

八乙基卟啉和四苯基卟啉合钌(II) 及锇(II)的二氧化加合物的红外光谱

OEP(八乙基卟啉阴离子)和 TPP(四苯基卟啉阴离子)合钌(II)和锇(II)的二氧化加合物由 matrix 分离技术得到($T=20-43\text{K}$, $P=10^{-5}-10^{-6}\text{torr}$). 为了确定 $\nu(\text{O}_2)$ 带的归属应用了同位素取代法 $^{16}\text{O}_2 / ^{18}\text{O}_2$. IR 谱说明对于钌的两种加合物(指 OEP 和 TPP)都有两种异构体, 其 $\nu(^{16}\text{O}_2)$ 频率为: $\text{Ru}(\text{OEP})\text{O}_2$, 1141 和 1103cm^{-1} ; $\text{Ru}(\text{TPP})\text{O}_2$, 1167 和 1114cm^{-1} . $\text{Os}(\text{TPP})\text{O}_2$ 只生成一种异构体, $\nu(^{16}\text{O}_2)=1090\text{cm}^{-1}$, 异构体 $\nu(^{16}\text{O}_2)$: $[\text{Ru}(\text{OEP})\text{O}_2]$, 1141cm^{-1} , $[\text{Ru}(\text{TPP})\text{O}_2]$, 1167cm^{-1} , 这些加合物约在 100K 时分解, 它们的结构指定为 end on, 而异构体 $[\text{Ru}(\text{OEP})\text{O}_2]$, 1103cm^{-1} , $[\text{Ru}(\text{TPP})\text{O}_2]$, 1114cm^{-1} 和 $[\text{Os}(\text{TPP})\text{O}_2]$, 1090cm^{-1} , 在 240-270K 分解, 它们的结构指定为桥联二聚体. 在加合物中, 将 OEP 换成 TPP 引起的钌加合物 $\nu(\text{O}_2)$ 频率的改变比铁和钴加合物更大. $\nu(\text{O}_2)$ 相对强度的变化顺序为: $\text{Fe}(\text{II}) \rightarrow \text{Ru}(\text{II}) \rightarrow \text{Os}(\text{II})$.

关键词: 卟啉钌(II)和锇(II)配合物的二氧化物 matrix 分离技术 红外光谱

INFRARED SPECTRA OF DIOXYGEN ADDUCTS OF RUTHENIUM(II) AND OSMIUM(II) OCTAETHYLPORPHINE AND TETRAPHENYLPORPHINE

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Dioxygen adducts of $\text{Ru}(\text{II})$ and $\text{Os}(\text{II})$ with OEP (octaethylporphyrinato anion) and TPP (tetraphenylporphyrinato anion) were obtained by using the matrix isolation technique ($T=20-43\text{K}$ and $P=10^{-5}-10^{-6}\text{torr}$). To assign $\nu(\text{O}_2)$ bands the isotope substitution $^{16}\text{O}_2 / ^{18}\text{O}_2$ has been applied. IR spectroscopy revealed that in the case of Ru adducts two isomers exist in both adducts for which $\nu(^{16}\text{O}_2)$ band frequencies amount to 1141 and 1103cm^{-1} for $\text{Ru}(\text{OEP})\text{O}_2$; for $\text{Ru}(\text{TPP})\text{O}_2$ they are 1167 and 1114cm^{-1} . $\text{Os}(\text{TPP})\text{O}_2$ forms one isomer only for which $\nu(^{16}\text{O}_2)=1090\text{cm}^{-1}$. Isomers of $\nu(^{16}\text{O}_2)$ frequencies: 1141cm^{-1} $[\text{Ru}(\text{OEP})\text{O}_2]$ and 1167cm^{-1} $[\text{Ru}(\text{TPP})\text{O}_2]$ which decompose at ca 100K have been assigned the end-on structure, while isomers 1103cm^{-1} $[\text{Ru}(\text{OEP})\text{O}_2]$, 1114cm^{-1} $[\text{Ru}(\text{TPP})\text{O}_2]$ and 1090cm^{-1} $[\text{Os}(\text{TPP})\text{O}_2]$ that decompose at 240-270K the bridging dimer structure. Substitution of OEP by TPP in adducts causes more considerable changes in $\nu(\text{O}_2)$ band frequencies in case of Ru, as compared with Fe and Co.

