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RESONANCE RAMAN SCATTERING STUDY ON THE π-CATION RADICALS OF MAGNESIUM, ZINC, AND COPPER TETRAPHENYLPORPHINES

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Resonance Raman spectra were measured for Mg, Zn, and Cu tetraphenylporphines and their π-cation radicals. On one-electron oxidation Raman bands from porphine ring modes show frequency shifts, the magnitudes of which depend on the kind of central metal ions and the nodal structure of the a_{2u} HOMO of the metalloporphines.

The π-cation radicals of metalloporphyrins and their derivatives play crucial roles in the redox reactions of horseradish peroxidase and catalase[1] and also in the electron transport chain of photosynthetic organisms[2]. The resonance Raman spectra have been reported for bacteriochlorophyll cation radicals by Lutz and Kleo[3] and Cotten *et al.*[4] They observed Raman bands characteristic of the cation radicals and tried to explain the spectral change due to the oxidation in terms of a molecular orbital calculation. Their discussion, however, is confined to the change observed for only a few bands. In this study we measured the resonance Raman spectra of the π-cation radicals of magnesium, zinc, and copper tetraphenylporphines (abbreviated to $MgTPP^{+\cdot}$, $ZnTPP^{+\cdot}$, and $CuTPP^{+\cdot}$) in the 1800-800 cm^{-1} region, where almost all the in-plane stretching vibrations of the porphine ring are observed, and compared the spectra with those of MgTPP, ZnTPP, and CuTPP.

Tetraphenylporphine(abbreviated to TPP) and the complexes were synthesized in the usual way[5]. The π-monocation radicals were obtained by controlled-potential electrolysis performed on the CH_2Cl_2 solutions of the metalloporphines containing tetrabutylammonium perchlorate(0.1 M)[5]. After the oxidation the absorption spectra of the sample solutions were measured, confirming that the spectral changes due to the oxidation are almost identical with those reported previously[5,6]. Raman spectra were recorded by a JEOL model 400D Raman spectrophotometer equipped with a Spectra Physics model 164 Ar^+ laser as an excitation source. As $MgTPP^{+\cdot}$ and $ZnTPP^{+\cdot}$ are photolabile at room temperature, we measured the Raman spectra at 80 K by a reflection method using a Oxford Instrument Co., Ltd., model CF-100 cryostat. In the case of $CuTPP^{+\cdot}$, the spectrum of its CH_2Cl_2 solution was measured by a spinning cell method. All the spectra reported in this letter were obtained with the

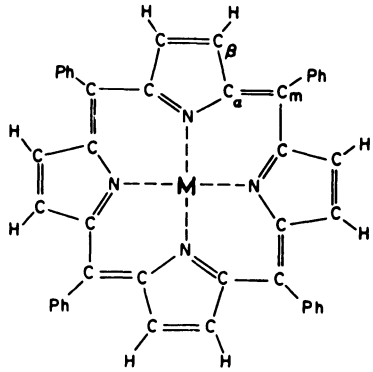

Fig.1. Structure of metal tetraphenylporphine.
(M, metal; Ph, phenyl)

excitation wavelength of 457.9 nm. The Raman spectra of the radicals with the 488.0- or 514.5-nm excitation have a very low S/N ratio although they are similar to the spectra reported in this letter.

