

The Infrared Spectra of Metalloporphyrins (4000–160 Cm^{-1})¹

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Abstract: Infrared spectra, in the region 4000–160 cm^{-1} , of the divalent metal (Co, Ni, Cu, Zn, Pd, Ag, Cd, and Mg) complexes of protoporphyrin IX dimethyl ester and hematoporphyrin IX dimethyl ester have been measured in the solid state and in solution. A strong absorption near 350 cm^{-1} probably arises from a coupling of the metal–nitrogen stretch with a porphyrin skeletal deformation. The intensity of the 350- cm^{-1} absorption is much greater for the Ni, Co, and Pd complexes than for the other metalloporphyrins. The intensity increase may arise from a weak metal→ligand π interaction. The frequencies of the porphyrin skeletal absorptions, particularly those at 970–920 and 530–500 cm^{-1} , are metal ion dependent. Frequency shifts can be linked to the order of metal–ligand coordinate bond strength: Pd > Co > Ni > Cu > Ag > Zn > Cd > Mg.

The biological and chemical importance of metalloporphyrins makes the nature of the metal–ligand linkage in these complexes of considerable interest. Since spectral properties provide pertinent information, the electronic spectra of these materials have been studied extensively. However, only a few infrared spectral studies have been carried out,³ and no systematic examination of divalent metal derivatives of naturally occurring porphyrins, in either the rock-salt region or in the far-infrared, has been reported. Metal-dependent frequency shifts of porphyrin skeletal absorptions as well as the frequencies of the metal–nitrogen vibration in the infrared region should give an indication of the metal–ligand coordinate bond strength. We have now studied the infrared spectra, in the region 4000–160 cm^{-1} , of complexes of the divalent metals Co, Ni, Cu, Zn, Pd, Ag, Cd, and Mg with protoporphyrin IX dimethyl ester and hematoporphyrin IX dimethyl ester (Figure 1).

Experimental Section

Materials. Protoporphyrin IX dimethyl ester (purity ~95%) was obtained from Sigma Chemical Co. and used without further purification. Hematoporphyrin IX dimethyl ester was prepared by the esterification⁴ of hematoporphyrin IX hydrochloride (Sigma Chemical Co.) and was separated from the unreacted acid by column chromatography on alumina. The divalent metal derivatives of the porphyrins were prepared by standard procedures⁵ and were separated from the metal-free ligand by column chromatography on alumina. The solids were recrystallized from chloroform-petroleum ether and dried under vacuum. The absence of metal-free and altered porphyrin impurities in the metalloporphyrins was established by thin layer chromatography on silica gel and by observation of the positions of the maxima and by the ratio of the absorbancies in the electronic spectra. The protoporphyrin complexes were judged to be very pure by chromatographic criteria. The hematoporphyrin derivatives contained small amounts (<5%) of hydroxyethyl compounds, which were found to affect the infrared spectra very slightly if at all. The metalloporphyrins, except the Mg(II) derivatives, were judged to be essentially anhydrous from the absence of coordinated water absorption peaks in the solution infrared spectra.

Infrared Measurements. The spectra in the region 4000–650 cm^{-1} were obtained with the materials dispersed in potassium bromide disks and were checked with mineral oil mulls with a Beckman IR-12 grating infrared spectrophotometer. Solution spectra, usually in methylene chloride (hematoporphyrins) and chloroform (protoporphyrins), were also obtained. A Perkin-Elmer No. 301 double-beam grating spectrophotometer (with a dry nitrogen purge) was used to study the 650–160- cm^{-1} region. Spectra were obtained with concentrated mineral oil mulls of the materials placed between thin disks of high-density polyethylene. Two disks of polyethylene were also placed in the reference beam. The spectra from 650 to 300 cm^{-1} were checked with concentrated potassium bromide pellets. The frequencies quoted could be reproduced to ± 2 cm^{-1} in the far-infrared and no greater than ± 4 cm^{-1} elsewhere.