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Introduction

The literature contains only fragmentary data concerning vibrational spectra of dioxygen adduct of Ru(II) and Os(II) with some porphyrins⁽¹⁻⁶⁾. G.A. Schick and D.F. Bocian⁽¹⁾ reported Resonance Raman (RR) spectra for the bis-pyridine adducts of metalloctaethylporphyrins [(OEP)M(py)₂], where M = Fe(II), Ru(II) and Os(II). Frequency variations in the porphyrin modes with metal substitution are interpreted in terms of changes in metal-porphyrin bonding (both δ and π), porphyrin core size, and metal charge. Ruthenium and osmium porphyrins are highly important as isoelectronic analogs of biologically important iron porphyrins.

The aim of the present study has been to investigate upon matrix isolation IR spectra of "base-free" dioxygen adducts of ruthenium and osmium octaethylporphyrine [Ru(OEP)] and tetraphenylporphyrine [Ru(TPP)] and to compare these results with data of analogous compounds of iron(II).

Experimental

The bis-pyridine complexes of Ru and Os porphyrins with OEP and TPP were prepared by the literature method^(1,7,8). The gases, ¹⁶O₂ (99.9%, Amerigas) and ¹⁸O₂ (97%, Monsanto Research) were used without further purification. During matrix IR measurements the bis-pyridine complex of Ru or Os porphyrin was placed in the graphite cell of our matrix-isolation system and irradiated by laser line 514.5 nm (with 200–800mW) under vacuum at 10⁻¹–10⁻⁶ torr for 15–60min. until the vacuum gauge indicated a complete dissociation of the axial base ligand from the complex. The resulting "base-free" complex was evaporated from graphite cell irradiated by laser (with 500–1500mW) and cocondensed with ¹⁶O₂ or ¹⁸O₂ on a CsI window which was cooled to ~20K by a CTI Model 21 closed cycle helium refrigerator. A thin film of complexes was prepared by the same procedure.

The application of a graphite cell heated by laser⁽⁹⁾ instead of a Knudsen cell⁽⁷⁾ enabled us to use small quantities (0.5–3mg) of unique substances for analyses. IR spectra were measured on a Beckman Model 4260 infrared spectrophotometer with a 50, 20 and 5cm⁻¹/min chart speed. Polystyrene bands were used for frequency calibration. The accuracy of frequency readings was $\pm 1\text{cm}^{-1}$.

Results and Discussion

Fig.1 shows the matrix isolation IR spectra of dioxygen adducts of Fe(TPP), Ru(TPP) and Os(TPP). When Ru(TPP) vapor was cocondensed with ¹⁶O₂, two bands appeared at 1167 and 1114cm⁻¹ (at ~45K) as is shown in trace C and Table I. These bands were shifted to 1101 and 1057cm⁻¹, respectively, when Ru(TPP) was reacted with ¹⁸O₂ (trace D). Upon addition

$^{16}\text{O}_2$ to $\text{Ru}(\text{OEP})$, two bands appear at 1141 and 1103cm^{-1} (Fig.2A). These bands were shifted to 1079 and 1046cm^{-1} , respectively, when $\text{Ru}(\text{OEP})$ was reacted with $^{18}\text{O}_2$ (Fig.2B).

