 400 ~ 450 °C using high laser power so that the 'base-free' porphyrin was deposited as a thin film on the CsI window. Next, the O_2 gas was introduced through a gas line (3) and deposited on top of the thin film of 'base-free' porphyrin. The temperature of the CsI window was controlled by a heater surrounding the cooling unit. The IR spectrum of a thin film thus prepared was recorded on a Beckman model 4260 IR spectrophotometer. Polystyrene bands were used for frequency calibration. The accuracy of frequency reading was ± 1 cm^{-1}.

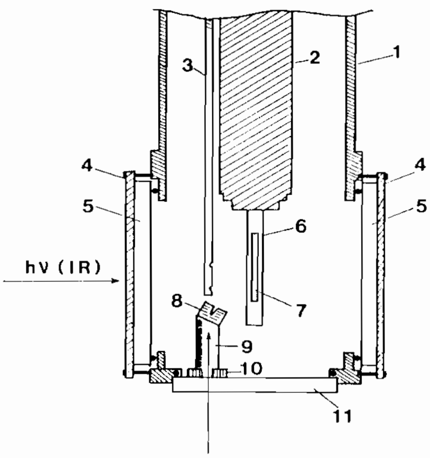


Fig. 1. Schematic diagram of the IR matrix isolation apparatus: 1, vacuum shroud; 2, cold tip; 3, gas line; 4, window holder; 5, CsI window; 6, metal frame; 7, CsI window for sample deposition; 8, miniature oven in aluminum radiation shield; 9, Pyrex glass tubing; 10, iron plate; 11, quartz window.

Results and discussion

As stated earlier, Ru(TPP) and Os(TPP) are known to exist as metal–metal bonded dimers in the solid state as well as in solution [10, 11]. To produce the monomeric porphyrin, we took special precautions in our experimental procedure. Namely, the oven temperature was quickly raised to 400 ~ 500 °C by using high power laser beam, and the Ru(TPP) or Os(TPP) vapor thus obtained was deposited on the CsI window (~30 K) and reacted immediately with O_2 gas. Slow heating (1 h or longer) of the oven at lower temperatures did not produce any vapor because the monomeric species was not produced under these conditions. We also noted that the majority of the sample remaining in the oven did no longer vaporize at 400 ~ 500 °C due to decomposition. The IR spectra of dioxygen adducts reported in this work are that of monomeric porphyrin since we obtained similar results for Ru(TMP) which is known not to dimerize due to steric hindrance between the mesityl groups on each porphyrin ring [15].

Figure 2 shows the IR spectra of Ru(TPP) cocondensed with $^{16}O_2$ and $^{18}O_2$ at ~30 K. The bands at 1167 and 1114 cm^{-1} are clearly shifted to 1101 and 1057 cm^{-1}, respectively, by $^{16}O_2/^{18}O_2$ substitution. The shift of the former band (66 cm^{-1}) is in perfect agreement with that expected for a diatomic harmonic oscillator (66 cm^{-1}) whereas that of the latter band (57 cm^{-1}) is slightly smaller than the theoretical value (63 cm^{-1}). Similar experiments with Ru(TMP) yielded two oxygen-isotope sensitive bands at 1166 and 1114 cm^{-1} (at ~45 K), thus confirming that

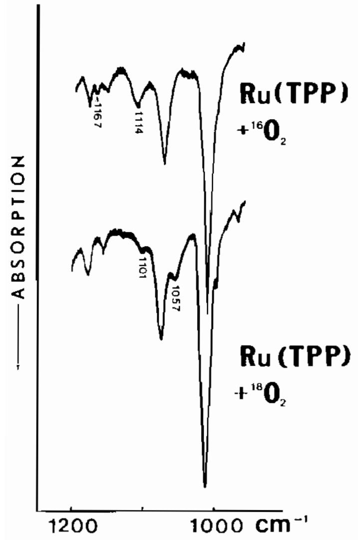


Fig. 2. IR spectra of Ru(TPP) cocondensed with $^{16}O_2$ and $^{18}O_2$ at ~30 K.