Results and Discussion

The 4000–650- Cm^{-1} Region. The principal infrared absorption bands in the rock-salt region for the porphyrins and metalloporphyrins are listed in Tables I and II. Representative solid-state spectra are shown in Figure 2. The spectra of the hematoporphyrin series and the protoporphyrin series closely resemble each other. The only obvious differences arise from absorption characteristic of the hydroxyethyl and vinyl substituents. The spectra of compounds of the protoporphyrin series are generally more highly resolved than those of the hematoporphyrins. The most prominent absorptions in the spectra of both series of compounds are associated with the vibrations of the porphyrin ring substituents. The absorptions that arise from motions of the macrocycle skeleton, on the other hand, are generally weak and not easily observed. A number of ligand absorption peaks, which are independent of the metal ion, can be readily assigned. Our assignments are in general agreement with those recently reported for a number of metal-free porphyrins.⁶

The O–H stretching vibration of the hydroxyethyl side chain of hematoporphyrin absorbs weakly at 3600 cm^{-1} in methylene chloride solution. The magnesium porphyrins show an additional broad absorption at 3300–3400 cm^{-1} in their solution spectra that can be assigned to the O–H stretch of coordinated water. Magnesium porphyrins invariably occur as solvates with one or two solvent molecules axially bound to the metal atom.⁷ The metal-free porphyrins show a weak

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Table I. Infrared Absorption Bands of Divalent Metal Derivatives of Protoporphyrin IX Dimethyl Ester

H ₂	Co	Ni	Cu	Zn	Pd	Ag	Cd	Mg
3315 w								
3095 w	3070 w	3080 w				3090 w	3090 w	3090 w
3010 w								
2958 w	2960 w	2955 w	2950 w	2950 w	2960 w	2960 w	2960 w	2965 w
2920 w	2930 w	2925 w	2920 w	2925 w	2930 w	2930 w	2920 w	2930 w
2865 w	2870 w	2860 w	2865 w	2860 w	2870 w	2865 w	2865 w	2870 w
1737 s	1741 s	1741 s	1739 s	1738 s	1739 s	1738 s	1738 s	1738 s
1670 w	1667 w					1665 w	1666 w	
1626 w		1621 w	1626 w	1622 w		1620 w	1622 w	1628 w
1589 w	1599 w				1594 w		1562 w	1562 w
1543 w	1561 w	1564 w	1550 w		1552 w	1557 w	1542 w	1547 w
1507 w						1516 w		1523 w
1440 m	1438 m	1436 m	1438 m	1438 m	1438 m	1436 m	1436 m	1456 m
1418 w								1419 w
1377 w	1390 w	1391 w	1390 w	1387 w	1386 w	1387 w	1377 w	1378 w
1324 w	1370 w	1368 w	1360 w	1358 w	1360 w	1358 w	1358 w	1354 w
1278 w						1260 w	1265 w	1272 w
1258 m	1240 m	1239 m	1238 m	1236 m	1240 m	1243 w	1246 w	1244 w
1230 w						1227 w		1223 w
1199 m	1200 w		1203 w	1200 w		1198 w	1198 w	1201 w
1184 m	1169 m	1168 m	1169 m	1167 m	1166 m	1167 m	1167 m	1165 m
1110 w	1130 w	1128 w	1129 w	1125 w		1127 w	1129 w	1130 w
1080 w	1084 w	1087 w	1085 w	1082 w	1084 w	1089 w	1088 w	1088 w
1066 w		1060 w	1058 w	1062 w	1060 w	1058 w	1055 w	1060 w
	1023 w	1020 w	1022 w	1022 w	1019 w	1015 w		
990 w			990 w			985 w	990 w	991 w
962 w			969 w	970 w		970 w		968 w
912 w	968 w	966 w	944 w	938 w	973 w	938 w	927 w	933 w
	897 w		897 w	906 w	898 w	897 w	898 w	907 w
787 w	757 w	755 w	756 w	757 w	759 w	754 w	752 w	755 w
739 w								
725 w	716 w	713 w	714 w	716 w	720 w	719 w	720 w	723 w
710 w								
683 w								

band at 3320 cm^{-1} that can be associated with an N-H stretching vibration. The N-H out-of-plane deformations give rise to sharp absorption peaks at 740 and 680 cm^{-1} .⁶ An in-plane N-H deformation has previously been assigned to an absorption band at 1110

symmetric deformations give rise to medium intensity absorption peaks at 1440 and 1380 cm^{-1} . Characteristic vinyl C-H bending modes cannot be assigned unequivocally in the spectra of the protoporphyrins

