The Resonance Raman Spectra of (*meso*-Tetraphenylporphinato)cobalt(II)-d_0 [Co (TPP)-d_0], -d_8, and -d_{20}

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Synopsis. The resonance Raman spectra of the title complexes were measured, and a normal coordinate analysis was carried out. The 1604 and 1243 cm^{-1} polarized bands of Co(TPP)-d_0 were assigned to resonance-enhanced phenyl modes. This suggests the presence of appreciable porphine-phenyl resonance interaction in this complex.

Many vibrational studies have been devoted to the TPP ligand. Since there is no physiological porphine with aromatic groups at its *meso* positions, it is important to check the TPP's characteritic features which are caused by the peripheral phenyl group. Recently, Burke *et al.* tentatively assigned the 1240 cm^{-1} band of Fe(TPP) and the corresponding bands of the analogues to a mode mainly associated with the C_m–Ph (mesocarbon-phenyl) stretching vibration and stated that the porphine-phenyl resonance interaction in the ground state was no required to interpret any of the RR data.[1,2] On the other hand, Fuchsman *et al.* assigned the halogen-sensitive resonance Raman (RR) bands (1100—1050 cm^{-1}) of tetra(*p*-halophenyl)porphine derivatives[3] and the 1234 cm^{-1} band of Cu(TPP)[4] to phenyl modes and pointed out that this was direct evidence of the resonance interaction. Adequate vibrational data to shed light on this controversial point were not found in the literature. Fortunately, however, our understanding of the fundamental vibration of the porphine core has been extensively advanced by Kitagawa *et al.*'s detailed experimental[5] and theoretical[6] studies of (octaethylporphinato)nickel(II) [Ni(OEP)]. Although the pattern of peripheral substitution in TPP is quite different from that in OEP, X-ray crystallographic studies suggest that the bonding within the porphine core is essentially the same in both porphines.[7,8] Hence, we tried to explain our RR data with reference to the results of normal coordinate analyses.

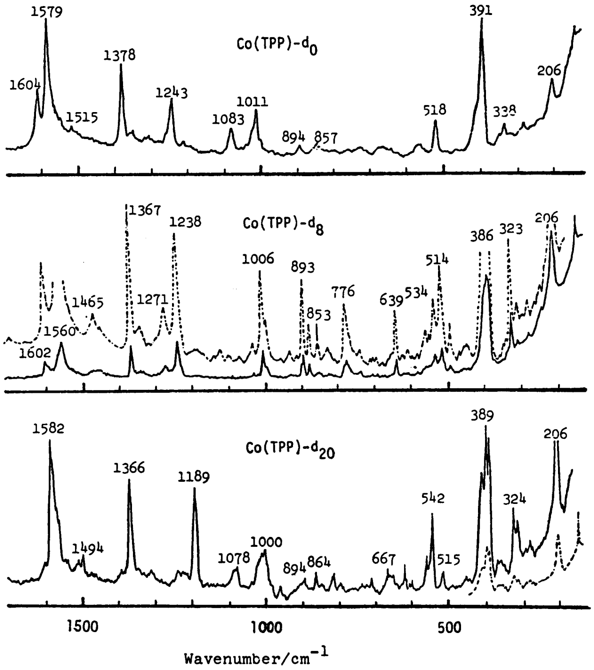

Fig. 1. RR spectra of Co(TPP)-d_0, -d_8, and -d_{20}. The samples were deposited on a cold tip at 10 K as films and excited by the 457.9 nm line of an Ar-ion laser.

Figure 1 shows the RR spectra of the well-purified samples, which were vaporized from a "miniature oven" and deposited onto a cold Cu tip to make films. The films at 10 K were excited by the 457.9 nm line of an Ar-ion laser. The details and the spectrometer have been described previously.[9] The spectra closely resemble those in Ar matrices.[9] All the strong bands were found to be polarized, as was expected from the fact that the RR spectra of metalloporphines were dominated by the totally symmetric modes (A_{1g} species

TABLE 1. CALCULATED AND OBSERVED A_{1g} FUNDAMENTAL FREQUENCIES (cm^{-1}) OF Co(TPP)-d_0, -d_8, -d_{20}, AND M(T_{piv}PP).