Table 1 Comparison of $\nu(^{16}\text{O}_2)$ and $\nu(^{18}\text{O}_2)$ IR Frequencies in Some $\text{Co}(\text{II})$, $\text{Mn}(\text{II})$ ⁽¹⁰⁻¹²⁾ and $\text{Fe}(\text{II})$, $\text{Ru}(\text{II})$ and $\text{Os}(\text{II})$ Dioxygen Adduct Complexes with OEP and TPP (cm^{-1})

species	$\nu(^{16}\text{O}_2)$	$\nu(^{18}\text{O}_2)$	$\nu(^{16}\text{O}_2) - \nu(^{18}\text{O}_2)$
$\text{Co}(\text{OEP})\text{O}_2$	1275	1202	73
$\text{Co}(\text{TPP})\text{O}_2$	1278	1209	69
$\text{Mn}(\text{OEP})\text{O}_2$	991	934	57
$\text{Mn}(\text{TPP})\text{O}_2$	983	933	50
$\text{Fe}(\text{OEP})\text{O}_2$	1190, 1104	1124, 1042	66, 62
$\text{Fe}(\text{TPP})\text{O}_2$	1195, 1106	1127, 1043	68, 63
$\text{Ru}(\text{OEP})\text{O}_2$	1141, 1103	1079, 1046	62, 57
$\text{Ru}(\text{TPP})\text{O}_2$	1167, 1114	1101, 1057	66, 57
$\text{Os}(\text{TPP})\text{O}_2$	1090	1030	60

Fig.1 IR spectra of

- (A) $\text{Fe}(\text{TPP}) + ^{16}\text{O}_2$,
 (B) $\text{Fe}(\text{TPP}) + ^{18}\text{O}_2$,
 (C) $\text{Ru}(\text{TPP}) + ^{16}\text{O}_2$,
 (D) $\text{Ru}(\text{TPP}) + ^{18}\text{O}_2$,
 (E) $\text{Os}(\text{TPP}) + ^{16}\text{O}_2$ and
 (F) $\text{Os}(\text{TPP}) + ^{18}\text{O}_2$ at $\sim 45\text{K}$

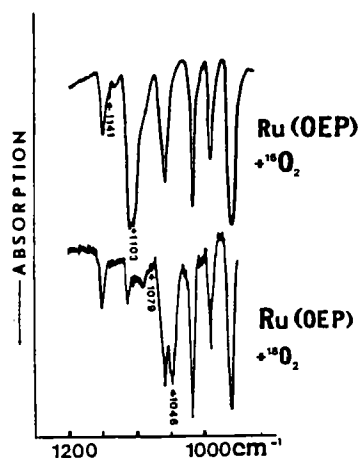
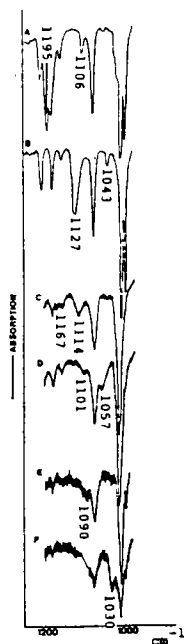


Fig.2 IR spectra of $\text{Ru}(\text{OEP}) + ^{16}\text{O}_2$ and $\text{Ru}(\text{OEP}) + ^{18}\text{O}_2$ at $\sim 45\text{K}$

The observed isotopic shifts of these two bands (66 and 57cm^{-1} , $\text{Ru}(\text{TPP})$; 62 and 57cm^{-1} $\text{Ru}(\text{OEP})$, respectively) are in agreement with that expected for the perturbed diatomic molecules. In the case of $\text{Os}(\text{TPP})$ reacted with $^{16}\text{O}_2$ and $^{18}\text{O}_2$ only one oxygen-isotope sensitive band at 1090cm^{-1} is observed (Fig.1E). It was shifted to 1030cm^{-1} by $^{16}\text{O}_2 / ^{18}\text{O}_2$ substitution (Fig.1F). $\text{Fe}(\text{TPP})$ (Fig.1A and B) and $\text{Fe}(\text{OEP})$ (Table 1) form two isomeric dioxygen adducts whose O_2 stretching frequencies are 1195 ; 1106cm^{-1} (isomer I) and 1106 ; 1104cm^{-1} (isomer II), respectively. These bands were shifted to 1127 , 1043cm^{-1} [$\text{Fe}(\text{TPP})$] and

