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Resonance Raman Characterization of Ferric and Ferryl Porphyrin π Cation Radicals and the Fe^{IV}=O Stretching Frequency

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Abstract: Resonance Raman (RR) spectra of porphyrin π cation radicals were investigated for the Fe^{III} and Fe^{IV} states by using (tetramesitylporphyrinato)iron complexes [(TMP)Fe]. Vibrational modes were assigned on the basis of the isotopic frequency shifts upon ^{15}N and meso-^{13}C substitution and the reported normal coordinate analysis. For both the Fe^{III} and Fe^{IV} porphyrin π cation radicals, the ν_4 band was significantly shifted to lower frequency and thus the previous assignment by Kincaid et al. (*J. Am. Chem. Soc.* **1989**, *111*, 735) should be modified. The RR spectra exhibited no temperature dependence between -100 and +10 °C and between -100 and -80 °C for the Fe^{III} and Fe^{IV} porphyrin π cation radicals, respectively, indicating the presence of one type of radicals, presumably the a_{2u} radical judging from the low-frequency shifts of the ν_2 mode. The controversy about the Fe^{IV}=O stretching mode ($\nu_{Fe=O}$) of the Fe^{IV}=O porphyrin π cation radical was clarified by demonstrating that the two $\nu_{Fe=O}$ RR bands appear at 829 and 801-802 cm^{-1} in the presence of EtOH and *n*-PrOH while a single band appears at 831 or 801 cm^{-1} in the presence of MeOH or *t*-BuOH, respectively. The difference between the $\nu_{Fe=O}$ frequencies in the presence and absence of MeOH were interpreted reasonably in terms of the effect of the fifth ligand.

Oxidation states of iron porphyrins higher than the ferric state play a key role in the catalytic reactions by heme enzymes[2] such as peroxidases, catalases, and cytochrome P-450 and also in epoxidation of olefins by oxoferryl porphyrins.[3] Localization of the oxidation equivalent particularly in the Fe^{V} oxidation state has been a matter of debate. The corresponding intermediate for horseradish peroxidase (HRP, compound I) is considered to have the Fe^{IV}=O porphyrin π cation radical on the basis of Mossbauer,[4] visible absorption,[5] ENDOR,[6] NMR,[7] EPR,[8] and EXAFS[9] spectroscopies, while that of cytochrome *c* peroxidase (CcP, compound ES)[10] was demonstrated to have the Fe^{IV}=O neutral porphyrin and protein cation radical.[11] A question to be answered is how the Fe^{IV}=O bond is affected by the localization of the oxidative equivalent to the porphyrin ring or the protein moiety. Furthermore, when the oxidative equivalent is localized in a porphyrin ring, the orbital occupancy of the unpaired electron is suggested to relate with the functional differences of enzymes; the intermediates of catalase and peroxidase were deduced to have the $^2A_{1u}$ and $^2A_{2u}$ ground states, respectively, on the basis of absorption spectra of model compounds.[5] However, recent studies with NMR[12] and ESR[13] assigned both reference model compounds to a_{1u} radicals.

Resonance Raman (RR) spectroscopy is a powerful technique for characterizing the iron porphyrins in heme proteins as well as in organic solvents.[14] While some in-plane vibrations exhibit frequency shifts depending on delocalization of π electrons between the iron ion and the porphyrin macrocycle, the frequency of the Fe^{IV}=O stretching vibration ($\nu_{Fe=O}$) serves as the most direct probe of the Fe^{IV}=O bond. The $\nu_{Fe=O}$ RR band was identified for HRP compound II,[15-17] CcP compound ES,[18] and even compound B of cytochrome oxidase.[19] The corresponding $\nu_{Fe=O}$ band for the Fe^{IV}=O porphyrins in organic solvents was also elucidated by several groups.[20-23] However, the RR spectra of HRP compound I with one more higher oxidation state than compound II has been controversial due to its photolability.[24-28] Therefore, it is quite important to establish in a model system how RR spectra are altered by further oxidation of the Fe^{IV}=O porphyrin and how the Fe^{IV}=O bond is affected by it.

Previously we reported the $\nu_{Fe=O}$ RR band of the Fe^{IV}=O porphyrin π cation radical,[29] but it was claimed by Kincaid et al.[30] who suggested that the previous $\nu_{Fe=O}$ RR band might arise from a photoreacted product. On the other hand, RR spectra of me-

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[†] Deceased October 10, 1990. This paper is dedicated to the memory of Dr. Yoshitaka Tatsuno.

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talloporphyrin π cation radicals were reported for (TPP)M (TPP = tetraphenylporphyrin) and (OEP)M (OEP = octaethylporphyrin) complexes,[31-33] in which M = Co^{II}, Cu^{II}, Zn^{II}, Ni^{II}, Co^{III}, and $V^{IV}{=}O$, and the RR spectral differences between the a_{1u} and a_{2u} radicals have been established. However, an iron porphyrin was not included in such studies. Accordingly, in the present study, we investigated the RR spectra of Fe^{III} and Fe^{IV} porphyrin π cation radicals by using (tetramesitylporphyrinato)iron complexes [(TMP)Fe]. Here we assign the vibrational modes of the cation radicals on the basis of ^{15}N and ^{13}C isotopic frequency shifts, explain how the porphyrin macrocycle is altered by removal of an electron, and solve the remaining controversy about the $\nu_{Fe=O}$ RR band stated above.

Experimental Section

Materials. ^{15}N-enriched pyrrole (95%) and ^{13}C-enriched potassium cyanide (99%) were purchased from Cambridge Isotope Laboratories and used without further purification. The latter was used after conversion to $Zn(^{13}CN)_2$ by using $ZnSO_4$.[34] $^{54}Fe_2O_3$ (97% enriched) was purchased from Rohstoff Einfuhr and converted to $^{54}FeSO_4$ with the method reported previously.[35] The ^{15}N-enriched $(TMP)H_2$ [$(TMP\text{-}^{15}N_4)H_2$] was synthesized from pyrrole-^{15}N and mesitaldehyde in the presence of BF_3Et_2O according to Lindsey et al.[36] Its mass spectrum gave a peak at m/e = 786.57 for the calculated value of 786.42 expected for $C_{56}H_{54}{}^{15}N_4$. The meso-^{13}C-incorporated $(TMP)H_2$ [$(TMP\text{-}^{13}C_4)H_2$] was obtained similarly from the ^{13}C-enriched mesitaldehyde, which was prepared in 77% yield from the $AlCl_3$-catalyzed Gattermann reaction of mesitylene with $Zn(^{13}CN)_2$.[37] The IR spectrum of mesitaldehyde gave the $^{13}CH{=}O$ stretching band at 1650 cm^{-1} but no band of the $^{12}CH{=}O$ stretching mode. The mass spectrum of $(TMP\text{-}^{13}C_4)H_2$ exhibited a single peak at m/e = 786.00 for the calculated value of 786.45 expected for $C_{52}H_{54}N_4{}^{13}C_4$.