Figure 2 gives the Raman spectra of MgTPP$^{+\cdot}$ and ZnTPP$^{+\cdot}$ in a solid state at 80 K (Figs.2(B) and (D)), together with the spectra of MgTPP and ZnTPP(Figs.2(A) and (C)) measured under the same condition. Figures 3(A) and (B) are the Raman spectra of the CH_2Cl_2 solutions of CuTPP and its π-cation radical, respectively. The depolarization ratios measured for the Raman bands of the CH_2Cl_2 solutions of the metalloporphines indicate that the Raman bands observed at 1487 cm^{-1} for MgTPP, at 1490 cm^{-1} for ZnTPP, and at 1497 cm^{-1} for CuTPP belong to the B_{1g} or B_{2g} species($\rho \fallingdotseq 0.75$) and that all the other bands in Figs.2(A), (C) and 3(A) belong to the A_{1g}($\rho \fallingdotseq 0.13$) (The D_{4h} symmetry is assumed to the samples.). Burke *et al.*7) studied the Raman spectra of iron tetraphenylporphine μ-oxo dimers and gave detailed assignments to the Raman bands. Based on their assignments it is known that the Raman bands at 1592, 1030, 1000, and 882 cm^{-1} observed for MgTPP(Fig.2(A)) and the corresponding bands of ZnTPP and CuTPP(Figs.2(C) and 3(A)) are due to the phenyl ring modes. With regard to the porphine ring in-plane modes there are nine A_{1g} vibrations. One of them is a CH stretching vibration and two are ring deformation vibrations which are expected in a frequency region below 800 cm^{-1}. Following the assignments made by Burke *et al.*, we can ascribe the Raman bands at 1539, 1348, 1233, 1075, and 1000 cm^{-1} in Fig.2(A) and the corresponding bands in Figs.2(C) and 3(A) to the remaining A_{1g} porphine ring stretching vibrations. In the frequency region around 1000 cm^{-1} in Figs. 2(A), (C), and 3(A) the Raman band from one of the porphine ring stretching modes overlaps with the band from the phenyl ring mode. In Table 1 the assignments are given by specifying vibrational modes whose contributions are major to each Raman band.

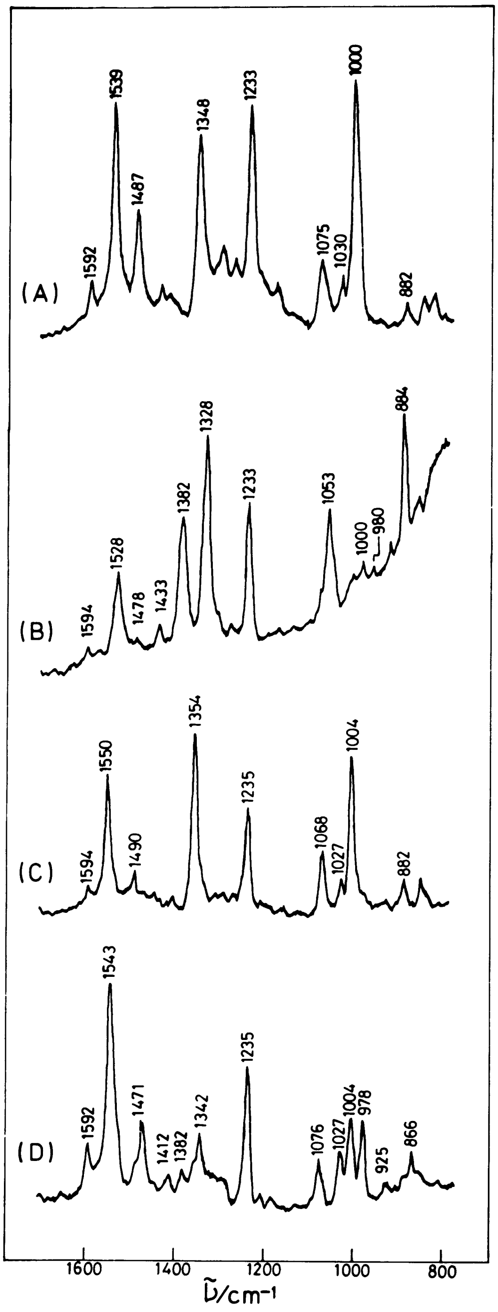

Fig.2. Resonance Raman spectra of (A) MgTPP, (B) MgTPP$^{+\cdot}$, (C) ZnTPP, and (D) ZnTPP$^{+\cdot}$ in a solid state at 80 K. Excitation wavelength, 457.9 nm (ca. 30 mW).

Presumably one-electron removal from the π-electrons of the metalloporphines does not give any appreciable effect on the peripheral phenyl groups. Therefore, the 1592-, 1027-, and 1004-cm^{-1} bands observed for ZnTPP$^{+\cdot}$ (Fig.2(D)) and the corresponding bands observed for

