mechanism of electron transfer involving metalloporphyrins.

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Registry No. Fe(*m*-CN)TPPCl, 64413-49-6; Fe(*p*-CN)TPPCl, 19570-49-1; Fe(*p*-$COOCH_3$)TPPCl, 64413-48-5; Fe(*p*-COOH)-TPPCl, 55266-17-6; Fe(*m*-Br)TPPCl, 64413-47-4; Fe(*m*-Cl)TPPCl, 64413-46-3; Fe(*m*-F)TPPCl, 64413-45-2; Fe(*m*-$OCH_2C_6H_5$)TPPCl, 64413-44-1; Fe(*p*-Br)TPPCl, 64413-43-0; Fe(*p*-Cl)TPPCl, 36965-70-5; Fe(*p*-F)TPPCl, 60250-86-4; Fe(*p*-C_6H_5)TPPCl, 64413-55-4; FeTPPCl, 16456-81-8; Fe(*m*-CH_3)TPPCl, 52155-49-4; Fe(*p*-CH_3)TPPCl, 19496-18-5; Fe(*p*-$C(CH_3)_3$)TPPCl, 64413-51-0; Fe(*p*-OCH_3)TPPCl, 36995-20-7; Fe(*p*-OH)TPPCl, 64413-57-6; Fe(*p*-$OCM_2C_6H_5$)TPPCl, 64413-56-5; H_2(*m*-CN)TPP, 64397-83-7; H_2(*m*-F)TPP, 50800-86-7; H_2(*m*-$OCH_2C_6H_5$)TPP, 64397-82-6; H_2TPP, 917-23-7; H_2(*m*-CH_3)TPP, 50849-45-1.

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Infrared Spectra of *N*-Methyltetraphenylporphyrin Complexes (1600–200 cm^{-1})[1]

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The infrared spectra of chloro-*N*-methyltetraphenylporphinato complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) as well as *N*-methyltetraphenylporphinatophenylmercury(II) are reported in the region 1600–200 cm^{-1}. Comparisons with infrared spectra of nonmethylated porphyrins in "metal-sensitive" regions near 1000 and 600–200 cm^{-1} indicate that the metal–ligand interactions are more similar among the *N*-CH_3TPP complexes than among corresponding series of nonmethylated porphyrin complexes. Use of the mass effect of *N*-CD_3TPP in comparing the spectra of ClCo-*N*-CH_3TPP, ClCo-*N*-CD_3TPP, and CoTPP allows assignment of peaks in spectra of *N*-CH_3TPP and TPP complexes which have significant C–N components. A comparison of the spectra of BrCo-*N*-CH_3TPP and ClCo-*N*-CH_3TPP allows assignment of metal–halide stretching bands. These bands occur, in cm^{-1}, at 314 (Cl–Mn), 332 (Cl–Fe), 318 (Cl–Co), 257 (Br–Co), 300 (Cl–Ni), 264 (Br–Ni), 313 (Cl–^{64}Zn), 309 (Cl–^{68}Zn), and 292 (Cl–Cd). The softening effect of the porphyrin ligand found for nonmethylated porphyrins (e.g., ν(Cl–Mn) at 271 cm^{-1} for ClMnTPP) is not evident for *N*-CH_3TPP complexes. With the exception of the Cl–Mn stretch, only very small shifts (<1 cm^{-1}) are evident in a comparison of the spectra of Cl^{64}Zn-*N*-CH_3TPP and Cl^{68}Zn-*N*-CH_3TPP. These shifts are smaller than those for ^{64}ZnTPP and ^{68}ZnTPP, indicating greater ionic character of the zinc–porphyrin bonding.

Introduction

In the systematic study of *N*-methylporphyrin complexes,[2–8] we have sought to make comparisons of properties of these species with corresponding nonmethylated porphyrin complexes. Like the nonmethylated porphyrins, *N*-methylporphyrins form complexes with a large variety of metal ions. Unlike the case of planar porphyrins, however, are the (1) tendency for the metal ion to form high-spin rather than low-spin complexes and (2) greater stability of some metal ions (e.g., Co(II) and Mn(II)) to oxidation in the *N*-methylporphyrin complex.[4] *N*-Methylporphyrin complexes may be converted to the corresponding nonmethylated porphyrin complex by a variety of nucleophiles.[3,8,11] This reaction is remarkably sensitive to the metal ion employed.

Structural analysis via x-ray diffraction is being undertaken for several complexes in order to understand the structural similarities and differences between *N*-alkyl and nonalkylated porphyrins.[6,7] Due to the size of these species, and the time and high cost involved in such investigations, however, the number of complexes which can be studied in this way is limited. Hence, infrared spectra are being used for the purpose of structural comparison. The spectra of a number of complexes of *N*-methyltetraphenylporphyrin (*N*-CH_3TPP) are reported herein. This species was chosen because of the

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simplicity of the substituents (only meso phenyl groups) on the porphine ring system and the ease of preparation of the ligand and complexes.