1124, 1042 cm^{-1} [Fe(OEP)] when iron porphyrins were reacted with $^{18}\text{O}_2$. In literature [7] it has been established that isomer I, in case of Fe(OEP) and Fe(TPP), is end-on and isomer II side-on type*. Isomer I is stable up to $\sim 200\text{K}$ (at which temperature it starts to decompose), whereas isomer II is converted to isomer I by raising the temperature to $\sim 100\text{K}$. It was found that the $\nu(\text{O}_2)$ of isomer I is far stronger than that of isomer II. Also in both spectra of Ru(TPP) O_2 and Ru(OEP) O_2 two $\nu(\text{O}_2)$ bands occur. These bands may be ascribed the existence of two isomers: bands within 1167–1141 cm^{-1} (isomer I) and 1114–1103 cm^{-1} (isomer II). In the case of Ru adducts the bands of isomer II are more intensive. Co(OEP) O_2 , Co(TPP) O_2 , Mn(OEP) O_2 and Mn(TPP) O_2 do not form two isomers (Table 1).

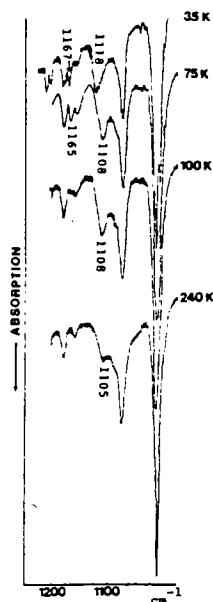


Fig.3 Temperature dependence of IR spectrum of Ru(TPP) cocondensed with $^{16}\text{O}_2$

Fig.3 shows, as an example, spectra of Ru(TPP) + $^{16}\text{O}_2$ at various temperatures. With the rise in temperature both in spectra of Ru(OEP) + $^{16}\text{O}_2$, Ru(OEP) + $^{18}\text{O}_2$ and in those of Ru(TPP) + $^{16}\text{O}_2$, Ru(TPP) + $^{18}\text{O}_2$ the frequencies of $\nu(\text{O}_2)$ of oxygen bands are decreased. Within the range of lower temperatures (20–45K) the frequency decrease is faster than that at higher temperatures (Fig.4). Also the relative intensity of bands $\nu(\text{O}_2)$ is changed. For Ru(TPP) +

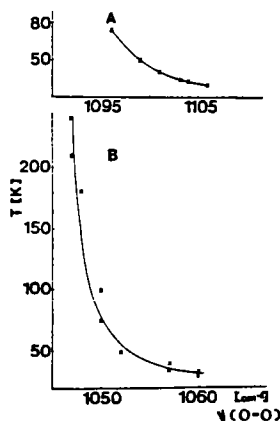
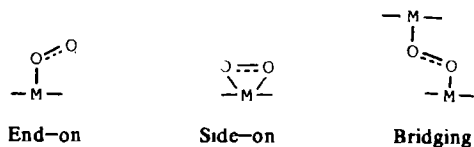


Fig.4 Dependence of $\nu(^{18}\text{O}_2)$ band frequencies on temperature in IR spectra of Ru(TPP) + $^{18}\text{O}_2$: isomer I, end-on, (A) and isomer II, bridging, (B)

* Structurally, dioxygen adducts are classified into three types:



O_2 the bands corresponding to isomer II [$\nu(^{16}O_2)$ at ~ 1114 and $\nu(^{18}O_2)$ at $\sim 1057cm^{-1}$] reach the maximum intensity within the temperature range from 100 to 150K, while the bands of isomer I [$\nu(^{16}O_2)$ at ~ 1167 and $\nu(^{18}O_2)$ at $\sim 1101cm^{-1}$] do not occur at 20–30K, but reach their maximum intensity at 45–65K. On the other hand, at 65–100K a decrease in intensity of isomer I bands takes place, accompanied by a simultaneous rise in intensity of isomer II bands. It might indicate a transformation from structure I into structure II. The bands of isomer II disappear at 270K, while the bands of isomer I disappear at the temperature of 100K.