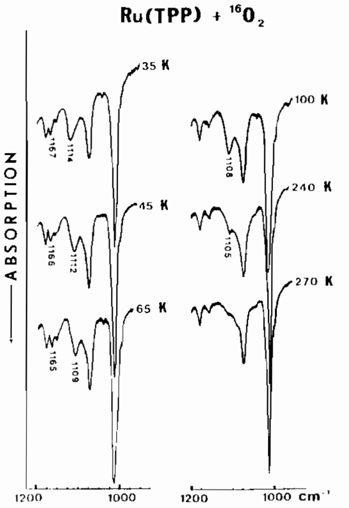
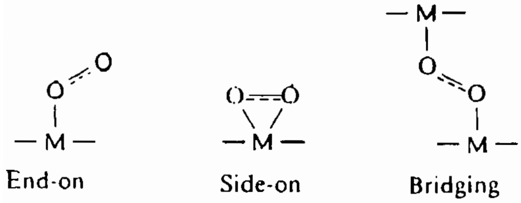


Fig. 3. Temperature dependence of IR spectrum of Ru(TPP) cocondensed with $^{16}O_2$.

these dioxygens are bonded to the monomeric porphyrins.

Structurally, dioxygen adducts are classified into three types:



We have previously shown by IR [9] and RR [16] spectroscopy that $Fe(TPP)O_2$ in O_2/Ar matrices exists in two isomeric forms: the end-on isomer which exhibits $\nu(O_2)$ at 1195 cm^{-1} and the side-on isomer which shows it at 1106 cm^{-1}. At ~15 K, the former is *c.* four times stronger than the latter, and gains its intensity at the expense of the latter when the matrix is warmed to ~110 K. At this temperature, the latter band disappears completely. On the other hand, $Ru(TPP)O_2$ exhibits $\nu(O_2)$ at 1167 and 1114 cm^{-1} at ~30 K, and the former is weaker than the latter. Furthermore, the former band disappears completely when the temperature is raised to ~100 K (Fig. 3).

As stated above, $\nu(O_2)$ of the end-on isomer of $Fe(TPP)O_2$ (1195 cm^{-1}) is higher than that of the side-on isomer (1106 cm^{-1}). Thus, $\nu(O_2)$ at 1167 cm^{-1} observed for the $Ru(TPP)O_2$ system can be assigned to the end-on isomer of $Ru(TPP)O_2$. Such a down-shift of $\nu(O_2)$ in going from Fe(II) to Ru(II) porphyrins has already been observed for six-coordinate 'base-bound' porphyrins [2, 4]. As mentioned earlier, this is due to the increased π-backbonding in the Ru(II)–O_2 bond relative to the Fe(II)–O_2 bond. It is interesting to note that $\nu(O_2)$ of five-coordinate $Ru(TPP)O_2$ is at 1167 cm^{-1} whereas that of a six-coordinate Ru(II) porphyrin having an axial base ligand (1, 3-dicyclohexylimidazole) is at 1103 cm^{-1} [3]. As noted for dioxygen adducts of Fe(II) porphyrins [2, 9], this downshift can be attributed to the base ligand effect which increases the negative charge on the O_2 via the σ and/or π donation.

The second $\nu(O_2)$ at 1114 cm^{-1} observed for Ru(TPP) cannot be attributed to the side-on isomer since its frequency is higher than that of $Fe(TPP)O_2$ (1106 cm^{-1}) which is known to be side-on. Furthermore, the 1114 cm^{-1} band of Ru(TPP) becomes stronger and its intensity is maximized near 100 K (Fig. 3) whereas the 1106 cm^{-1} band of Fe(TPP) disappears when the temperature is raised to ~100 K. These observations suggest that the dioxygen adduct responsible for the 1114 cm^{-1} band of Ru(TPP) is not of side-on type.

Figure 4 shows the IR spectra of Os(TPP) reacted with $^{16}O_2$ and $^{18}O_2$ at ~35 K. In this case, we observed only one oxygen-isotope sensitive band at 1090 cm^{-1} which was shifted to 1030 cm^{-1} by $^{16}O_2/^{18}O_2$ substitution. This frequency is 24 cm^{-1} lower than that of Ru(TPP) (1114 cm^{-1}). Thus, the structure of the dioxygen adduct responsible for the 1090 cm^{-1} band is similar to that of $Ru(TPP)O_2$ which exhibits the $\nu(O_2)$ at 1114 cm^{-1}.

