Infrared Study on Interaction between Porphyrin and Divalent Metal Ion

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(Received March 3, 1971)

In contrast to the NMR, ESR, and electronic spectra of metalloporphyrins, their infrared spectra have not been understood because of complication. Although only empirical assignment has been done for some observed infrared bands of the naturally occurring porphyrin complexes,[1,2] no systematic band assignment has been made for metalloporphyrins. However, the highly symmetrical metalloporphyrin enables us to assign some characteristic absorptions. Here we reprot the interaction between aromatic ligand and metal ion in the ground state in terms of the aromatic C–H bending vibrations.

The aromatic meso protons of porphyrins are easily exchanged with deuterium in D_2O–D_2SO_4. The band at 835 cm^{-1} of metal-free octaethylporphyrin has been assigned to the meso C–H out-of-plane bending vibration since it disappears on deuteration.[3] It was found that three absorptions for Zn(II)-octaethylporphyrin at 3110, 1220, and 836 cm^{-1} were found to disappear upon deuteration. They are assigned to the C–H stretching (ν(C–H)), in-plane bending (δ(C–H)), and out-of-plane bending (π(C–H)) vibrations, respectively. Zn(II)-octaethylporphyrin-d_4 shows three new bands at 2260, 942, and 638 cm^{-1}. Similarly the bands at 3040, 1227, and 836 cm^{-1} of Zn(II)-octamethylporphyrin are shifted to 2245, 916, and 638 cm^{-1} upon deuteration.

The δ (C–H) and π (C–H) frequencies of various divalent metal complexes of cotaethylporphyrin are listed in Table 1. The stronger coordination between aromatic ligand and metal ion results in the higher frequency shift in the order Pd>Ni>Co>Cu>Zn>Mg. The δ (C–H) frequency is more dependent on the nature of the metal ion than the π (C–H) frequency. The order of the frequency shift is similar to that of the metal sensitive vibration around 1000 cm^{-1} [1,4] and vibrations appearing in the far-infrared region.[1,5] Thus, the frequency shifts of the δ (CH) and π (CH) show clearly the effect of metal ion on aromatic ligand. The order found for the frequency shift is the same as that for the stability replacement reaction,[6] for the one electron-oxidation potential[7] and for the hypsochromic shift in electronic spectrum.[5,7] The shifts of the δ (C–H) and π (C–H) might be related to the changes of the electronic structure of the porphyrin ring. The higher electronegativity of the metal ion or the less ionic character of the metal-porphyrin bond causes the larger shift towards higher frequencies.

Table 1. Frequencies of the in-plane and out-of-plane bending vibrations of the aromatic C–H bond[a)]

Complex	In-plane (cm^{-1})	Out-of-plane (cm^{-1})
Mg(II)-OEP	1217	834
Zn(II)-OEP	1220	836
Cu(II)-OEP	1223	837
Co(II)-OEP	1228	837
Ni(II)-OEP	1229	837
Pd(II)-OEP	1229	839

a) Spectra were measured for KBr pellets and frequencies were calibrated with polystyrene.

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