Resonance Raman Spectroscopy of Transition Metal Protoporphyrin IX Dimethyl Ester Complexes and its Interpretation in Terms of d-Orbital Interaction

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Resonance Raman (RR) spectra are reported for Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pd^{II}, and Cd^{II} protoporphyrin IX dimethyl ester (PP) complexes. The reduction in frequency of their structure-sensitive bands are in the order $Ni^{II} > Co^{II} > Pd^{II} > Cu^{II} > Zn^{II} > Cd^{II}$, while the values of λ_{max} for their electronic absorption spectra increase in the order $Pd^{II} < Ni^{II} < Co^{II} < Cu^{II} < Zn^{II} < Cd^{II}$. Empirical assignments for some of the stronger Raman bands of some metalloporphyrins are given. A detailed examination of the interaction between metal ions and the porphyrin ring shows that in planar metalloporphyrins, in addition to the fundamental co-ordinate bonds, both core-expansion effects and π-back-bonding effects exist. When the outer $d_{x^2-y^2}$ orbital is occupied by metal electrons, core expansion predominates; if no outer $d_{x^2-y^2}$ orbital electron is present, π-back-bonding contributes more than core expansion. Using this assumption, we can explain the spectral changes in both Raman and electronic absorption spectra satisfactorily. We suggest that the essence of the core-expansion mechanism is the multiplex result of the interactions between the outer electrons of metal ions with the electrons of the porphyrin ring and their steric interactions.

Since the initial application of resonance Raman spectroscopy to porphyrins and metalloporphyrins in the early seventies,[1] it has become a powerful tool with which to investigate biomacromolecules, especially hemoproteins and cytochromes, *etc.*[2,3] Several papers on the interaction between metal ions and the porphyrin ring have been published.[3–6] The controversial interpretations of the spectral changes in Raman frequency with various central metal atoms, as summarised by Felton *et al.*[7] were as follows. (*a*) Spiro and co-workers suggested that the 'doming' or 'ruffling' of the porphyrin ring, accompanying the out-of-plane displacement of metal, partially interrupted the conjugation in the porphyrin skeleton, thus lowering the structure-sensitive frequencies.[3,4] (*b*) Spaulding *et al.* proposed a 'core-expansion' mechanism, demonstrating structural changes in the porphinato core, due to the retention of planar pyrrole units modulating the geometry of the 16-membered inner ring and thus inducing the vibrational frequency shifts. A third interpretation, given by Kitagawa *et al.*,[6] was that the conjugation interaction between the metal $4p_z$ orbital and the porphyrin a_{2u} orbital lowered the energy level of the a_{2u} orbital, and thus caused the shift to high wavenumber.

In this paper we attempt to probe the interaction between metal ions and the porphyrin ring by means of spectral changes in the RR spectra and the optical absorption spectra of a series of transition metal protoporphyrin IX dimethyl ester complexes (metalloPPs).

Experimental

NiPP, PdPP, and CdPP were prepared from free base PP (Sigma Chemical Co., used without further purification) by the DMF method[8] and were purified on Al_2O_3 chromatographic columns. CoPP, CuPP, and ZnPP were prepared as described in ref. 9. The elemental analyses of the complexes are consistent with the calculated values.

The electronic absorption spectra were obtained on a Shimazu UV–VIS spectrophotometer, model UV-365. RR spectra were determined on an assembled and computerized Raman spectrometer, a GDM-1000 double monochromator (Jena Zeiss), coupled with a model 1112 photon counter (Princeton Applied Research), a Cromemco Z80A microcomputer and a Spectra Physics 165 Argon ion-laser exciting lines at 457.9, 488.0, and 514.5 nm. A laser filter monochromator (Applied Photophysics) was used to filter out the laser plasma lines. All Raman spectra were obtained in KBr pellets using a rotating-cell technique to avoid local heating and decomposition of the samples during laser irradiation. The structural formula of the metalloporphyrins are given in Figure 1.