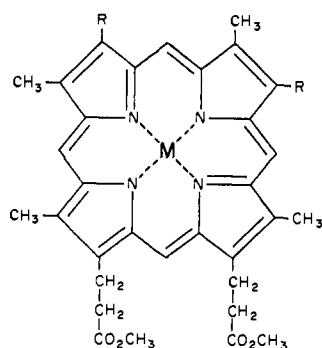


Figure 1. Structural representation of metalloporphyrins: R = $\text{CH}=\text{CH}_2$ for protoporphyrin IX; R = CHOHCH_3 for hematoxylin IX; M = Co, Ni, Cu, Zn, Pd, Cd, Ag, and Mg.

cm^{-1} . As expected, the N-H bands are absent from the spectra of the metalloporphyrins. Bands of medium-to-weak intensity are found in the $3100\text{--}2800\text{ cm}^{-1}$ region, and these can be assigned to C-H stretching modes. The 2960-- , 2925-- , and 2875 cm^{-1} peaks are associated with antisymmetric and symmetric alkyl C-H vibrations. The protoporphyrin compounds show very weak vinyl C-H stretching absorptions at 3090 and 3010 cm^{-1} . The alkyl C-H antisymmetric and

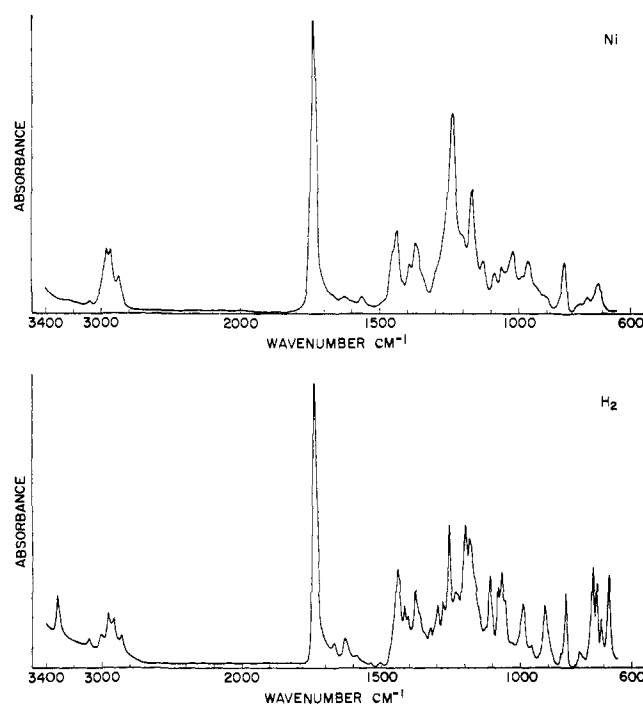


Figure 2. Infrared absorption and spectra of protoporphyrin IX dimethyl ester and nickel protoporphyrin IX dimethyl ester in potassium bromide disks.

Table II. Infrared Absorption Bands of Divalent Metal Derivatives of Hematoporphyrin IX Dimethyl Ester