The points emphasized in this report are the following: (1) comparisons which can be made between assignments for porphyrin complexes, based on a normal-coordinate analysis,[9] empirical assignments for tetraphenylporphyrin complexes,[10] and the bands found for N-CH_3TPP and N-CD_3TPP complexes; (2) the effect of various metal ions on the so-called "metal-sensitive" bands, especially near 1000 cm^{-1} and in the 400–200-cm^{-1} region; and (3) the metal–halide stretches near 300 cm^{-1}.

The deuteration of the N-methyl group gives rise to a mass effect which allows assignment of bands involving the N-methyl nitrogen atom. Since the bands of the N-methylporphyrin complexes are very close in energy and intensity to those of corresponding nonmethylated complexes, the assignments for N-methylporphyrin complexes are used to make assignments for the nonmethylated complexes. Comparison is then made with previous assignments. The "metal-sensitive" bands are used to investigate whether or not complexes of N-methylporphyrin exhibit more similar metal–ligand interactions than a corresponding series of nonmethylated porphyrins. The metal–halide stretches are used to investigate direct metal–halide bonding vs. ion-pair formation and to see if the N-methylporphyrin ligand exhibits the "softening" effect postulated for nonmethylated porphyrins.

Experimental Section

Preparation of the Complexes. Preparation and characterization of the N-CH_3TPP ligand,[2] chloromanganese(II),[5] chlorozinc(II),[5] chlorocobalt(II),[2] chlorocopper(II),[11] and chloronickel(II)[8] complexes have been reported previously. BrCo-N-CH_3TPP was prepared like ClCo-N-CH_3TPP and characterized by visible–UV spectroscopy. The chlorocadmium(II) complex was prepared in a similar manner, with the following analysis (Bernhardt, West Germany): Calcd for $ClCdC_{45}H_{31}N_4$: C, 69.69; H, 4.03; N, 7.22; Cl, 4.57. Found: C, 69.94; H, 4.27; N, 7.08; Cl, 4.44. $FeCl_2$ was synthesized from anhydrous $FeCl_3$ and iron wire in dry THF for the preparation of the chloroiron(II) complex, which, in turn, was synthesized under inert atmosphere. In the solid state, ClFe-N-CH_3TPP is air stable. The magnetic susceptibility of the product is that expected for high-spin Fe(II) (5.4 ± 0.1 μ_B at 298 °C using the Faraday method) and the absorption spectrum is very much like other N-CH_3TPP complexes of 2+ metal ions.[5] Anal. Calcd for $ClFeC_{45}H_{31}N_4$: C, 75.17; H, 4.35; N, 7.79; Cl, 4.93. Found: C, 75.18; H, 4.39; N, 7.91; Cl, 4.85.

The phenylmercury(II) complex was prepared from phenylmercury nitrate (Alfa-Ventron) and recrystallized from CH_2Cl_2/CH_3CN. The proton NMR spectrum verified the formula of the complex. The visible–UV spectrum of this complex is easily distinguished from the spectrum of the free ligand or protonated N-CH_3TPP species and is unchanged by the addition of noncoordinating bases such as 2,6-lutidine.

N-CD_3TPP was prepared from CD_3FSO_3 (Aldrich) and TPP and chromatographed on alumina.[2] The ClCo-N-CD_3TPP complex was then prepared from a fivefold excess of $CoCl_2 \cdot 2H_2O$ in CH_3CN added to an equal volume of CH_2Cl_2 containing 100 mg of N-CD_3TPP and 100 μL of 2,6-lutidine. The complex was recrystallized twice from CH_2Cl_2/CH_3CN and gave a visible–UV spectrum identical with that of an analyzed sample of ClCo-N-CH_3TPP.

Tetraphenylporphinatozinc(II) was prepared by the method of Adler et al.[12] from $ZnCl_2$ and TPP in dimethylformamide and verified by its UV–visible spectrum.[13] NiTPP and CuTPP were prepared similarly.

Infrared Spectra. For the Mn(II), Fe(II), Co(II), Cd(II), and Hg(II), complexes of N-CH_3TPP, 1.25% dispersions in CsI (Alfa-Ventron, 99.9%) pellets were prepared. The TPP complexes were 0.90–1.00% dispersions in CsI.

Upon pressing pellets of ClNi-N-CH_3TPP and ClCu-N-CH_3TPP, the corresponding TPP complexes, NiTPP and CuTPP, were obtained as evidenced by the dramatic green to orange color change (verified by dissolving the porphyrin with benzene and recording the visible–UV spectrum). For these complexes, CH_2Cl_2 solutions were rapidly evaporated on polyethylene film. Spectra were obtained in segments. The samples were then dissolved from the polyethylene film and tested for demethylation from visible–UV spectra. Solution spectra of the Cu(II) complex (1% by weight) were also taken in CH_3CN and CH_2Cl_2 using 2-mm polyethylene cells in reference and sample beams.