The bands in the oxygen adducts Ru(TPP) and Ru(OEP) of structure I (at 1167 and $1141cm^{-1}$, respectively) in view of their frequency ought to be interpreted as "end-on". Such a down-shift of $\nu(O_2)$, in comparison with Fe(TPP) and Fe(OEP) (1190), in passing from Fe(II) to Ru(II) porphyrins has already been observed for six-coordinate "base-bound" porphyrins⁽²²⁾. The second $\nu(O_2)$ at 1103 and $1114cm^{-1}$ observed for Ru(OEP) and Ru(TPP), respectively, cannot be attributed to the side-on isomer. The ~ 1103 and $\sim 1114cm^{-1}$ bands of Ru(OEP) and Ru(TPP) become stronger and their intensities are maximized near 100K, whereas the ~ 1104 and $\sim 1106cm^{-1}$ bands of Fe(OEP) and Fe(TPP) (which are known to be side-on) disappear when the temperature is raised to $\sim 100K$. These observations suggest that the dioxygen adduct responsible for the 1103 and $1114cm^{-1}$ bands of Ru(OEP) and Ru(TPP) are not of side-on type. The structure of the dioxygen adduct of Os(TPP) responsible for the $1090cm^{-1}$ band is similar to that of Ru(TPP) O_2 and Ru(OEP) O_2 which exhibits the $\nu(O_2)$ 1114 and $1103cm^{-1}$, respectively.

In the literature [13] IR spectra of iron(II), salen (salen = N, N-ethylenebis(salicylideneiminato)) dianion was investigated. IR spectra of Fe(salen) cocondensed with O_2 exhibit two $\nu(O-O)$ bands at 1104 and $1001cm^{-1}$. The band at $1104cm^{-1}$ has been assigned to the "side-on" dioxygen adduct, Fe(salen) O_2 . The band at $1001cm^{-1}$ has been assigned to the $\nu(O-O)$ of the bridging dimer $[Fe(salen)]_2O_2$ based on the following observations: (a) this band becomes stronger as the concentration of Fe(salen) relative to dioxygen is increased, (b) Fe(salen) film exposed to O_2 at 15K exhibits one $\nu(O-O)$ at $1102cm^{-1}$ but an additional $\nu(O-O)$ at $1000cm^{-1}$ when the film is warmed to 40K (increased diffusion of dioxygen into Fe(salen) layers promotes the formation of the dimeric complex at 40K).

The behavior of the 1003, 1114 and $1090cm^{-1}$ bands of Ru(OEP), Ru(TPP) and Os(TPP), respectively, are similar to that of $1001cm^{-1}$ band in $[Fe(salen)]_2O_2$. Hence, we attribute these bands to $\nu(O_2)$ of the O-bridging dimers, $[Ru(OEP)]_2O_2$, $[Ru(TPP)]_2O_2$ and $Os(TPP)_2O_2$, respectively (Table 2). The lowering of $\nu(O_2)$ on passing from the Ru(1103 and $1114cm^{-1}$) to Os ($1090cm^{-1}$) complexes is expected since π -back-bonding effect* increases on going from Ru to Os.

* π back-bonding donation from $dz^2(M)$ to $2p\pi^*(O_2)$ (π -back-bonding effect) is increased in the series Fe(II) \rightarrow Ru(II), Os(II)^(1,14).

Table 2 Structural Assignment of $\nu(\text{O}_2)$ IR Frequencies in $\text{Fe}(\text{II})$, $\text{Ru}(\text{II})$, and $\text{Os}(\text{II})$ of Dioxygen Adduct Complexes with OEP and TPP (cm^{-1})

species	assignment		
	end-on	side-on	bridging
$\text{Fe}(\text{OEP})\text{O}_2$	1190(1124) ^a	1104(1042)	
$\text{Fe}(\text{TPP})\text{O}_2$	1195(1127) ^a	1106(1043)	
$\text{Ru}(\text{OEP})\text{O}_2$	1141(1079)		1103(1046) ^a
$\text{Ru}(\text{TPP})\text{O}_2$	1167(1101)		1114(1057) ^a
$\text{Os}(\text{TPP})\text{O}_2$			1090(1030) ^a

The number in parentheses indicates the $\nu(^{18}\text{O}_2)$ frequency.