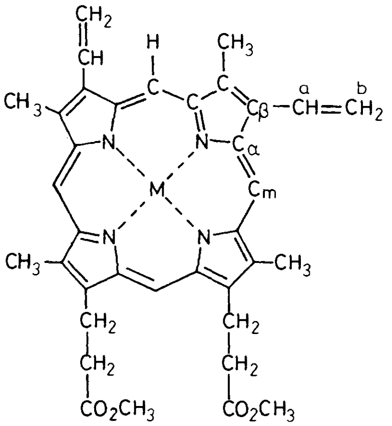

Figure 1. Structural formula of metalloprotoporphyrin IX dimethyl ester.

Results and Discussion

Electronic Absorption Spectra.—The absorption bands of CoPP, NiPP, CuPP, ZnPP, PdPP, and CdPP are listed in Table 1. According to Gouterman's four-orbit model,[10] the electronic transition from top-filled ring orbitals $a_{1u}(\pi)$ and $a_{2u}(\pi)$ to the empty $e_g(\pi^*)$ orbital *via* configuration interaction gives rise to one strong absorption band (Soret band), an α band, [$Q(0,0)$]; and a vibronic transition band, β[$Q(1,0)$]. These are

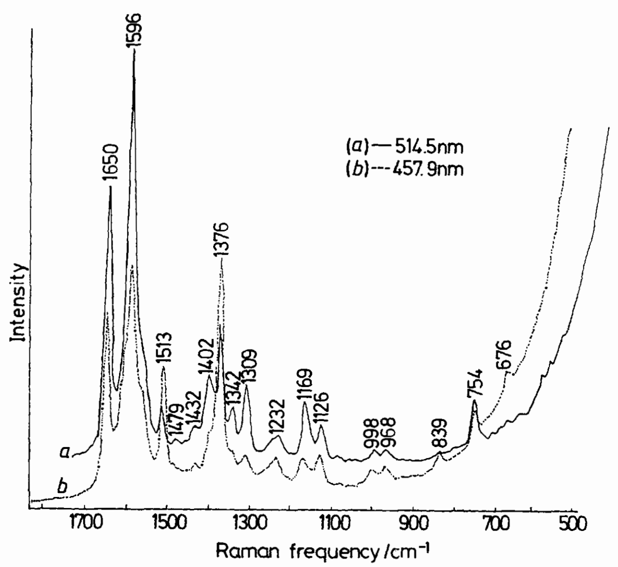

Figure 2. RR spectra of CoPP in KBr pellet; (*a*) laser power: 400 mW, slit width: 500 μm, scanning speed: 24 cm^{-1} min^{-1}; (*b*) laser power: 130 mW, slit width: 600 μm, scanning speed: 24 cm^{-1} min^{-1}.

typical for metalloporphyrins with D_{4h} molecular symmetry (*cf.* Table 1).

Resonance Raman Spectra.—Figure 2 is an illustration of the RR spectra of CoPP, which is one of the metalloPPs we examined. It is clear that certain Raman intensities were enhanced when the excitation frequencies were in resonance or close to the electronic absorption bands. With irradiation at 457.9 nm, near resonance with the Soret band, the polarized 1 376 and 1 513 cm^{-1} bands are strongly enhanced; while with 514.5 nm excitation, which is close to the α,β bands, enhancement of the 1 650 and 1 597 cm^{-1} bands (and the anomalously polarized 1 308 and 1 169 cm^{-1} bands) is obvious. The band at 839 cm^{-1}, however, almost only ever appears in the spectrum following irradiation at 457.9 nm. Using refs. 11–13 and the rule of spectral changes in the series of metalloPPs under investigation, we give the empirical assignment for their major Raman bands in Table 2.

Table 1. Soret, α, and β bands in the UV–VIS spectra of the metal complexes (in $CHCl_3$).