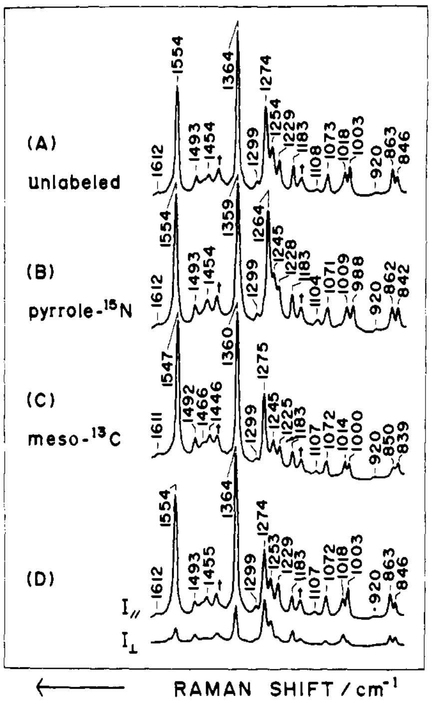

Figure 1. Resonance Raman spectra of $(TMP)Fe^{III}Cl$ and its isotopomers in CH_2Cl_2 at room temperature: (A) unlabeled species, (B) pyrrole-^{15}N derivative, (C) meso-^{13}C derivative, (D) polarized spectra for unlabeled species. Raman bands marked by a dagger are due to solvent.

Table I. Observed Frequencies, Isotopic Frequency Shifts, and the Mode Assignments for Raman Bands of $(TMP)Fe^{III}Cl$ and the Corresponding Data for $(TPP)Ni^{II}$

$(TMP)Fe^{III}Cl$					$(TPP)Ni^{II}$		
ν_i[a]	P[b]	$\Delta\nu(^{15}N)$[c]	$\Delta\nu(^{13}C)$[d]	assignt[e]	ν_i[f]	$\Delta\nu(^{15}N)$	$\Delta\nu(^{13}C)$
1612	p	0	−1	phenyl (ν_{8a})			
1554	p	0	−7	ν_2	1572	0	−8
1493	dp	0	−1	ν_{11}	1504	0	0
1454	p	0	−8	ν_3	1470	0	−6
1364	p	−5	−4	ν_4	1374	−6	0
1274	dp	−10	+1	ν_{12}	1302	−11	0
1254	dp	−9	−9	ν_{27}	1269	−8	−5
1229	p	−1	−4	ν_1	1235	−1	−6
1183	dp	0	0	ν_{34} (ν_{17})	1190	0	0
1073	p	−2	−1	ν_9	1079	−1	−1
1018	dp	−9	−4	ν_{15}	1005	−10	−8
1003	p	−15	−3	ν_6	1004	−20	−2
863	dp	−1	−13	ν_{32}	869	−2	−4
846	dp	−4	−7	ν_{16}	846	−7	−10

[a] Observed frequencies. [b] Polarization. [c] Isotopic frequency shift for ^{15}N substitution. [d] Isotopic frequency shift for ^{13}C substitution. [e] Mode number is based on ref 41. [f] All data for $(TPP)Ni^{II}$ were observed values reported in ref 41.

$(TMP)Fe^{III}Cl$ was obtained from the reaction of $FeSO_4$ with $(TMP)H_2$ in *N*,*N*-dimethylformamide (DMF), followed by the treatment with 3 N HCl according to Kobayashi et al.[38] The $(TMP)Fe^{III}Cl$ was converted to $(TMP)Fe^{III}ClO_4$ by treatment with $AgClO_4$ and then oxidized to a porphyrin π cation radical [$(TMP^{\bullet+})Fe^{III}(ClO_4)_2$] by $Fe(ClO_4)_3$. This exhibited dark green color, and its absorption spectrum was in agreement with that reported.[39] The oxo ferryl porphyrin π cation radical [$(TMP^{\bullet+})Fe^{IV}{=}O$] was prepared through oxidation of $(TMP)Fe^{III}Cl$ by *m*-chloroperoxybenzoic acid (*m*CPBA) in the Raman cell kept in the ethanol bath at −80 °C according to Groves et al.,[40] and its formation was confirmed by the color change to the characteristic green color. For the experiments with alcohol-containing solvents, the mixing ratio of alcohol to CH_2Cl_2 was 1:19 in volume. Since this complex was

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not so stable, its RR spectrum was measured within 6 min after formation.

Raman Measurements. Raman scattering was excited at 406.7 nm with a Kr^+ ion laser (Spectra Physics, 2016) and detected with a photodiode array (PAR 1420) attached to a double monochromator (Spex 1404). The spectral resolution in terms of the width/pixel was 1.4 cm^{-1}. Raman shifts were calibrated with indene as standard with the accuracy of ±1 cm^{-1}. All measurements were carried out with a spinning cell with a diameter of 2 cm. The cell was spun at 1600 rpm in a cryostat that was cooled to −80 °C by cold N_2 gas. The laser power was brought to the lowest possible (5 mW) to avoid photoreaction except for the experiments of power dependence.

Results

Ferric Neutral Compounds. Figure 1 shows the RR spectra of $(TMP)Fe^{III}Cl$ and its pyrrole-^{15}N and meso-^{13}C isotopomers. In order to draw any structural information from the observed RR spectra, it is indispensable to characterize the vibrational properties of some marker bands to be used in this study. The vibrational properties of the porphyrin skeleton of (TMP)M would be close to those of (TPP)M, for which Spiro and co-workers[41] and Bocian and co-workers[42] worked out the normal coordinate analyses with $M = Ni^{II}$ and $M = Cu^{II}$, respectively. Even though the absolute frequencies depend on a metal ion coordinated, the isotopic frequency shifts should generally be close between the corresponding vibrational modes if these modes were alike. Accordingly, we assign the observed RR bands of $(TMP)Fe^{III}Cl$ on the basis of the isotopic frequency shifts upon ^{15}N [$\Delta\nu(^{15}N)$] and ^{13}C substitutions [$\Delta\nu(^{13}C)$]. Since the observed frequency shifts are closer to those of $(TPP)Ni^{II}$ than to those of $(TPP)Cu^{II}$, we adopt the mode numbering by Spiro and co-workers.[41]

The observed frequency shifts for $(TMP)Fe^{III}Cl$ and plausible assignments are summarized in Table I together with the corresponding reported data of $(TPP)Ni^{II}$.[41] Two polarized (p) bands at 1364 and 1003 cm^{-1} exhibit large $\Delta\nu(^{15}N)$ and therefore are assigned to ν_4 and ν_6, respectively. They involve mainly the $C_\alpha N$ and $C_\alpha C_\beta$ stretching vibrations.[41] The p bands at 1554 and 1454 cm^{-1} give large $\Delta\nu(^{13}C)$ and zero $\Delta\nu(^{15}N)$, in agreement with the properties of the ν_2 and ν_3 modes of $(TPP)Ni^{II}$. These frequencies reflect mainly the strength of the $C_\beta C_\beta$ and $C_\alpha C_m$ bonds. The p band at 1073 cm^{-1} shows little shift upon both ^{15}N and ^{13}C substitutions and is assigned to ν_9, which mainly involves the in-plane C_β–H bending vibration. It is puzzling that the 1080-cm^{-1} band of $(TPP)Cu^{II}$ shows large isotopic frequency shifts [$\Delta\nu(^{15}N) = 6$ and $\Delta\nu(^{13}C) = 3$ cm^{-1}][42] contrary to small shifts for $(TPP)Ni^{II}$ and the present iron complexes. The highest frequency depolarized (dp) band at 1493 cm^{-1} is insensitive to both ^{15}N and ^{13}C substitutions and is assigned to ν_{11}, which is predominantly associated with the $C_\beta C_\beta$ stretching mode.[41] The dp band at 1274 cm^{-1} gives large $\Delta\nu(^{15}N)$ and small $\Delta\nu(^{13}C)$, while the dp band at 1254 cm^{-1} shows large shifts for both ^{15}N and ^{13}C substitutions. These properties are in agreement with those of ν_{12} and ν_{27}, respectively.[41] The ν_{12} and ν_{27} frequencies reflect primarily the strength of the $C_\alpha N$ bond, although the latter contains significantly the C_m–phenyl stretching character. The dp band at 1183 cm^{-1} shows little shift for both ^{15}N and ^{13}C substitutions, and this is anticipated for ν_{17} and ν_{34}.[41] Since the absolute frequency is closer to ν_{34} of $(TPP)Ni^{II}$, the band is tentatively assigned to ν_{34}, which contains mainly the C_β–H in-plane bending vibration. The dp band at 1018 cm^{-1} exhibits large $\Delta\nu(^{15}N)$ and moderate $\Delta\nu(^{13}C)$, and is assigned to ν_{15}, which arises mainly from the $C_\alpha C_\beta$ stretching vibration. The dp band at 863 cm^{-1} shows very large $\Delta\nu(^{13}C)$ and small $\Delta\nu(^{15}N)$. This is incompatible with the property of ν_{32}, but around the 800–900-cm^{-1} region there is no dp band of $(TPP)Ni^{II}$ that shows such a large $\Delta\nu(^{13}C)$. In contrast, the dp band at 846 cm^{-1} exhibits moderate sizes of $\Delta\nu(^{15}N)$ and $\Delta\nu(^{13}C)$ that are smaller than those of ν_{16} of (TPP)Ni. Therefore, with regard to ν_{32} and ν_{16}, the actual vibrational mode would be appreciably different between $(TMP)Fe^{III}Cl$ and (TPP)Ni, but this vagueness would have no problem in this study, since these modes contain mainly the angle deformation character.