H ₂	Co	Ni	Cu	Zn	Pd	Ag	Cd	Mg
3610 w	3610 w	3610 w	3600 w	3600 w	3605 w	3610 w	3605 w	3590 w
3320 w								
2958 w	2955 w	2955 w	2950 w	2950 w	2955 w	2960 w	2975 w	2970 w
2925 w	2930 w	2925 w	2920 w	2925 w	2930 w	2925 w	2930 w	2930 w
2870 w	2870 w	2870 w	2870 w	2870 w	2870 w	2870 w	2870 w	2870 w
1737 s	1740 s	1739 s	1738 s	1737 s	1736 s	1738 s	1737 s	1736 s
1667 w	1668 w	1670 w	1665 w	1670 w		1668 w		
1610 w			1610 w	1627 w		1623 w		1620 w
	1608 w	1606 w			1594 w	1582 w	1572 w	1583 w
1548 w		1573 w			1562 w			
1509 w		1525 w				1515 w		1523 w
1447 m	1440 m	1438 m	1436 m	1440 m	1439 m	1439 m	1439 m	1457 m
	1387 w	1384 w	1387 w	1384 w	1388 w	1382 w	1383 w	1390 w
1366 m	1368 m	1369 w	1363 w	1360 w	1364 w	1368 w	1371 w	1380 w
1345 w				1342 w				1357 w
1268 w	1239 m	1240 m	1237 m	1248 m	1247 m	1248 m	1265 m	1268 w
1230 w				1228 w		1228 w		1223 w
1198 w	1200 w		1198 w	1200 w	1206 w	1200 w	1199 w	
1168 m	1168 m	1169 m	1167 m	1165 m	1169 m	1168 m	1166 m	1163 m
1108 w	1129 w	1128 w	1224 w	1130 w	1136 w	1128 w	1123 w	1126 w
1071 m	1086 w	1085 w	1082 w	1089 w	1085 w	1080 m	1073 m	1072 m
	1060 w	1062 w	1058 w	1058 w	1057 w			
1032 w	1026 w	1021 w	1019 w	1025 w	1030 w	1035 w	1036 w	
988 w		990 w	992 w	990 w		992 w	990 w	980 w
960 w							971 w	
918 w	969 w	961 w	945 w	935 w	970 w	939 w	927 w	933 w
879 w	908 w	896 w				890 w	881 w	883 w
836 w	839 w	835 w	836 w	837 w	839 w	836 w	833 w	836 w
	757 w	754 w	753 w	755 w	759 w	750 w		
744 w								
685 w	718 w	728 w	725 w	718 w	721 w	726 w	722 w	728 w

because of the overlap of these bands in the 9000–1000-cm⁻¹ region with other ligand bands. A sharp peak at 840 cm⁻¹ can be assigned to the methine C–H bend.

The strongest absorption peak in the spectra at 1738 cm⁻¹ can be associated with the methyl propionate ester carbonyl stretch. The solid-state spectrum of magnesium protoporphyrin shows a splitting of the ester carbonyl band with peaks of nearly equal intensity appearing at 1735 and 1700 cm⁻¹. Chloroform or tetrahydrofuran solution spectra, however, only show one ester band. Intermolecular hydrogen bonding between coordinated water and the ester carbonyl could give rise to the observed splitting in the spectra of the solids. The splitting could also arise from the direct intermolecular interaction of a carbonyl oxygen and a magnesium atom of another molecule in a manner analogous to that observed in the aggregation of chlorophyll.⁸ Magnesium hematoporphyrin shows only one ester band both in the solid state and in solution. The methyl propionate carbon–oxygen single bond stretching vibration gives rise to a medium intensity absorption band at 1170 cm⁻¹. No definite assignment can be made for the C–O stretch of the hydroxyethyl group in the hematoporphyrins. There is, however, an increase in intensity of the absorption near 1070 cm⁻¹ in going from the protoporphyrin to the hematoporphyrin derivatives, and this may be the region in which the C–O absorption occurs.