$CuTPP^{+\cdot}$ (Fig.3(B)) can be ascribed to the phenyl ring modes. The C_m-C_ϕ (C_ϕ denotes the carbon atom belonging to the phenyl group. See Fig.1.)stretching vibration observed near 1250 cm^{-1} for the metalloporphines are observed also for the cation radicals in the same frequency region(Figs.2(B), (D), and 3(B)). This result indicates that the one-electron oxidation yields no appreciable change in the order of the C_m-C_ϕ bonds. According to ESR and magnetic susceptibility measurements[5,6,8], the ground state of $MgTPP^{+\cdot}$, $ZnTPP^{+\cdot}$, and $CuTPP^{+\cdot}$ is the $^2A_{2u}$ state, *i.e.*, the electron is removed from the a_{2u} highest occupied molecular orbital. The optical spectra of the radicals exhibit a strong Soret band near 410 nm and a broad featureless absorption in a 450-700 nm region. As discussed by Fajer *et al.*[5], the absorption bands mentioned above are from the $^2A_{2u} \rightarrow ^2E_g$ transitions. Therefore, the intensity enhancement of Raman bands with visible excitation is expected for the porphine ring in-plane vibrations with the A_{1g}, A_{2g}, B_{1g}, and B_{2g} symmetries. The depolarization ratios of the Raman bands observed for the CH_2Cl_2 solution of $CuTPP^{+\cdot}$ (Fig.3(B)) indicate that the 1539- and 1236-cm^{-1} bands belong to the A_{1g} mode and that there are no band with anomalous polarization. Although the depolarization ratio of the other bands in Fig.3(B) cannot be determined due to their low intensity, we assume that, as in the case of the metalloporphines, the vibrational modes of the Raman bands observed for the cation radicals belong to the A_{1g} (and possibly B_{1g}) species. Presumably the frequency shifts

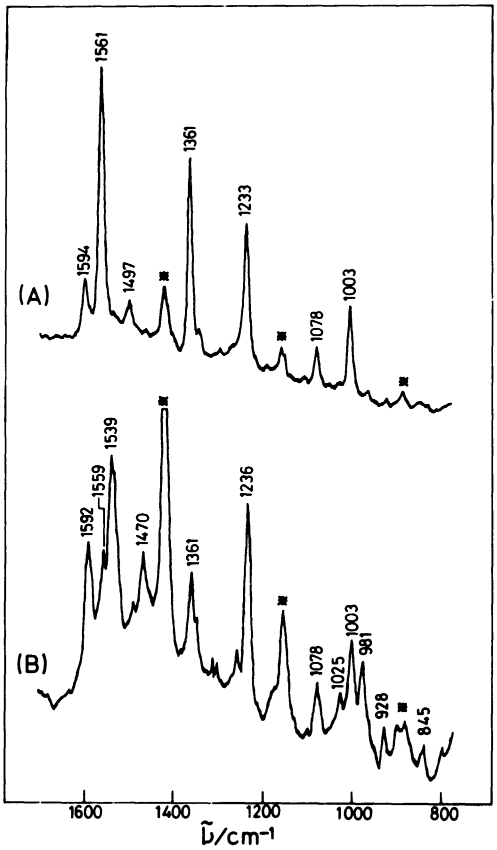

Fig.3. Resonance Raman spectra of the CH_2Cl_2 solutions(ca. 1.8 mM) of (A) CuTPP and (B) $CuTPP^{+\cdot}$ at room temperature. Excitation wavelength, 457.9 nm(ca. 30 mW). The asterisk denotes the Raman band from the solvent.

Table 1. The frequencies(cm^{-1}) and assignments of Raman bands observed for MgTPP, ZnTPP, and CuTPP and their cation radicals.

MgTPP	$MgTPP^{+\cdot}$	$\Delta\nu$[a]	ZnTPP	$ZnTPP^{+\cdot}$	$\Delta\nu$	CuTPP	$CuTPP^{+\cdot}$	$\Delta\nu$	Assignments[b]
1592	1594	-2	1594	1592	-2	1594	1592	-2	phenyl
1539	1528	-11	1550	1543	-7	1561	1539	-22	$\nu(C\beta-C\beta)+\delta(C\beta-H)$
1487	1478	-9	1490	1471	-19	1497	1470	-27	$\nu(C\beta-C\beta)$ (B_{1g})
	1433			1412					
	1382			1382					
1348	1328	-20	1354	1342	-12	1361	1361	0	$\nu(C\alpha-N)+\delta(C\beta-H)$
1233	1233	0	1235	1235	0	1233	1236	+3	$\nu(Cm-C\phi)$
1075	1053	-22	1068	1076	+8	1078	1078	0	$\delta(C\beta-H)$
1030			1027	1027	0		1025		phenyl
1000	1000		1004	1004	0	1003	1003	0	phenyl, $\nu(C\alpha-Cm)$
	980	-20		978	-26		981	-22	$\nu(C\alpha-Cm)$
				925			928		$\nu(ClO_4^-)$
882			882						phenyl
	884			866			845		

a) $\Delta\nu$, frequency shift(cm^{-1}) due to one-electron oxidation. b) Phenyl, ν, and δ denote a phenyl ring mode, a stretching mode, and a bending mode, respectively.