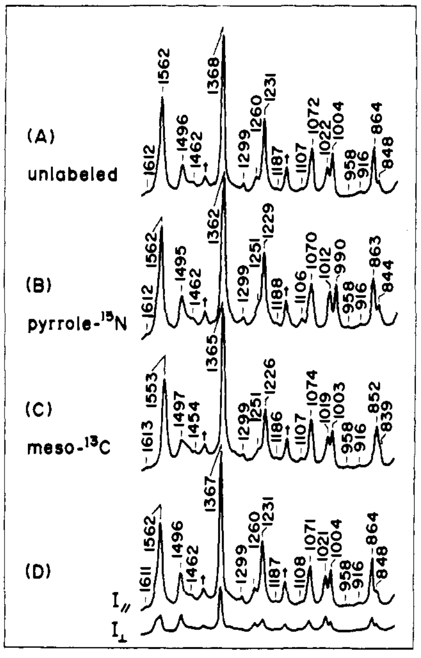

Figure 2. Resonance Raman spectra of $(TMP)Fe^{III}(Im)_2$ and its isotopomers in CH_2Cl_2 at room temperature: (A) unlabeled species, (B) pyrrole-^{15}N derivative, (C) meso-^{13}C derivative, (D) polarized spectra for unlabeled species. Raman bands marked by a dagger are due to solvent.

Table II. Observed Frequencies, Isotopic Frequency Shifts, and the Mode Assignments for Raman Bands of $(TMP)Fe^{III}(Im)_2$

ν_i	P	$\Delta\nu(^{15}N)$	$\Delta\nu(^{13}C)$	assignt
1612	p	0	+1	phenyl (ν_{8a})
1562	p	0	−9	ν_2
1496	dp	−1	+1	ν_{11}
1462	p	0	−8	ν_3
1368	p	−6	−3	ν_4
1260	dp	−9	−9	ν_{27}
1231	p	−2	−5	ν_1
1072	p	−2	+2	ν_9
1022	dp	−10	−3	ν_{15}
1004	p	−14	−1	ν_6
864	dp	−1	−12	ν_{32}
848	dp	−4	−9	ν_{16}

The RR spectra of a six-coordinate low-spin derivative with imidazole (Im) as axial ligands are shown in Figure 2, where the spectra of pyrrole-^{15}N and meso-^{13}C derivatives are also contained. The assignments of bands based on the polarization properties and isotopic frequency shifts are summarized in Table II. The skeletal double bond stretching frequencies such as ν_2, ν_{11}, ν_3, and ν_4 are shifted to higher frequency by 4–8 cm^{-1} upon the change from the five-coordinate high-spin to six-coordinate low-spin state, while other bands exhibit smaller shifts. The ν_{34} band seems to exist at 1187 cm^{-1}, but it is too weak to confirm. It is interesting that the intense ν_{12} band of $(TMP)Fe^{III}Cl$ is missing for $(TMP)Fe^{III}(Im)_2$. General behaviors about the isotopic frequency shifts are similar between the two kinds of complexes. Therefore, the vibrational modes themselves are little altered by the change of coordination number and the spin state of the iron ion.

Ferric π Cation Radical. Figure 3 shows the RR spectra of $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ and its isotopomers. As seen from the relative intensity to the solvent peak at 1423 cm^{-1}, Raman intensities of $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ are noticeably weak despite the fact that the absorbance of the Soret band of the π cation complex is not low.[39] This ferric porphyrin π cation was stable against laser illumination, and accordingly, the use of the higher laser power did not yield any RR spectral changes. The RR band at 1325 cm^{-1} (p) exhibits a frequency shift by −6 cm^{-1} upon ^{15}N

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[41] Li, X. Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Su, Y. O.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 31–47.

[42] Atamian, M.; Donohoe, R. J.; Lindsey, J. S.; Bocian, D. F. *J. Phys. Chem.* **1989**, *93*, 2236–2243.

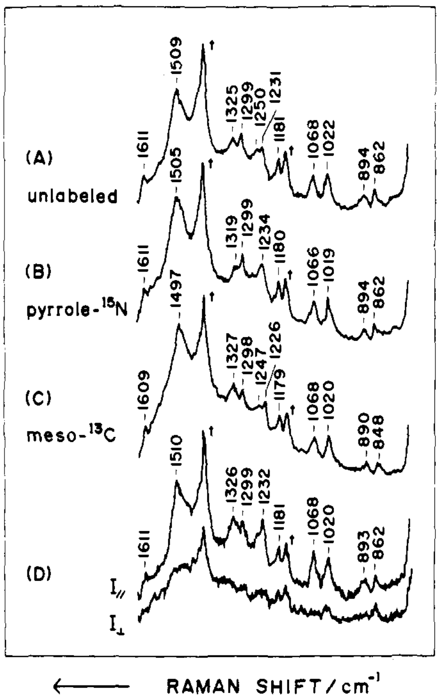

Figure 3. Resonance Raman spectra of (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$ and its isotopomers in dried CH$_2$Cl$_2$ at room temperature: (A) unlabeled species, (B) pyrrole-^{15}N derivative, (C) meso-^{13}C derivative, (D) polarized spectra for unlabeled species. Raman bands marked by a dagger are due to solvent. The spectra were observed with the spinning cell.

Table III. Observed Frequencies, Isotopic Frequency Shifts, and the Mode Assignments for Raman Bands of (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$

ν_i	P	$\Delta\nu(^{15}N)$	$\Delta\nu(^{13}C)$	assignt
1611	p	0	-2	phenyl (ν_{8a})
1509	p	-4	-12	ν_2
1325	p	-6	+2	ν_4
1299	p	0	-1	
1250	p	-	-3	ν_{12}
1231	p	+3	-5	ν_1
1181	dp	-1	-2	ν_{34}
1068	p	-2	0	ν_9
1022	dp	-3	-2	ν_{15}
894	p	0	-4	
862	dp	0	-14	ν_{32}

substitution and is therefore assignable to ν_4. Note that the ν_4 frequency of the π cation radical is distinctly lower than that of the ferric neutral porphyrins shown in Figures 1 and 2 (1364–1368 cm^{-1}), although the vibrational mode itself might be slightly altered from them. The dp band at 1250 cm^{-1}, which is probably buried under the 1234-cm^{-1} band for the ^{15}N derivative but can be identified at 1247 cm^{-1} with the ^{13}C derivative, has large $\Delta\nu(^{15}N)$ and small $\Delta\nu(^{13}C)$, suggesting to assign the 1250 cm^{-1} band to ν_{12}, which also arises from the C$_\alpha$N stretching vibrations. This is also downshifted from that of (TMP)Fe^{III}Cl. Thus, all the vibrations containing the C$_\alpha$N stretching character are shifted to lower frequencies in the π cation radical.