The C=C and C=N stretching vibrations of the porphyrin macrocycle give rise to as many as five weak absorption peaks in the region from 1700 to 1500 cm⁻¹. For the most part, the frequencies and intensities of the bands are dependent on the metal ion present. The

study of these weak and poorly resolved peaks is considerably facilitated by using highly concentrated KBr disks. Such spectra show an absorption peak at 1665 cm⁻¹ occurring as a shoulder on the strong ester band. The metal-free porphyrins show four absorption peaks below 1630 cm⁻¹: a peak of highest intensity at 1610–1630 cm⁻¹, one or two moderate intensity bands in the region 1540–1610 cm⁻¹; and finally a very weak band at 1500–1540 cm⁻¹. The spectra of the Mg, Zn, and Cd derivatives are similar to those of the metal-free porphyrins, and only minor frequency shifts are observed. Copper and silver porphyrins show increased absorption in the 1540–1610-cm⁻¹ region, while the Co, Ni, and Pd complexes show their most intense absorptions in this region. The chlorophylls and other dihydro porphyrins also show the C=C and C=N stretches in the 1500–1650-cm⁻¹ region.⁹ The absorption peaks of the chlorins are, however, relatively much more intense than those of the porphyrins. The protoporphyrin complexes show an absorption band near 1620 cm⁻¹ which is relatively more intense than for the hematoporphyrin complexes. The increase in absorption could arise from the C=C stretching vibration of the vinyl substituent.

A weak absorption band at 1350 cm⁻¹ has been assigned to a C–N stretching mode for a series of tetraphenylporphyrins.¹⁰ A weak absorption appears in protoporphyrin and hematoporphyrin complexes in this region. Its exact frequency is difficult to assign since it overlaps with the strong alkyl bending absorption. This band also falls within a relatively small

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(10) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).

Table III. Far-Infrared Absorption Bands of Divalent Metal Derivatives of Protoporphyrin IX Dimethyl Ester

H ₂	Co	Ni	Cu	Zn	Pd	Ag	Cd	Mg
	649 w	640 w	641 m	644 w	646 w	632 m	640 m	634 m
615 m	608 m	610 m	609 m	608 m	611 m	608 w	606 w	
590 w			581 w			588 w		588 w
558 w								556 w
500 w	522 m	521 m	512 m	506 m		509 m	506 m	504 m
452 w						491 w		491 w
432 m	436 m	436 m	436 m	438 m	438 m	438 m	438 m	440 w
382 m	380 m	379 m	380 m	380 m	382 m	380 m	380 m	376 m
360 m	349 s	353 s	348 m	349 s	352 s	350 s	352 s	342 s
332 m			330 m					319 m
319 m	309 m	306 m	304 m	299 m	308 m	298 m	301 m	
294 m								
236 w	221 m	234 w		230 w				
182 m	198 w	196 w	194 m		189 m	194 m	189 m	189 w

Table IV. Far-Infrared Absorption Bands of Divalent Metal Derivatives of Hematoporphyrin IX Dimethyl Ester

H ₂	Co	Ni	Cu	Zn	Pd	Ag	Cd	Mg
	647 w	635 w	640 w	641 w		640 w		638 w
604 m	608 m	611 m	611 m	605 m	608 m	606 m	606 m	604 m
579 w	574 w						582 w	581 w
558 w							559 w	
529 w			531 w			538 w	538 w	536 w
502 m	529 m	520 m	515 w	501 m		502 m	498 m	493 m
454 m				464 w		460 m	456 m	466 w
438 m	438 m	436 m	436 m	438 m	444 m	437 m	442 m	
384 m	382 m	384 m	382 m	380 m	382 m	383 m	378 m	
361 m	348 s	352 s	346 m	346 s	346 s	348 s	346 s	337 s
333 m			330 m					
318 w	301 m	309 w	303 m	300 m		298 w	296 w	
298 w								
273 w								261 w
205 w	203 w			226 w		206 w	204 w	217 w
195 w		189 m	195 m		220 m	188 w	189 w	189 w