due to the one-electron oxidation are not so large that one-to-one correspondence is possible between the Raman bands of the radicals and those of the corresponding metalloporphines. Based on these reasonings, we considered that the prominent bands at 1543, 1471, 1342, 1076, and 978 cm^{-1} observed for $ZnTPP^{+\bullet}$ (Fig.2(D)) correspond to those at 1550, 1490, 1354, 1068, and 1004 cm^{-1} in the spectrum of ZnTPP(Fig.2(C)). In a similar way we made the assignments of the bands observed for $MgTPP^{+\bullet}$ and $CuTPP^{+\bullet}$. The results are summarized in Table 1. The bands at 1433, 1382, and 884 cm^{-1} in Fig.2(B) and those at 1412, 1382, and 866 cm^{-1} in Fig.2(D) do not have the corresponding bands in the spectra of MgTPP and ZnTPP(Figs.2(A) and (C)). As Figures 2(B), (D) and 3(B) show, the relative intensities of Raman bands observed for $MgTPP^{+\bullet}$ are different from those observed for $ZnTPP^{+\bullet}$ and $CuTPP^{+\bullet}$. These results suggest that there exist considerable differences in the enhancement mechanism of Raman bands between the metalloporphines and their cation radicals and also between the radical of MgTPP and those of ZnTPP and CuTPP.

The frequency shifts due to the one-electron oxidation summarized in Table 1 should be explained in terms of the electronic structure in the ground state of the metalloporphines and their cation radicals. From the calculated nodal structure of the a_{2u} molecular orbital[9)] it is known that the orbital is bonding with regard to the C_β-C_β and C_α-C_m bonds and anti-bonding with regard to the C_α-C_β and C_α-N bonds. Then the removal of one electron from the a_{2u} orbital causes the decrease in the order of the C_β-C_β and C_α-C_m bonds, which seems to be consistent with the shift to lower frequency side observed for the Raman bands due to the C_β-C_β and C_α-C_m bonds near 1550, 1480, and 990 cm^{-1}(See Table 1). The shift to lower frequency side observed for the Raman bands near 1350 cm^{-1}(to which the C_α-N stretching mode mainly contributes), however, does not correspond to the nodal structure of the a_{2u} orbital. These results clearly indicate that, to explicitly explain the origins of the frequency shifts and their dependence on the type of central metal ions summarized in Table 1, we need to calculate both the MO's and the normal vibrations of the metalloporphines and their cation radicals. In spite of the above features it is clear that the one-electron oxidation of the metalloporphines causes similar frequency shifts for each porphine stretching mode, and that the measurement of the shifts gives us a clue to determine the ground electronic structure of the cation radicals(the $^2A_{2u}$ state in this case) of the metalloporphines.

References

1) L. K. Hanson, Chi K. Chang, M. S. Davis, and J. Fajer, *J. Am. Chem. Soc.*, 103, 663 (1981).
2) R. H. Felton, " The Porphyrins " Vol.5, edited by D. Dolphin, p.53, Academic Press(1978).
3) M. Lutz and K. Kleo, *Biochim. Biophys. Acta* 546, 365(1979).
4) T. M. Cotten, K. D. Parks, and R. P. Van Duyne, *J. Am. Chem. Soc.*, 102, 6399(1980).
5) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, 92, 3451(1970).
6) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, 92, 2982(1970).
7) J. M. Burke, J. R. Kincaid, and T. G. Spiro, *J. Am. Chem. Soc.*, 100, 6077(1978).
8) J. Fajer, D. C. Borg, A. Forman, R. H. Felton, L. Vegh, and D. Dolphin, *Ann. N. Y. Acad., Sci.*, 206, 349(1973).
9) G. M. Maggiora, *J. Am. Chem. Soc.*, 95, 6555(1973).

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