The nearby band at 1231 cm^{-1} (p) is assignable to ν_1. The assignment of an intense polarized band at 1509 cm^{-1}, which shows a large shift (-12 cm^{-1}) upon ^{13}C substitution, is a key of this spectrum and will be discussed later. Note that the 1509-cm^{-1} band exhibits an appreciable shift upon ^{15}N substitution contrary to expectation to the ν_2 mode. Frequencies of other bands below 1240 cm^{-1} are not greatly different from those of (TMP)Fe^{III}Cl. The frequency of the phenyl ring mode at 1611 cm^{-1} remains unaltered by ionization of the porphyrin ring, suggesting that the electronic states of phenyl rings are almost completely separated from those of porphyrin rings. Plausible assignments of Raman bands of (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$ are summarized in Table III. Although the mode numbers are commonly used in the neutral porphyrins and the π cation radical, actual vibrational modes would be appreciably different between them. The results indicate that removal of an electron from the porphyrin ring causes changes of a relatively limited number of double bond stretching frequencies. The RR spectrum little changed between +10 and -100 °C.

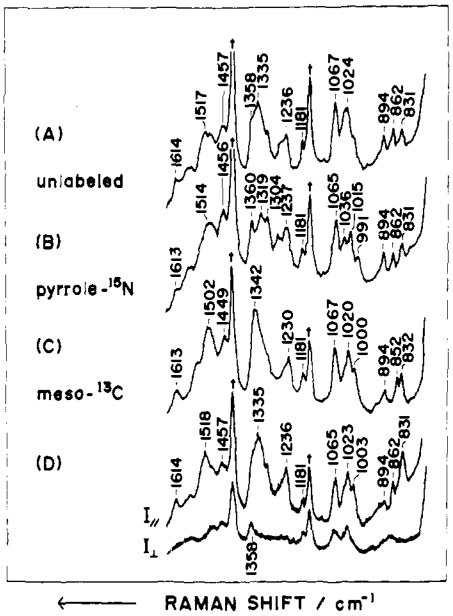

Figure 4. Resonance Raman spectra of (TMP$^{\bullet+}$)Fe^{IV}=O(MeOH) and its isotopomers in CH$_2$Cl$_2$ containing MeOH at -80 °C: (A) unlabeled species, (B) pyrrole-^{15}N derivative, (C) meso-^{13}C derivative, (D) polarized spectra for unlabeled species. The spectra were observed with the spinning cell. Raman bands marked by a dagger are due to solvent. The ratio of *m*CPBA to porphyrin was ca. 20.

Ferryl π Cation Radicals. Figure 4 shows RR spectra of (TMP$^{\bullet+}$)Fe^{IV}=O and its isotopomers in CH$_2$Cl$_2$ containing methanol (MeOH). The formation of the target compound was confirmed with visible absorption spectrum.[29] The Raman intensity is considerably weak, probably due to low Soret absorbance. In contrast with (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$, (TMP$^{\bullet+}$)Fe^{IV}=O was readily photodecomposed upon stopping of spinning of the Raman cell, and the RR spectrum of the photoproduct observed then was the same as that of (TMP)Fe^{III}OH.

Recently Kincaid et al.[30] assigned the RR band of (TMP$^{\bullet+}$)-Fe^{IV}=O at 1358 cm^{-1} to the ν_4 band. However, as evident from Figure 4D and A, this band is depolarized and exhibits no frequency shift upon ^{15}N substitution. Therefore, the 1358-cm^{-1} band cannot be ν_4. On the other hand, the RR band at 1335 cm^{-1} is shifted to 1319 cm^{-1} upon ^{15}N substitution and is therefore assigned to ν_4. This frequency is significantly lower than that (1371 cm^{-1}) of the oxoferryl neutral porphyrin [(TMP)Fe^{IV}=O] reported previously.[23] If there were contaminated any ferric TMP derivatives, a polarized band corresponding to their ν_4 band should be observed around 1364–1368 cm^{-1} as seen in Figures 1 and 2. Since such a band is not seen in Figure 4A, this sample seems to contain scarcely the photodecomposed ferric compounds.

The polarized band at 1517 cm^{-1} is shifted to 1514 and 1502 cm^{-1} upon ^{15}N and meso-^{13}C substitutions, respectively, and is assignable to the ν_2 mode. However, similar to the 1509-cm^{-1} band of (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$, it would not be the same mode as that expected from ν_2 of (TPP)Ni^{II} due to the appreciable ^{15}N shift. The weak dp band at 1457 cm^{-1} might arise from ν_{11} although it gives large $\Delta\nu(^{13}C)$. The RR spectrum of (TMP$^{\bullet+}$)Fe^{IV}=O did not change between -100 and -80 °C, although at higher temperature the decomposed compounds appeared. Tentative assignments of other RR bands of (TMP$^{\bullet+}$)Fe^{IV}=O are summarized in Table IV together with the observed frequencies of the corresponding bands of oxoferryl neutral porphyrin [(TMP)Fe^{IV}=O].[23]

In our previous report,[29] the RR band at 831 cm^{-1}, which is seen at similar frequencies for the ^{15}N and ^{13}C derivatives in Figure 4, was assigned to the Fe^{IV}=O stretching vibration ($\nu_{Fe=O}$) of

Table IV. Observed Frequencies, Isotopic Frequency Shifts, and the Mode Assignments for Raman Bands of $(TMP^{\bullet+})Fe^{IV}{=}O(MeOH)$ and the Corresponding Data for $(TMP)Fe^{IV}{=}O$

$(TMP^{\bullet+})Fe^{IV}{=}(MeOH)$					$(TMP)Fe^{IV}{=}O$
ν_i	P	$\Delta\nu(^{15}N)$	$\Delta\nu(^{13}C)$	assignt	ν_i
1614	p	−1	−1	phenyl (ν_{8a})	
1517	p	−3	−15	ν_2	1570
1457	dp	−1	−8	ν_{11}	
1358	dp	+2	−16		
1335	p	−16		ν_4	1371
1236	p	+1	−6	ν_1	1229
1181	dp	0	0	ν_{34} or ν_{17}	
1067	p	−2	0	ν_9	1071
1024	dp	−9	−4	ν_{15}	
1003	p	−12	−3	ν_6	
894	p	0	0		
862	dp	0	−10	ν_{32}	862
831	p	0	+1	$\nu_{Fe=O}$	843

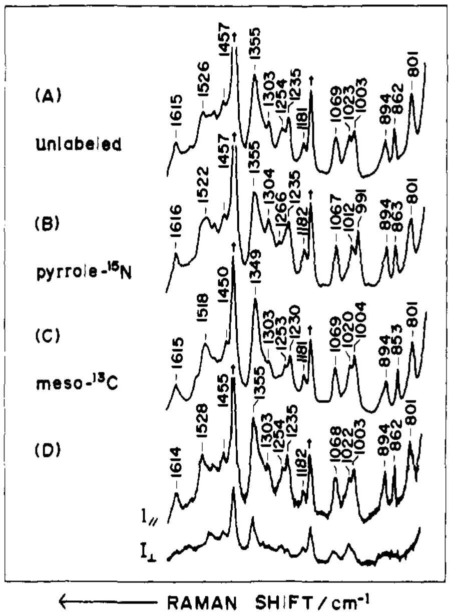

Figure 5. Resonance Raman spectra of $(TMP^{\bullet+})Fe^{IV}{=}O(m\text{CBA})$ and its isotopomers in dried CH_2Cl_2 at −80 °C: (A) unlabeled species, (B) pyrrole-^{15}N derivative, (C) meso-^{13}C derivative, (D) polarized spectra for unlabeled species. Raman bands marked by a dagger are due to solvent. The spectra were observed with a spinning cell. The ratio of *m*CPBA to porphyrin was 2.