frequency range and its intensity appears to be independent of the particular metal ion present. This, however, is not true for the medium intensity absorption peak at $\sim 1240\text{ cm}^{-1}$. For the Mg, Cd, Zn, Cu, and Ag complexes, the intensity of this absorption peak is less than that of the ester band at 1170 cm^{-1} . Conversely, for the Ni, Co, and Pd complexes, the intensity of this peak is greater than that of the ester band. The Cu and Ni etioporphyrin bands at $\sim 1240\text{ cm}^{-1}$ ¹¹ show an intensity difference which appears to be entirely analogous to that described here. The $\sim 1240\text{-cm}^{-1}$ absorption probably arises from a ligand deformation (breathing) vibration. There are two medium-to-weak intensity absorption bands in the spectra of the metal-free porphyrins at 990 and 915 cm^{-1} . The metalloporphyrins, however, show only one prominent absorption peak in this region at $973\text{--}926\text{ cm}^{-1}$. A number of very weak absorption peaks at 990 , 970 , and 900 cm^{-1} lie under this intense band. The metal-dependent band can be assigned to an in-plane porphyrin deformation mode. An analogous metal-dependent band at somewhat higher frequency, $\sim 1010\text{ cm}^{-1}$, has previously been observed for the divalent metal derivatives of the tetraphenylporphyrins.¹⁰

Far-Infrared Spectra. The positions of the far-infrared absorption bands, $650\text{--}160\text{ cm}^{-1}$, for the porphyrins and metalloporphyrins are listed in Tables III and IV and representative solid-state spectra are shown in Figure 3. The intensities of the far-infrared

absorption peaks are approximately one-tenth the intensities of the high-frequency bands. The spectra of the hematoporphyrin and protoporphyrin complexes are similar, except that the protoporphyrin spectra are

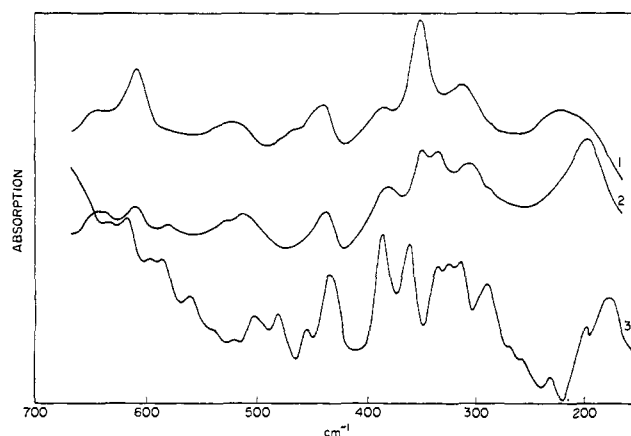


Figure 3. Far-infrared absorption spectra of protoporphyrin IX dimethyl ester compounds: (1) cobalt complex; (2) copper complex; and (3) metal-free ligand in mineral oil mulls.

more highly resolved. A number of common absorption peaks can be assigned to ligand vibrations. For example, bands at 640 , 610 , 440 , and 300 cm^{-1} can be assigned to methyl propionate ester deformations.¹²

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Prominent absorption peaks at 382 and 360 cm^{-1} (for the metal-free porphyrins) can be associated with porphyrin macrocycle deformation modes. Analogous absorptions appear in this frequency range for the chlorophylls.¹³

The far-infrared spectra of the metalloporphyrins show a series of metal-dependent ligand absorption bands. The broad, medium intensity porphyrin deformation band at 500 cm^{-1} is shifted to higher frequency in the metalloporphyrins. The frequency, but not the intensity, of this band is metal ion dependent. This absorption is not resolved in the spectra of the palladium porphyrins. The most intense band in the far-infrared spectra of the metalloporphyrins appears at $\sim 350 \text{ cm}^{-1}$. This band, and the adjacent weaker band at $\sim 380 \text{ cm}^{-1}$, can be considered as analogous to the two porphyrin deformations that appear at 382 and 360 cm^{-1} for the metal-free ligands. While the frequency of these absorptions are not strongly dependent on the metal ion, the intensity is. The intensity of the 350- cm^{-1} peak, relative to that of the 380- cm^{-1} peak, is greatest for the Pd, Ni, and Co complexes and somewhat less for the other metals. The Cu complexes show a splitting of this band, with an additional peak at 330 cm^{-1} . Metal-free derivatives show several absorptions in the 335–315- cm^{-1} region. In the metalloporphyrin spectra, these ligand bands are shifted to lower frequency and collapse to a single broad band. The metal-free porphyrins show two peaks in the 200–180- cm^{-1} region, which are generally shifted to higher frequency for the metalloporphyrins. In some cases, the intensity of this band is weak and the band is extremely broad. The zinc complexes do not show any absorptions at 200 to 180 cm^{-1} .