^a stable form

The frequency of $\nu(\text{O}_2)$ bands in complexes of: iron, cobalt and ruthenium with OEP is lower than that with TPP (Table 1). This indicates a decrease in bond force constants of O—O in complexes of the above metals with OEP. It follows from the literature⁽²⁾ that bridging and dioxo species of $\text{Ru}(\text{OEP})$ are more unstable than those of corresponding $\text{Ru}(\text{TPP})$ complexes. In the case of Fe complexes, however, the differences in $\nu(\text{O}_2)$ band frequencies, when OEP is substituted instead of TPP, are not considerable, whereas for Ru they are more distinct (for $\Delta\nu(^{16}\text{O}_2)$: 3cm^{-1} , Co; $5, 2\text{cm}^{-1}$ Fe; $26, 11\text{cm}^{-1}$ Ru and for $\Delta\nu(^{18}\text{O}_2)$: 7cm^{-1} Co; $3, 1\text{cm}^{-1}$ Fe; $22, 11\text{cm}^{-1}$ Ru). We may suggest the following way of explaining considerable differences in $\nu(\text{O}_2)$ frequencies between $\text{Ru}(\text{TPP})\text{O}_2$ and $\text{Ru}(\text{OEP})\text{O}_2$: π -back-bonding effect increases in the order $\text{Fe} < \text{Ru} < \text{Os}$. The Ru complexes are stronger than those of Fe in view of the increase in π -bonding capabilities of $4d$ orbitals as compared with $3d$. Shorter and stronger bondings and the increase in π -bonding capabilities of Ru—O (in comparison to Fe—O) makes possible a stronger coupling between the electron clouds in the ligand (TPP or OEP) and those in the oxygen molecule added. That is why the differences in charge distribution, caused by substitution of OEP instead of TPP, are transmitted more easily to O_2 by the intermediary of Ru than of Fe, this resulting in larger differences in $\nu(\text{O}_2)$ band frequencies.

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References

- [1] Schick, S.A., Bocian, D.P., *J. Am. Chem. Soc.*, **106**, 1682(1984).
- [2] Paeng, I.R., Nakamoto, K., *J. Am. Chem. Soc.*, **112**, 3289(1990).
- [3] Collman, J.P., Brauman, J.I., Fitzgerald, J.F., Sparapany, J.W., Ibers, J.A., *J. Am. Chem. Soc.*, **110**, 3486(1988).
- [4] Groves, J.T., Ahn, K.H., *Inorg. Chem.*, **26**, 3831(1987).
- [5] Che, C.M., Chung, W.C., Lai, T.F., *Inorg. Chem.*, **27**, 2801(1988).
- [6] Proniewicz, L.M., Paeng, I.R., Lewandowski, W., Nakamoto, K., *J. Mol. Struct.*, **219**, 335(1990).
- [7] Watanabe, T., Ama, T., Nakamoto, K., *J. Phys. Chem.*, **88**, 440(1984).
- [8] Antipas, A., Bucher, J.W., Gouterman, M., Smith, P.D., *J. Am. Chem. Soc.*, **100**, 3015(1978).
- [9] Scheuermann, W., Nakamoto, K., *Appl. Spectrosc.*, **32**, 251(1978).
- [10] Urban, M. W., Nakamoto, K., Busolo, F., *Inorg. Chem.*, **21**, 3406(1982).
- [11] Urban, M.W., Nakamoto, K., Kincaid, J., *Inorg. Chem. Acta*, **61**, 77(1982).
- [12] Watanabe, T., Ama, T., Nakamoto, K., *Inorg. Chem.*, **22**, 2470(1983).
- [13] Proniewicz, L.M., Isobe, T., Nakamoto, K., *Inorg. Chem. Acta*, **155**, 91(1989).
- [14] Choi, S., Spiro, T.G., Langry, C.K., Smith, K.M., Budd, D.L., La Mar, G.N., *J. Am. Chem. Soc.*, **104**, 4345(1982).