$(TMP^{\bullet+})Fe^{IV}{=}O$ on the basis of the ^{18}O and ^{54}Fe isotopic frequency shifts. However, Kincaid et al.[30] claimed that this band arised from a photodecomposed compound and the $\nu_{Fe=O}$ band of $(TMP^{\bullet+})Fe^{IV}{=}O$ was located at 801 cm^{-1}. As noted previously, when the spinning of the cell was abolished, the 831-cm^{-1} band disappeared, and therefore, it cannot be ascribed to a stable photoproduct. Furthermore, the relative intensity of the 831-cm^{-1} band to other porphyrin bands was not altered by the laser power change between 5 and 0.5 mW that was the lowest possible power for the Raman measurements, and a Raman band was not recognized around 800 cm^{-1} with the weakest laser power. In this regard, the reported results shown in Figure 1 of ref 30 were partly nonreproducible. According to the initial report on $(TMP^{\bullet+})Fe^{IV}{=}O$ by Groves et al.,[40] this compound is more stabilized in the presence of MeOH than in its absence. Therefore, in the previous study,[29] we carried out the experiments for the solution containing MeOH. However, MeOH might have coordinated to the trans position of the oxo oxygen and altered the $\nu_{Fe=O}$ frequency. In order to solve this controversy, we prepared the π cation radical without MeOH. The results are shown in Figure 5.

A prominent RR band at 1355 cm^{-1} shows no shift upon ^{15}N substitution but is shifted to a lower frequency by 6 cm^{-1} upon ^{13}C substitution. The ν_4 band, which should be polarized and is expected to shift upon ^{15}N substitution, cannot be identified in Figure 5. This band might be buried in a wing of the 1355-cm^{-1} band, but difference calculation failed to reveal the presence of the ^{15}N isotope sensitive band. A new band appears at 1526 cm^{-1}, which exhibits -4- and -8-cm^{-1} shifts upon ^{15}N and ^{13}C substitutions, respectively, similar to the 1509-cm^{-1} band of $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ and is considered to arise from the modified ν_2. Frequencies of other bands and their behaviors upon isotopic substitutions bear close resemblance between Figures 4 and 5, although the relative intensity of the band at 1003 cm^{-1} to others is slightly higher. It is noted that an intense band is observed at 801 cm^{-1} in Figure 5.

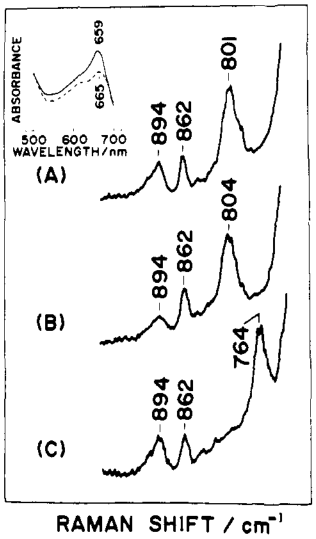

Figure 6. Resonance Raman spectra of $(TMP^{\bullet+})Fe^{IV}{=}O(m\text{CBA})$ in dried CH_2Cl_2 at −80 °C: (A) derived from ^{56}Fe porphyrin and ordinary *m*CPBA, (B) derived from ^{54}Fe porphyrin and ordinary *m*CPBA, (C) derived from ^{56}Fe porphyrin and $[^{18}O]m$CPBA. Others are the same in the caption of Figure 5. The inset figure shows the absorption spectra in the α band region of $(TMP^{\bullet+})Fe^{IV}{=}O(MeOH)$ (solid line) and $(TMP^{\bullet+})Fe^{IV}{=}O(m\text{CBA})$ (broken line).

The inset of Figure 6 compares the visible absorption spectra of $(TMP^{\bullet+})Fe^{IV}{=}O$ observed in the presence and absence of MeOH. Difference in the α band is clear, although the difference was little in the Soret band. Figure 6 shows the behavior of the 801-cm^{-1} band for the use of $(TMP)^{54}FeCl$ and ^{18}O-labeled *m*CPBA. The 801-cm^{-1} band shifts to a higher frequency by 3 cm^{-1} with the ^{54}Fe porphyrin and to a lower frequency by 37 cm^{-1} with the ^{18}O derivative. These agree closely with the expected shifts of $\Delta\nu(^{54}Fe) = 3.3$ cm^{-1} and $\Delta\nu(^{18}O) = -35.2$ cm^{-1} calculated for a diatomic Fe=O harmonic oscillator. Therefore, this band is assigned to the $\nu_{Fe=O}$ band of $(TMP^{\bullet+})Fe^{IV}{=}O$, in agreement with Kincaid et al.[30] When the laser power was raised, the 831-cm^{-1} band did not appear but the 801 cm^{-1} band simply disappeared. To gain an insight into the compound obtained in the presence of MeOH, we added various kinds of alcohols to the solvent, and the results are summarized in Figure 7.

As shown by spectra B and C in Figure 7, the two bands around 831 and 801 cm^{-1} are coexistent for the solvent containing ethanol (EtOH) (precisely, 829 and 802 cm^{-1}) and 1-propanol (*n*-PrOH) (829 and 801 cm^{-1}), while frequencies of other bands are little altered. For the solution with 2-methyl-2-propanol (*t*-BuOH) (D), the 831-cm^{-1} band was missing but a band was present at 801 cm^{-1} similar to the case of the absence of alcohol (E). In a separate study for $(OEP)Fe^{III}(2\text{-MeIm})$,[43] coordination of MeOH, EtOH, and *n*-PrOH to the sixth coordination position of the Fe^{III} ion was confirmed by observations of the Fe^{III}-alcohol stretching RR band and a CT absorption band around 570–590 nm, but *t*-BuOH did not give such evidence for coordination. Accordingly, it is deduced

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[43] (a) Fidler, V.; Ogura, T.; Sato, S.; Aoyagi, K.; Kitagawa, T. *Bull. Chem. Soc. Jpn.*, in press. (b) Ogura, T.; Fidler, V.; Ozaki, Y.; Kitagawa, T. *Chem. Phys. Lett.* **1990**, *169*, 457–459.