Complex	λ/nm		
NiPP	400.0	561.2	524.1
CoPP	405.0	565.0	529.0
CuPP	406.0	570.4	532.5
ZnPP	415.6	581.6	544.6
PdPP	398.0	553.0	517.0
CdPP	424.0	590.0	555.0

Rule for Spectral Changes in Electronic Absorption Bands and Raman Bands with Metal Ions.—The bands labelled with asterisks in Table 2 are the so-called 'structure-sensitive' bands. The frequencies of these Raman bands and the values of λ_{max} vary with the metal ions in the following order:

$$Pd^{II} < Ni^{II} > Co^{II} > Cu^{II} > Zn^{II} > Cd^{II} \text{ and } Pd^{II} > Cd^{II}$$

Decrease in structure-sensitive frequencies with metal ions

$$Pd^{II} < Ni^{II} < Co^{II} < Cu^{II} < Zu^{II} < Cd^{II}$$

Increase in λ_{max} values with metal ions

(*a*) *Spectral changes in metals of the same period but in different groups.* The metalloPPs examined form square-planar co-ordination complexes with the metal ion in the centre.[14,15] In accordance with the principle of orbital splitting in ligand-field theory, the metal ion outer d orbitals are as shown in Table 3. Since the $d_{x^2-y^2}$ orbital points directly towards the four nitrogen atoms,[16] when the $d_{x^2-y^2}$ orbital is filled with electron(s), repulsion towards the four nitrogen atoms takes place, causing porphinato core expansion, and a decrease in certain bond intensities. As a result of the increase in the C_α–C_m bond length and the $C_\alpha C_m C_\alpha$ bond angle, the structure-sensitive frequencies decrease. If the $d_{x^2-y^2}$ orbital is occupied by one or more electrons, then greater core expansion takes place, with the Raman frequencies shifting toward the lower wavenumber side in the following order: Co^{2+},Ni^{2+} > Cu^{2+} > Zn^{2+}, and Pd^{2+} > Cd^{2+}. In addition, the radius[17] of Co^{2+} (0.072 nm) is larger than that of Ni^{2+} (0.069 nm); core expansion in CoPP is therefore larger than in NiPP, and thus, the structure-sensitive frequencies in CoPP are lower than in NiPP.

The size of metal ion and the electronic repulsion of the $d_{x^2-y^2}$ orbital can also account for the rule governing the spectral

Table 2. Raman frequencies/cm^{-1} and assignments[a]

NiPP	CoPP	CuPP	ZnPP	PdPP	CdPP	Assignment[c] of ν
*1 662	1 650	1 638	1 618	1 635	1 609	C_α–C_m
*1 609	1 596	1 581	1 564	1 586	1 549	C_α–C_m
1 580	1 573sh	1 553sh	1 536sh			
*1 524	1 513	1 502	1 487	1 502	1 480	C_α–C_m, C_α–C_β
1 435	1 432	1 429	1 430			C_s=CH_2(V)[b]
1 403	1 402	1 395	1 393	1 404	1 391	C_α–C_β
*1 380	1 376	1 374	1 369	1 380	1 359	C_α–N
1 346	1 342	1 341	1 342	1 340	1 336	C_s=CH_2(V)[b]
1 306	1 308	1 315	1 318			C_m–H, C_α–C_β
		1 246	1 247	1 245	1 243	C_α–C_β, C_β–C_s
1 233	1 232			1 230		
1 169	1 169	1 171	1 175	1 174	1 169	C_β–C_α(V)[b]
1 124	1 126	1 132	1 141	1 126	1 126	C_α–C_β, C_β–C_β
839	839	839	840	839	840	Ring deformation
754	753	753	756	760	758	
676	675	675	676	676	675	

* Structure-sensitive band. [a] Spectra determined in KBr pellets. [b] V = vinyl group in PPs, C_s = carbon on the peripheral substituted groups. [c] See Figure 1 for explanation of α, β, a, m, and b.