Metal-Dependent Absorptions. The frequencies of the metalloporphyrin absorptions that arise from metal–nitrogen vibrations are expected to appear in the far-infrared. Transition metal complexes of similar ligands that contain unsaturated nitrogen donor atoms have been extensively examined in the far-infrared. Thus, metal–nitrogen stretching modes have been assigned to absorption peaks in the 200–300- cm^{-1} region for divalent metal complexes of the pyridines, quinoline,¹⁴ and bipyridine.¹⁵ The high stability of the metalloporphyrins suggests a somewhat higher frequency for the metal–nitrogen stretching mode. The far-infrared spectra reported here do not show any prominent absorption peaks that can be unambiguously assigned to a metal–nitrogen vibration. In addition, a careful search in the 160–80- cm^{-1} region does not show any medium or strong absorption peaks. The failure to observe the M–N band in the far-infrared is probably a consequence of a variety of factors. The multiplicity of the porphyrin ligand absorptions makes detection of any new absorption bands for the complexes difficult. The complexity of the metalloporphyrin molecule and the strong interaction of the ligand and metal ion also make it likely that there will be considerable coupling of the ligand and metal–ligand vibrations. It is unlikely, therefore, that there is any vibration that even approximately represents a pure metal–nitrogen stretching or bending mode. On the other

hand, certain of the low-frequency ligand deformation vibrations that involve motions of the carbon–nitrogen framework would also involve motions of the metal atom. It is possible that the porphyrin band which is shifted from 360 to $\sim 350 \text{ cm}^{-1}$ for the metalloporphyrins contains a large contribution from a metal–nitrogen stretching motion. Unfortunately, the frequency of this intense absorption is only weakly dependent on the particular metal ion present and only varies a few wavenumbers over the entire series of complexes. This spread is within the experimental uncertainty of our measurements, and therefore no stability order can be extracted from these data. Magnesium porphyrins, however, show the lowest frequency metal–ligand band at $\sim 340 \text{ cm}^{-1}$, as expected from the relatively poor coordinating properties of magnesium. The chlorophylls show the magnesium–nitrogen band at somewhat lower frequency, 295 cm^{-1} .¹³ This shift is consistent with the lower stability of metal–chlorin linkage as compared to the metal–porphyrin linkage.¹⁶

The positions of the high-frequency porphyrin skeletal vibrations should be a function of the metal ion that is coordinately bound to the macrocycle. The magnitude of the frequency shift then depends on the extent to which the ligand electron distribution is altered when bound to a metal ion. The magnitude of the frequency shift presumably can be related to the strength of the metal–porphyrin coordinate band. The metal-dependent porphyrin frequency shifts noted here are, for the most part, small and within the experimental uncertainty of our measurements. This is true for the skeletal stretching and breathing modes in the region 1500–1700 and at 1240 cm^{-1} . On the other hand, the ligand deformation absorptions at 920–980 and 500–525 cm^{-1} show measurable metal-dependent frequency shifts. The bands shift to higher frequency in the order Pd > Co > Ni > Cu > Ag > Zn > Cd > Mg. This agrees approximately with the order derived from the frequency shifts of the ligand infrared absorptions for divalent metal derivatives of the tetraphenylporphyrins: Pd > Ni > Co > Cu¹⁰ > Zn¹⁷ > Mg.¹⁸ The infrared stability order follows the order of stability of the metalloporphyrins as derived from consideration of replacement reactions, dissociation reactions, and various electronic spectral data.¹⁹ The data, however, for the first transition series metalloporphyrins are not in agreement with the Irving–Williams stability order for complexes of nitrogen-containing ligands,²⁰ for the position of Co and Ni and the position of Cu are reversed. Finally, the frequency shifts are about the same for the hematoporphyrin and protoporphyrin complexes, indicating that our infrared measurements are not able to distinguish between the expected basicity differences of these ligands.