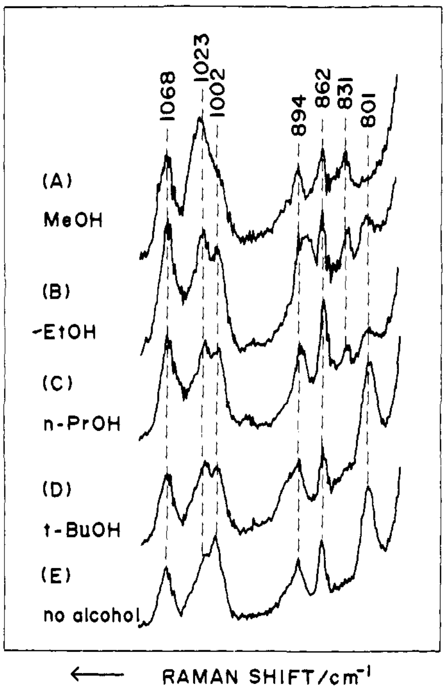

Figure 7. Resonance Raman spectra of $(TMP^{\bullet+})Fe^{IV}{=}O$(alcohol) and $(TMP^{\bullet+})Fe^{IV}{=}O$(*m*CBA) at -80 °C in dried CH_2Cl_2 with methanol (A), ethanol (B), *n*-propyl alcohol (C), or *tert*-butyl alcohol (D) and in the absence of any alcohol (E). The spectra were observed with the spinning cell.

that steric hindrance between bulky alkyl group and pyrrole nitrogens interferes with coordination of *t*-BuOH. The frequency difference in $\nu_{Fe=O}$ between the presence and absence of alcohol might be attributed to the difference between the alcohol-coordinated and noncoordinated compounds. However, this is not compatible with a general idea that the five-coordinate oxoferryl complexes give rise to higher $\nu_{Fe=O}$ frequency than the six-coordinate complexes.[20-23]

An alternative idea comes from the fact that the RR spectra in Figure 7B, C, and D are very alike except for the 801/831-cm⁻¹ features. Comparison of RR spectra between the five- and six-coordinate ferric complexes shown in Figures 1 and 2 suggests that the structural difference appears in the intensity of the ν_{16} band (846 cm⁻¹ in Figure 1 and 848 cm⁻¹ in Figure 2), which is noticeably weaker for the six-coordinate complex, while frequencies of RR bands below 1100 cm⁻¹ are almost the same between the two kinds of complexes. The absence of the ν_{16} band in Figure 7 despite of the presence of the ν_{32} band, which is characterized by a large $\Delta\nu(^{13}C)$ in Figures 4 and 5, suggests that the compound in question adopts the six-coordinate structure irrespective of the presence or absence of alcohol. Previously, Groves et al.[40] inferred that the reaction product of *m*CPBA, that is, *m*-chlorobenzoic acid (*m*CBA), was coordinated to the trans position of the oxo oxygen. In the presence of alcohol, *m*CBA would compete with alcohol for coordination at the axial position but the equilibrium becomes biased to alcohol. In this interpretation, the frequency difference in $\nu_{Fe=O}$ is ascribed to the difference in σ donation of the trans ligand; the larger the σ donation is, the lower the $\nu_{Fe=O}$ frequency is. If the σ donation from *m*CBA is larger than that of alcohol, the lower $\nu_{Fe=O}$ in the absence of alcohol is reasonably interpreted. In fact, for oxoferryl neutral complexes, the $\nu_{Fe=O}$ frequency is lower when the trans ligand is N-MeIm (807 cm⁻¹) than when it is THF (829 cm⁻¹).[21] One may argue that the ligand with higher σ donor property wins in the competition for coordination. It would be true if the concentration of *m*CBA were the same as that of alcohol. Actually, however, the concentration of alcohol is much higher than that of *m*CBA.

Discussion

Nature of the Fe=O Bond in the Ferryl π Cation Radical. An oxoferryl porphyrin π cation radical has a catalytic activity as a monoxygenase in contrast to the oxoferryl neutral porphyrins. We are curious to know an origin of the differences in nature of the Fe=O bond between the two kinds of complexes. The $\nu_{Fe=O}$ RR bands have been studied for various Fe porphyrins,[20-23] and they can be categorized into three groups: five-coordinate complexes ($\nu_{Fe=O}$ = 852 cm⁻¹ for O_2 matrix[20] and 843 cm⁻¹ in toluene solution[23]), six-coordinate with a weak trans ligand ($\nu_{Fe=O}$ = 829-820 cm⁻¹),[21] and those with a strong trans ligand ($\nu_{Fe=O}$ = 807 cm⁻¹).[21] In the present study, the $\nu_{Fe=O}$ frequency of the π cation radicals was located at 831 cm⁻¹ for a weak trans ligand (alcohol) and at 801 cm⁻¹ for a stronger trans ligand (*m*CBA). Consequently, the difference in $\nu_{Fe=O}$ frequencies between the porphyrin π cation radical and neutral porphyrin is smaller than the effect from the trans ligand.

Recently, Su et al.[44] observed the upshift of the $V^{IV}{=}O$ stretching frequency ($\nu_{V=O}$) of $(OEP)V^{IV}{=}O$ upon formation of π cation radical (a_{1u}) and ascribed it to the polarization effect of π electrons. They observed 1.00% downshift of the $\nu_{V=O}$ band of $(OEP)V^{IV}{=}O$ when the solvent was changed from benzene to CH_2Cl_2 and 1.52% upshift of it upon the formation of a π cation radical without a change of the coordination number. Upon coordination of alcohol or a strong ligand like imidazolate to the trans position of oxygen, they observed a 2.35% or 5.99% decrease of the $\nu_{V=O}$ frequency. If the same rate is applied to $(TMP)Fe^{IV}{=}O$ with $\nu_{Fe=O}$ at 843 cm⁻¹ in toluene,[23] the $\nu_{Fe=O}$ frequency of the five-coordinate neutral state in CH_2Cl_2 would be 835 cm⁻¹, and the hypothetical five-coordinate $(TMP^{\bullet+})Fe^{IV}{=}O$ would have $\nu_{Fe=O}$ = 848 cm⁻¹. If *m*CBA were regarded as a strong ligand like imidazolate, the $(TMP^{\bullet+})Fe^{IV}{=}O$(alcohol) and $(TMP^{\bullet+})Fe^{IV}{=}O$(*m*CBA) would have $\nu_{Fe=O}$ = 828 and $\nu_{Fe=O}$ = 797 cm⁻¹, respectively. These are unexpectedly in good agreement with the observed values. Therefore, the difference between two frequencies is reasonably ascribed to the trans effect.

Macor et al.[45] pointed out that the $\nu_{V=O}$ frequency is different between the a_{1u} and a_{2u} radicals; it is lower than that of the neutral mode by 16 cm⁻¹ for the a_{2u} radical $[(TPP^{\bullet+})V^{IV}{=}O]$ and higher than it by 15 cm⁻¹ for the a_{1u} radical $[(OEP^{\bullet+})V^{IV}{=}O]$. However, one cannot rule out a possibility that difference in porphyrin peripheral substituents (ethyl vs phenyl) causes some differences in coordination of the trans ligand, which yields some difference in the $\nu_{V=O}$ frequency without direct interaction with the half-occupied a_{1u} or a_{2u} orbital.

State of Porphyrin Macrocycle in the π Cation Radical. The characteristic feature of $(TMP^{\bullet+})Fe^{IV}{=}O$(MeOH) is the considerable downshift of the ν_4 frequency, and this is also true with $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$. Since the peak position for $([^{13}C]$-$TMP^{\bullet+})Fe^{IV}{=}O$(MeOH) is not clear, it is difficult to deduce how close to that of (TPP)Ni the ν_4 vibrational mode of $(TMP^{\bullet+})Fe^{IV}{=}O$(MeOH) is. However, judging from the large value of $\Delta\nu(^{15}N)$ compared with those of ferric compounds, the ν_4 mode of $(TMP^{\bullet+})Fe^{IV}{=}O$(MeOH) should involve significant $C_\alpha N$ stretching character. Accordingly, the formation of the π cation radical with $(TMP)Fe^{III}$ and $(TMP)Fe^{IV}{=}O$ is accompanied by weakening of the $C_\alpha N$ bonds, and/or the vibrational mode itself became a more pure $C_\alpha N$ stretching vibration. This contrasts with the case of $(TPP)V^{IV}{=}O$, which exhibited only a 2-cm⁻¹ downshift of ν_4 upon formation of the π cation radical.[45]

It is also noted that the phenyl mode becomes noticeably stronger upon formation of the π cation radical for $(TPP)V^{IV}{=}O$ but it remains weak for the $(TMP^{\bullet+})Fe$ system. The intensification of the phenyl band is also seen for $(TPP^{\bullet+})Cu^{II}$.[33] This may imply that, in the electronic excited state or both the ground and excited states, the peripheral phenyl rings of TPP become more coplanar to the porphyrin plane and thus π electrons of the phenyl group are more delocalized to the half-filled radical orbital for $(TPP^{\bullet+})M$. Since the orbital density at C_m is high for the a_{2u}

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(44) Su, Y. O.; Czernuszewicz, R. S.; Miller, L. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4150–4157.