Modes	Co(TPP)-d_0		Co(TPP)-d_8		Co(TPP)-d_{20}		Fe(T_{piv}PP)[a]	Co(T_{piv}PP)
	Obsd	Calcd	Obsd	Calcd	Obsd	Clacd	Obsd	Calcd
ν_1	—	3057	—	2264	—	3057	—	3057
ν_2	1579(vs)	1578	1560(vs)	1569	1582(vs)	1578	1566(vs)	1578
ν_3	1497(w)[b]	1493	1465(mw)	1471	1494(mw)	1493	1480(vw)	1493
ν_4	1378(s)	1378	1367(ms)	1356	1366(s)	1378	1370(s)	1377
ν_5	1083(m)	1092	776(m)	769	1078(m)	1092	1080(mw)	1092
ν_6	1011(ms)	1000	1006(ms)	1017	1000(ms)	1000	996(m)	994
ν_7	894(w)	886	893(mw)	883	894(w)	885	—	881
ν_8	391(vs)	385	386(vs)	379	389(s)	384	372(s)	375
ν_9	206(m)	208	206(s)	208	206(s)	203	—	143

a) The data were cited from Ref. 6. b) This band was distinctly detected in Ar matrices, but was smeared out in films (Ref. 9).

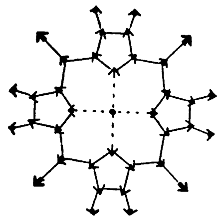

Fig. 2. The eigenvector of the Co(TPP)-d_0's ν_9 mode (A_{1g}, 206 cm^{-1}).

under D_{4h} symmetry) when the exciting frequency approaches that of the Soret band.[10] An experimental assignment is shown in Table 1, along with the calculated frequencies.

To carry out the normal coordinate calculation, the following assumptions were adopted: the symmetry of the porphine core is D_{4h}, and the phenyl group is regarded as a single dynamic unit with a mass of 77 (-d_0 and -d_8) and 82 (-d_{20}). The structural parameters were taken from the result of X-ray crystallographic analysis of Co(TPP),[8] but slightly modified to keep the D_{4h} symmetry. The potential energy was expressed with the same type of modified Urey-Bradley force field as that used for (NiOEP) by Abe *et al.*[6] The calculations were carried out by means of a NEAC-ACOS 1000 computer system at Tohoku University with AXSMZ and LSMX programs.[11]

The A_{1g}-calculated frequencies are in good agreement with the observed frequencies. The determined stretching and repulsive force constants were slightly different from those of Ni(OEP) in a manner roughly corresponding to their structural change. The experimental Teller-Redlich A_{1g} product ratios of Co(TPP)-d_8 and -d_{20} to -d_0 were 0.499 and 0.970, which were close to the theoretical values of 0.500 and 0.969 respectively.[12] The 1604 and 1243 cm^{-1} bands (-d_0) were not included in the A_{1g} mode. Some other weakly observed bands were explained with B_{1g}, A_{2g}, and B_{2g} frequencies calculated at the same time.

Although Fuchsman *et al.* supposed that some porphine-core modes of Cu(TPP) shifted to a frequency range lower by about 35 cm^{-1} upon the phenyl deuteration,[4] the calculated frequencies of Co(TPP)-d_0 and -d_{20} show that the maximum frequency shift is only 5 cm^{-1} in the ν_9 mode (Fig. 2). In this mode, the phenyl groups vibrate in-phase with each other and with the largest amplitude, while those in the other core modes are negligibly small. The mesocarbons vibrate in the same phase as do the phenyl groups, but with a slightly smaller amplitude. From the calculation, it is now evident that the 1243 cm^{-1} band (-d_0) shifted to 1189 cm^{-1} (-d_{20}). This large frequency shift and the disappearance of the 1604 cm^{-1} band upon the phenyl deuteration suggest that they are phenyl modes.

To confirm this assignment, a normal coordinate treatment for [*a,a,a,a-meso*-(*o*-pivaloylamidophenyl)porphinato]cobalt(II), [Co(T_{piv}PP)], was also carried out, where the same structural parameters and force constants as those used for Co(TPP) were employed. The calculated frequencies well explained the observed frequencies of Fe(T_{piv}PP)[2] in Table 1. A comparison between the calculated frequencies of Co(TPP)-d_0 and Co(T_{piv}PP) shows that the drastic changes in the mass (from 77×4 to 176×4 amu) and structure in the periphery do not substantially affect the A_{1g} normal frequencies, except for the ν_9 mode. This means that the second assumption, or the separation of the phenyl modes from the porphine-core modes, is appropriate. If the 1240 cm^{-1} band of Fe(TPP) is one of the core modes, as assigned by Burke *et al.*,[2] its counterpart in Fe(T_{piv}PP) should be found in a slightly lower frequency region. However, this is not the case.

The present work thus supports Fuchsman *et al.*'s results.

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