Table 3. The metal ion outer d orbitals.

	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Pd^{II}	Cd^{II}
d electron configuration	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$	$4d^8$	$4d^{10}$
No. of electrons occupying $d_{x^2-y^2}$ orbital	0	0	1	2	0	2

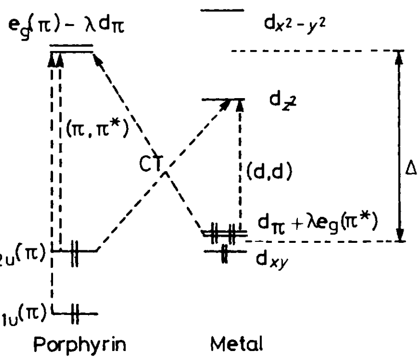

Figure 3. Schematic illustration of porphyrin and metal orbitals.[18]

changes in the electronic absorption bands. Gouterman[18] explained the changes in the position of the absorption peaks by the interaction of different metal ions with the porphinato ring (Figure 3). He suggested that the existence of π back-bonding, *i.e.*, the mixing of metal dπ orbitals with the $e_g(\pi^*)$ orbitals of the porphyrin ring raises the energy of $e_g(\pi^*)$, thus increasing the energy gap between $e_g(\pi^*)$ and $a_{1u}(\pi)$ and $a_{2u}(\pi)$, resulting in a blue-shift of the absorption spectrum. The energy of π back-bonding decreases along the series $Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$, so that the wavelengths of the absorption bands in CuPP and ZnPP are higher. Gouterman had not related his argument to the Raman frequency shifts; according to him, the formation of strong back-bonding obviously weakens the bond strength of the porphyrin ring, which, in turn, decreases the Raman frequencies. One expects, therefore, to observe the positions of the structure-sensitive bands of CoPP and NiPP at the lower wavenumber side of CuPP and ZnPP. But in fact the structure-sensitive Raman frequencies of the former are higher than the latter, as shown in Table 2.

Our interpretation is as follows: the repulsion of the $d_{x^2-y^2}$ electrons in Cu^{2+}, Zn^{2+}, and Cd^{2+} leads to porphinato core expansion and weakens the bond strength of the porphyrin ring, thus raising the energies of the bonding orbitals $a_{1u}(\pi)$ and $a_{2u}(\pi)$ and reducing the gap between $e_g(\pi^*)$ and $a_{1u}(\pi)$ and $a_{2u}(\pi)$, so that red shifts occur in the absorption spectra. In line with the magnitude of core expansion, the variation in the values of λ_{max} is $Ni^{2+} < Co^{2+} < Cu^{2+} < Zn^{2+}, Pd^{2+} < Cd^{2+}$. By invoking the core expansion caused by the size of the metal ions and also by the repelling effect of the $d_{x^2-y^2}$ orbital, we can satisfactorily explain the rules governing both absorption and Raman spectral changes in transition metalloPPs of the same period and different groups.

(*b*) *Spectral changes in metals of the same groups but in different periods.* Since the outer $d_{x^2-y^2}$ orbitals of Zn^{2+} and Cd^{2+} are occupied by two electrons, and the $4d_{x^2-y^2}$ orbital of Cd^{2+} extends further than the $3d_{x^2-y^2}$ orbital of Zn^{2+}, the repulsion of the $4d_{x^2-y^2}$ electrons on the four nitrogen atoms should be greater than that of $3d_{x^2-y^2}$, thus, the structure-sensitive frequencies of CdPP should lie at lower positions than in ZnPP, and the values of λ_{max} for the absorption spectra should follow the order CdPP > PdPP, which agrees with the experimental data we obtained. As for Ni^{2+} and Pd^{2+}, although the radius of Pd^{2+} is greater than that of Ni^{2+}, which implies that greater core expansion may exist, we believe that since the outer $d_{x^2-y^2}$ orbitals of Pd^{2+} and Ni^{2+} are empty, π back-bonding will be the dominant factor: the $4d_{x^2-y^2}$ orbital of Pd^{2+} extends further than the $3d_{x^2-y^2}$ orbital, so the π interaction between this orbital and the $e_g(\pi^*)$ orbital of the porphyrin ring is greater and stronger π back-bonding is formed, thus weakening the bond strength of the porphyrin ring. As a result, both the wavelengths of the absorption bands and the structure-sensitive Raman frequencies are less in PdPP than in NiPP. Following a comparison of the RR spectra of Os^{II}- and Fe^{II}OEP, Boldt *et al.*[19] proposed that the back donation of Os^{II} to the porphyrin ring is stronger than in Fe^{II}, which supports our view: in metalloPPs of the same group with an empty outer $d_{x^2-y^2}$ orbital, π back-bonding is dominant.