(45) Macor, K. A.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* **1990**, *29*, 1996–2000.

(46) Song, H.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1989**, *111*, 6865–6866.

radical, although it is zero for the a_{1u} radical, a slight change of the C_m-C_{phenyl} dihedral angle easily changes an amount of π delocalization. If it occurs only in the excited state, the Soret excitation causes a change of π electron distribution and thus strength of C=C bonds of the phenyl ring. Then more resonance enhancement of the phenyl mode is reasonably interpreted. In the case of $(TMP^{\bullet+})M$ π cation radicals, however, the internal rotation around the C_m-C_{phenyl} bond is interfered by the steric hindrance between two o-CH_3 groups of the phenyl ring and the pyrrole groups of the porphyrin, and therefore, the π conjugation between the phenyl and porphyrin rings remains unchanged upon electronic excitation even for the π cation radical. This would be a reason why the RR intensity of the phenyl mode is unaltered with $(TMP^{\bullet+})Fe$ radicals.

If such torsion around the C_m-C_{phenyl} bond also took place in the ground state of $(TPP^{\bullet+})M$ radicals, the radical property might be slightly diluted due to the delocalized electrons of the phenyl group. In the EPR study of $(TPP^{\bullet+})Zn^{II}$, leakage of the electron spin density to the phenyl rings has been detected.[47a-c] A theoretical calculation on phenyl hyperconjugation,[48] which describes π-σ spin delocalization into twisted phenyl rings, predicts larger leakage of the spin density for larger torsion around the C_m-C_{phenyl} bond. In a crystal, the phenyl group of (TMP)M is nearly perpendicular to the porphyrin plane[46] but that of (TPP)M is slightly rotated around the C_m-C_{phenyl} axis.[39] If similar torsion is present for $(TPP^{\bullet+})M$ in solutions, this would affect frequencies of double bond stretching modes of porphyrins and cause some difference between RR spectra of $(TMP^{\bullet+})Fe^{IV}{=}O$ and $(TPP^{\bullet+})V^{IV}{=}O$ porphyrin π cation radicals. Indeed, the ^1H NMR shift of the meta protons of the phenyl ring is appreciably different between $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$[40] and $(TPP^{\bullet+})Fe^{III}(ClO_4)_2$.[39] In the case of heme proteins, there should be no inflow of π elecrons at C_m upon formation of the π cation radical. In this regard, the results from the RR studies on $(TPP)V{=}O$[45] should be carefully applied to heme proteins.

Vibrational Modes of π Cation Radicals. According to the reports on the porphyrin π cation radicals of a divalent metal,[31-33] the ν_2 band is the most intense RR band upon the Soret excitation. Therefore, it is likely that the 1507-cm^{-1} band of $(TMP^{\bullet+})$-$Fe^{III}(ClO_4)_2$ arises from the ν_2 mode. The ν_2 mode of neutral metalloporphyrins contains mainly the $C_\alpha C_m$ stretching character and is expected to show no shift upon ^{15}N substitution but a large shift upon ^{13}C substitution.[41] Indeed, such a feature was confirmed in this study for the five-coordinate high-spin and six-coordinate low-spin ferric (TMP)Fe complexes as shown in Tables I and II. However, the 1507-cm^{-1} band of $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ exhibited an appreciable shift upon ^{15}N substitution as well as upon meso-^{13}C substitution. Therefore, the ν_2 mode of the porphyrin π cation radical is inferred to contain the $C_\alpha N$ stretching character, which is different from the ν_2 mode of (TPP)Ni and $(TMP)Fe^{III}Cl$. Since an electron is removed from the π orbital, which is bonding or antibonding regarding a given bond, it is rather natural that the force constants and thus vibrational energy distributions for the π cation radicals are appreciably altered from those of the neutral state. The low-frequency shift of ν_2 might be partly due to weakening of the $C_\alpha N$ bond. When the difference in the vibrational mode is admitted, the corresponding bands of the $Fe^{IV}{=}O$ porphyrin π cation radical observed at 1517 cm^{-1} for $(TMP^{\bullet+})$-$Fe^{IV}{=}O(MeOH)$ (Figure 4) and at 1526 cm^{-1} for $(TMP^{\bullet+})$-$Fe^{IV}{=}O(mCBA)$ (Figure 5) are also assignable to ν_2. Then, they are significantly lower than the ν_2 frequency (1570 cm^{-1}) of the $Fe^{IV}{=}O$ neutral porphyrin.

The ν_{11} band, which arises from the nearly pure $C_\beta C_\beta$ stretching vibration for Ni(TPP) and is expected to give no shift upon meso-^{13}C and ^{15}N substitutions,[41] is considered to appear at 1458 cm^{-1} for $(TMP^{\bullet+})Fe^{IV}{=}O(MeOH)$ and at 1457 cm^{-1} for $(TMP^{\bullet+})Fe^{IV}{=}O(mCBA)$, although they exhibited the meso-^{13}C isotopic shift of -8 cm^{-1}. These frequencies are significantly lower than that of $(TMP)Fe^{III}(Im)_2$ (1496 cm^{-1}), but it is not unreasonable from the fact that ν_2 band is significantly downshifted. We rather infer that this mode of the π cation radical contains the $C_\alpha C_m$ stretching character and therefore shows the meso-^{13}C isotopic frequency shift. Such changes of vibrational modes in the π cation radical are also apparent from the observed differences in the ^{15}N and meso-^{13}C isotopic frequency shifts between the ferric neutral porphyrins and π cation radicals studied here.

Czernuszewicz et al.[33] strengthened little change of vibrational modes between the neutral porphyrin and π cation radicals on the basis of similarity in deuteration shifts. They investigated $(TPP^{\bullet+})Cu^{2+}$ and observed -10- and -32-cm^{-1} shifts for ν_4 and ν_2, respectively, upon formation of the π cation radical in contrast with -36 and -52 cm^{-1} for $(TMP^{\bullet+})Fe^{IV}{=}O$ (see Table IV). One of the plausible explanations for the smaller shifts for $(TPP^{\bullet+})Cu^{II}$ is that the radical character is reduced for $(TPP^{\bullet+})Cu^{II}$ due to the torsion around the C_m-C_{phenyl} bond, and accordingly, its vibrational modes are closer to those of neutral porphyrins. However, there have been no experimental data about ^{13}C and ^{15}N isotopic frequency shifts for $(TPP^{\bullet+})Cu^{II}$, and a correlation between the frequencies of the core size marker bands and the core sizes has not been investigated for $(TPP^{\bullet+})M$ yet. Detailed discussion about the vibrational modes of $(TPP^{\bullet+})Cu^{II}$ should be postponed until such data are provided. Currently this is a sole study that gives the ^{13}C and ^{15}N isotopic shift data for (TPP)M-type π cation radicals.

a_{1u} and a_{2u} Radicals. Czernuszewicz et al.[33] revealed the RR spectral characteristics of the a_{1u} vs a_{2u} π cation radicals of metalloporphyrins. According to them, $(OEP^{\bullet+})M$ gives the a_{1u}-like radical and brings about an upshift of ν_2 and a downshift of ν_4, while $(TPP^{\bullet+})M$ gives the a_{2u}-like radical and brings about a downshift of ν_2 and a smaller but variable downshift of ν_4. The oxoferryl radical obtained in the present study is characterized by large downshifts of both ν_4 and ν_2. Therefore, this radical is categorized to the typical a_{2u} radical. This is consistent with the NMR and Mossbauer studies,[40,49] which pointed out that $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ has the a_{2u} radical character. Since the RR spectrum did not show any temperature dependence for both Fe^{III} and $Fe^{IV}{=}O$ porphyrin π cation radicals, coexistence of two kinds of radicals[50] is unlikely. In other words, the energy difference between the a_{1u} and a_{2u} radicals is fairly large.