The substantial intensity differences of the metal-dependent absorptions noted here are of interest. In general, the porphyrin bands for the Co, Ni, and Pd porphyrins are more intense than those of the other complexes. For example, the intensity of the 350- cm^{-1}

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absorption, relative to the ligand band at 380 cm^{-1} , varies in the order: $\text{Ni} \gtrsim \text{Co} > \text{Pd} > \text{Cu} \sim \text{Zn} \sim \text{Ag} \sim \text{Cd}$ (Figure 4). This order is the one generally observed for the high-frequency ligand absorptions at $1500\text{--}1700$, 1240 , and $1000\text{--}900\text{ cm}^{-1}$ except that the relative intensity differences are smaller. The increase in integrated intensity of the metal-carbon and $\text{C}\equiv\text{N}$ stretches for transition metal cyanides have been related to the increase in the extent of the back π donation by the metal.²¹ A similar intensity- π interaction relationship has been shown to be operative for the substituent²² and ring vibrations²³ of substituted benzenes. The data presented here, therefore, suggest that the metal ion is involved in π bonding with the ligand in the case of the Ni, Co, and Pd metalloporphyrins. With the other metal atoms, e.g., Cu and Zn, this interaction must then be considerably weaker. Molecular orbital calculations²⁴ on the Co, Ni, Cu, and Zn porphyrins lend some support to this proposal. Although the energy difference between the filled metal $\pi(e_g)$ and lowest unfilled ligand $\pi(e_g)$ orbital is relatively large in the case of the Co and Ni complexes, the metal-to-ligand π interaction is energetically much more favorable in these cases than for the Cu and Zn complexes. Yet this π interaction must be weak, because the electronic spectra (and presumably the ligand π orbitals) are not very sensitive to the particular metal ion present. Evidence for this kind of metal \rightarrow ligand π bonding has also been derived from contact shift nmr measurements²⁵ on Ni and Co dipyrromethenes. The added stability afforded by the metal \rightarrow ligand π interactions may thus explain the anomalous position of Co and Ni in the stability order of metalloporphyrins.

The observed intensity differences could, it is true, also arise from other factors. Solid-state effects as such are ruled out by the observation that the 350-cm^{-1} band intensity order is the same in the solid state as in methylene chloride solution. Solution spectra also indicate that solid-state effects are not large in the high-frequency spectra. Molecular structure differences, on the other hand, could lead to differences in the infrared absorption behavior of the metalloporphyrins. The crystal structures²⁶ of a number of metalloporphyrins indicate that some of the porphyrins are planar, while others are more or less ruffled. Structural

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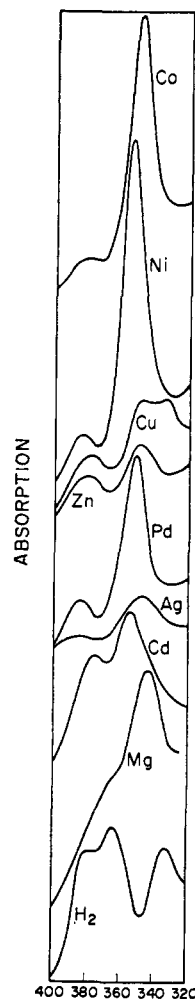


Figure 4. Far-infrared absorption spectra of protoporphyrin IX dimethyl ester compounds in potassium bromide pellets (8 mg/200 mg of KBr).

differences, however, do not appear to parallel the intensity differences reported here. That the presence of axially coordinated ligands may be an important factor is pointed up by the observation that hydrated magnesium porphyrins show a 340-cm^{-1} band of enhanced intensity. Nonetheless, the intensity differences for the metalloporphyrins cannot be explained on this basis, since only Co and Zn tend to add ligands while Cu and Ni do not.¹⁹ The intensity arguments presented here are based on relative peak heights in the solid-state spectra. A more accurate picture of the intensity differences can, of course, be obtained from solution spectra absorption coefficients. Such measurements are now in progress for the protoporphyrin metal complexes.