In metalloporphyrins, besides the co-ordinate bonding, π back-bonding and core-expansion effect, in some circumstances—especially in five co-ordinated complexes with axial ligands—the metal ion can be out-of-plane of with respect to the porphinato ring and 'doming' and 'ruffling' can take place. Therefore, by means of a study of the RR spectra and electronic absorption spectra of metalloporphyrins, integrated with their far IR spectra, one can deduce the interactions between the metal ions and the porphyrin ring and thus predict the relative stability of the metalloporphyrins. According to our experimental results and the analysis of the above mentioned interactions, we believe the relative stability should be: PdPP > NiPP > CoPP > CuPP > AgPP ~ ZnPP > CdPP, which corroborates ref. 20.

(*c*) *Application of our viewpoint to the interpretation and prediction of the rules governing spectral changes in other metalloporphyrins.* In AgPP, the $4d_{x^2-y^2}$ orbital is occupied by one electron, so core expansion effects should play the leading role. The frequencies should therefore follow the order CuPP > AgPP > CdPP. The absorption bands of AgPP given in ref. 16(*b*) (Soret 418 nm, α 517 nm, β 538 nm) confirmed our prediction. Since the rules for the spectral changes in metallo-octaethylporphyrins and mesoporphyrins[5,6,21] are similar to the metalloPPs being investigated here, we can also explain the rules governing these metalloporphyrins from our viewpoint.

As for the Raman spectral changes in iron porphyrins or hemeproteins with different oxidation and spin states, we consider that since the $d_{x^2-y^2}$ orbital is empty in low spin-state, the main cause of the spectral changes in different oxidation states is the varying degree of back-donation from Fe to the porphyrin ring. This is consistent with the arguments of Spiro *et al.*[3,4] In iron porphyrins with the same oxidation state, since the $d_{x^2-y^2}$ orbital is occupied by an electron in high spin-state, core-expansion effects will cause a decrease in the Raman frequencies.

Conclusions

The RR and electronic spectra of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Pd^{II}, and Cd^{II} protoporphyrin IX dimethyl ester complexes were studied and an analysis of the interactions between metal ion and porphyrin ring was made. The rules governing the spectral changes can be explained satisfactorily by means of the core-expansion effect and the relative strength of the π back-bonding effect. We believe that the essence of the mechanism of core expansion is the multiplex result of the electrostatic repulsion of the metal outer d electrons on the porphyrin ring and their steric interactions.

Core expansion is the major factor influencing the bonding energy of the porphyrin ring in a series of transition metal ions from the same period but in different groups, *i.e.*, the core expansion effect is greater than π back-bonding. For metal ions of the same group but in different periods, with empty outer

$d_{x^2-y^2}$ orbitals, π back-bonding is greater than the core-expansion effect. For metalloporphyrins with electrons in the outer $d_{x^2-y^2}$ orbital, core expansion is dominant, and the core expansion caused by the electrons in the $4d_{x^2-y^2}$ orbital is greater than that in the $3d_{x^2-y^2}$ orbital.

Acknowledgements

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