Mossbauer, NMR, and X-ray crystallographic analyses of the six-coordinate $(TPP^{\bullet+})Fe^{III}(ClO_4)_2$ and five-coordinate $(TPP^{\bullet+})Fe^{III}(SbCl_6)$ revealed the presence of the ferro- and antiferromagnetic coupling between the high-spin iron and the unpaired electron in the a_{2u} orbital.[39,49] Since the a_{2u} orbital has a large density at nitrogen,[51] the planarity of the FeN_4 core is expected to affect the spin arrangement; if it were domed, overlapping between the d_π orbitals of iron and the a_{2u} orbital at nitrogen would increase and it would stabilize the antiferromagnetic structure. The structure of $(TMP^{\bullet+})M$ is reported to be planar,[46] and accordingly the ferromagnetic coupling would be dominant. Since the frequencies of the single bond stretching and deformation mode frequencies below 1240 cm^{-1} are scarcely altered between $(TMP^{\bullet+})Fe^{III}(ClO_4)_2$ and $(TMP^{\bullet+})Fe^{IV}{=}O$-(MeOH), the planar structure would be maintained in the ferryl state, too.

Czernuszewicz et al.[33] observed a novel feature characteristic of π cation radicals. They observed an anomalously polarized (ap) band around 1000 cm^{-1} upon Soret excitation for both $(TPP^{\bullet+})Cu^{II}$ and $(OEP^{\bullet+})Ni^{II}$ and explained it in the following way: The $^2A_{1u}$ and $^2A_{2u}$ states are mixed through a vibration with the A_{2g} symmetry, and the ap band around 1000 cm^{-1} corresponds to this mode. If so, the π cation radicals that yield the ap band around 1000 cm^{-1} can be regarded as the a_{1u}/a_{2u} admixture that should

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be distinguished from the a_{1u}/a_{2u} thermal mixture.[50] Unfortunately, we failed to detect it for both (TMP$^{\bullet+}$)Fe^{III}(ClO$_4$)$_2$ and (TMP$^{\bullet+}$)Fe^{IV}=O. (TPP$^{\bullet+}$)Cu^{II} and (TPP$^{\bullet+}$)Fe^{III}Cl(SbCl$_6$) are known to adopt a ruffled structure in a crystal[52] and probably so in solution. In contrast, (TMP$^{\bullet+}$)M are considered to adopt a planar structure.[39,46,49] This feature and the hindrance of the torsion around the C_m–C_{phenyl} bond stated above may suggest that the (TMP$^{\bullet+}$)M system gives more pure a_{2u} radical than the (TPP$^{\bullet+}$)M system.

Since the $C_\beta C_\beta$ bond is antibonding and bonding for the a_{1u} and a_{2u} HOMOs, respectively,[51] removal of an electron from the a_{1u} or a_{2u} orbital is expected to cause the up- or downshift of the $C_\beta C_\beta$ stretching vibrations. On the other hand, the $C_\alpha N$ bond is nonbonding and antibonding for the a_{1u} and a_{2u} HOMOs;[51] the downshift of the $C_\alpha N$ stretching frequency is never expected upon formation of a cation radical from the simple consideration. This implies that significant configuration interaction occurs in the cation radical state and the resultant electronic state cannot be easily inferred from the ground-state wave functions of neutral porphyrins.

In conclusion, it became evident that both the ν_4 and ν_2 bands are shifted significantly to lower frequency in the π cation radical of Fe^{III} and Fe^{IV} porphyrins. Little shift of the ν_4 frequency upon the formation of compound I of HRP raises a question about the established assignment of the π cation radical at ambient temperatures. The RR spectrum of oxoferryl porphyrin π cation radical is along the extension of the a_{2u}-type divalent metalloporphyrin π cation radicals, but it might be different from other a_{2u}-type π cation radicals given by (TPP$^{\bullet+}$)M with regard to the torsion around the C_m–C_{phenyl} bond. The $\nu_{Fe=O}$ frequency is not greatly perturbed by formation of the π cation radical, but is more sensitive to its trans ligand. The controversy between Kincaid et al.[30] and our previous report[29] was reasonably explained in terms of the difference of the trans ligand.

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Porphyrin Sponges: Structural Systematics of the Host Lattice

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Abstract: Analysis of the crystal structures of over 100 tetraarylporphyrin-based lattice clathrates reveals the extent to which van der Waals interactions between host molecules govern the crystal packing. In all these materials, corrugated sheets of tightly packed porphyrin molecules stack to form arrays of parallel channels in which a remarkable variety of guest species are accommodated. Conservation of the host structure in the absence of any covalent or hydrogen-bonding connection between host molecules suggests an engineering strategy for the designed construction of molecular solids. This strategy is based on the use of rigid molecular building blocks with self-complementary shapes. Identification of the features of the molecular structure responsible for the versatility of tetraarylporphyrin-based clathrates lays the groundwork for the development of new microporous materials. X-ray structural data are provided for 34 new materials.

Introduction

The utility of microporous solids in many scientific and technological applications has led to the development of several strategies for the designed construction of lattice clathrates. The host lattices targeted in these efforts include three-dimensional extended solids, networks of hydrogen-bonded molecules, and molecular solids in which only van der Waals forces maintain the host structure. The large class of tetraphenylporphyrin (TPP)-based clathrates previously identified in this laboratory[1] fall into the last category. In materials of this kind, control of the clathrate properties of the solid is based primarily on the control of molecular shape.

Although the clathrate properties of most molecular host materials (including the TPP-based hosts) have been discovered by chance, rational efforts in the design of new host systems have been successful. Notable in this regard is the work of MacNicol,[2] which focuses primarily on the maintenance of high symmetry in the molecular building blocks. Large rigid molecules of high symmetry have few degrees of conformational and orientational freedom and are thus unlikely to pack efficiently in a three-dimensional lattice. Any inefficiency in the packing produces a driving force for clathrate formation. Clathrate properties of many molecular materials can be rationalized on this basis. Among these are the Werner complexes,[3] the cyclophosphazenes,[4] perhydrotriphenylene,[5] the cyclotriveratrylenes,[6] the triphenylmethanes,[7] tri-*o*-thymotide,[8] numerous "hexa-hosts" prepared by MacNicol and co-workers,[2] as well as the "porphyrin sponges".[1] Tetraphenylporphyrin-based hosts differ in one important way from most of the others. While they do not pack efficiently in three dimensions, TPP molecules pack quite efficiently in two dimensions. As a consequence one finds in a large number of such clathrates a common host structure shown in Figure 1. This observation provides the basis for the development of a more controlled approach to the design of microporous molecular solids based on rigid symmetric building blocks with self-complementary shapes.

The investigation reported herein includes a detailed analysis of the molecular packing in over 100 TPP-based clathrates. This

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