Previously, we [17] observed two $\nu(O_2)$ bands at 1104 and 1001 cm^{-1} (IR) when Fe(salen)(salen: *N*, *N'*-ethylenebis(salicylideneiminato dianion) vapor was cocondensed with O_2 or O_2/Ar at ~25 K. The former was assigned to the side-on isomer [9] whereas

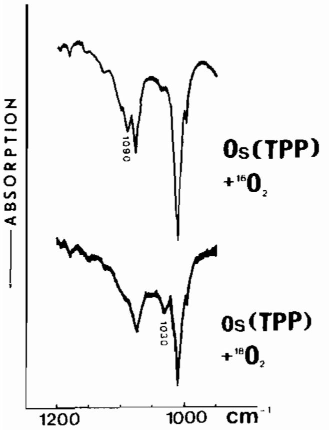


Fig. 4. IR spectra of Os(TPP) cocondensed with $^{16}O_2$ and $^{18}O_2$ at ~35 K.

TABLE 1. $\nu(O_2)$ of dioxygen adducts (cm^{-1})

	End-on	Side-on	Bridging
$Fe(TPP)O_2$	1195 (1127)[a]	1106 (1043)	
$Ru(TPP)O_2$	1167 (1101)		1114 (1057)[a]
$Os(TPP)O_2$			1090 (1030)[a]

The number in parentheses indicates the $\nu(^{18}O_2)$ frequency.
[a]Stable form.

the latter was assigned to the bridging dimer, $[Fe(salen)]_2O_2$ [17]. This is based on the observation that the 1001 cm^{-1} band becomes stronger as the $Fe(salen)/O_2$ ratio increases and as the temperature is raised. This behavior is similar to that of the 1114 and 1090 cm^{-1} bands of Ru(TPP) and Os(TPP), respectively. Hence, we attribute these bands to $\nu(O_2)$ of the O_2-bridging dimers, $[Ru(TPP)]_2O_2$ and $[Os(TPP)]_2O_2$, respectively (Table 1). The lowering of $\nu(O_2)$ on going from the Ru (1114 cm^{-1}) to Os (1090 cm^{-1}) complexes is expected since π-back-bonding from the metal to the O_2 increases on going from Ru to Os. Finally, relatively low intensities of these $\nu(O_2)$ bands in IR spectra suggest that the structures of these dimers are not completely centrosymmetric due to random orientation and limited mobility of metalloporphyrins in the film state at low temperatures.

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References

1 T. S. Srivastava, *Biochim. Biophys. Acta, 491* (1970) 599.
2 K. Nakamoto, I. R. Paeng, T. Kuroi, T. Isobe and H. Oshio, *J. Mol. Struct., 189* (1988) 293.
3 J. P. Collman, J. I. Brauman, J. P. Fitzgerald, J. W. Sparapany and J. A. Ibers, *J. Am. Chem. Soc., 110* (1988) 3486.
4 I. R. Paeng and K. Nakamoto, *J. Am. Chem. Soc., 112* (1990) 3289, and refs. therein.
5 D. Kim, Y. O. Su and T. G. Spiro, *Inorg. Chem., 25* (1986) 3993.
6 L. M. Proniewicz, K. Bajdor and K. Nakamoto, *J. Phys. Chem., 90* (1986) 1760.
7 J. T. Groves and K.-H. Ahn, *Inorg. Chem., 26* (1987) 3831.
8 C.-M. Che, W.-C. Chung and T.-F. Lai, *Inorg. Chem., 27* (1988) 2801.
9 T. Watanabe, T. Ama and K. Nakamoto, *J. Phys. Chem., 88* (1984) 440.
10 J. P. Collman, C. E. Barnes, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc., 106* (1984) 3500.
11 J. P. Collman, C. E. Barnes and L. K. Woo, *Proc. Natl. Acad. Sci. U.S.A., 80* (1983) 7684.
12 C. D. Tait, J. M. Garner, J. P. Collman, A. P. Sattelberger and W. H. Woodruff, *J. Am. Chem. Soc., 111* (1989) 7806 and 9072.
13 A. Antipas, J. W. Bucher, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc., 100* (1978) 3015; *102* (1980) 198.
14 W. Scheuermann and K. Nakamoto, *Appl. Spectrosc., 32* (1978) 251.
15 J. T. Groves and R. Quinn, *Inorg. Chem., 23* (1984) 3844.
16 L. M. Proniewicz, I. R. Paeng and K. Nakamoto, *J. Am. Chem.Soc., 113* (1991) 3294.
17 L. M. Proniewicz, T. Isobe and K. Nakamoto, *Inorg. Chim. Acta, 155* (1989) 91.