Table I. Some Infrared Absorption Bands for N-Methyltetraphenylporphyrin Complexes (1600–200 cm^{-1})[a]

ClMn	Rel absorbbance[b]	ClFe	Rel absorbbance[b]	ClCo	Rel absorbbance[b]
1596	0.27	1596.5	0.31	1596.5	0.27
1457	0.29	1462	0.22	1468	0.24
1440.5	0.59	1441.5	0.59	1441	0.59
1401.5	0.18	1403	0.13	1405.5	0.14
1348	0.18	1352	0.11	1353	0.16
1335	0.12	1333	0.04	1329	0.12
1188	0.43	1188	0.19	1186	0.41
1178	0.24	1175.5	0.24	1178	0.29
1082	0.18	1080	0.17	1082	0.18
1073	0.31	1072	0.37	1074	0.49
1004	1.00	1002	1.00	1005	1.00
1000	0.90	999	1.28	999	0.63
987	0.88	991	0.73	987	0.43
		986	0.84		
958	0.10	960	0.04	965	0.08
796	1.00	798	0.91	797	1.08
755	0.63	754	0.57	756	0.57
715	0.85	716	0.70	715	0.90
699	0.21	669	0.15	669	0.21
513	0.11	515	0.09	515	0.12
314	0.20	332	0.17	318	0.20
255	0.04	255	0.05	255	0.05
231	0.03	231	0.03	232	0.03
214	0.02	214	0.02	214	0.02
205.5	0.02	205.5	0.02	205.5	0.02

[a] Some of the more intense peaks. A complete listing, including peak positions for ClNi(II), ClCu(II), ClZn(II), ClCd(II), phenylmercury(II) and the free ligand is available as supplementary material. [b] Relative to the absorbance of the "metal-sensitive" peak near 1005 cm^{-1}.

A Beckman Instrument 180 spectrometer was used for this study. The sample compartment was flushed continuously with dry, CO_2-purged air, and background due to H_2O or CO_2 was negligible. Spectra were recorded at 2.5 cm^{-1}/cm with 10-cm^{-1} markers (and at 0.15 cm^{-1}/cm with 1-cm^{-1} markers for ^{64}Zn and ^{68}Zn complexes) to obtain accurate peak positions. Spectra were obtained in the absorbance mode. Positions are specified as the midpoint at half-height. Relative absorbances are given as the peak height minus baseline with deconvolution for overlapping peaks.

Results

The peaks in the region from 3000 to 2000 cm^{-1} are weak and are very similar for these complexes. A complete list of the absorption bands for N-methyltetraphenylporphyrin complexes in the 1600–200-cm^{-1} region is available as supplementary material. The relative absorbances for the chloromanganese(II), chloroiron(II), and chlorocobalt(II) complexes are tabulated therein for comparison. Table I lists a few peaks with relative absorbance that are illustrative of the complete data set. A perusal of these data shows that relative intensities are quite similar with notable exceptions of the peaks at 1188, 1002, 999, and 987 cm^{-1}. The nature of these peaks will be addressed in the Discussion section.

Data for BrCo-N-CH_3TPP are very similar to these reported for ClCo-N-CH_3TPP with the significant exception of the band at 318 cm^{-1} which shifts to 257 cm^{-1} upon replacement of chloride by bromide. This shift establishes the assignment of the metal–halide stretch.

The data for the deuterated complex, ClCo-N-CD_3TPP, are not reported in Table I since they are so similar to the data for ClCo-N-CH_3TPP. A complete listing of the peaks which are found for ClCo-N-CH_3TPP complexes but not CoTPP or which are significantly shifted are reported as supplementary

Table II. Comparison of Infrared Spectra of Tetraphenylporphinatocobalt(II) and Chloro-*N*-methyltetraphenylporphinatocobalt(II) (1600–750 cm^{-1})[a]

Peak positions, cm^{-1}		Assignments		
ClCo-*N*-CH$_3$TPP	CoTPP	Thomas and Martell[b]	Ogoshi et al.[c]	This work
1542 w	1541 w	–C=C pyrrole	$\nu(C_p'{-}N)$, $(C_p{-}C_p)$	$(C_p{-}C_p)$ of three pyrroles since intensity is lowered in *N*-CH$_3$TPP complex
1485 w–m				$(C_p{-}C_p)$ unique pyrrole
1406 w				$C_p{-}H$
1353 w	1350 s	=C–N stretch	$\delta(C_p{-}H)$	$\delta(C_p{-}H)$, three pyrroles
1329 w				$\delta(C_p{-}H)$, unique pyrrole
1252 vw				Some $(C_p{-}N)$
1186 m				δ(Cp–H), unique pyrrole
1178 m	1177 m		$\delta(C_p{-}H)$	$\delta(C_p{-}H)$, three pyrroles
1074 s	1072 m		$\delta(CCN)$, $\nu(C_p'{-}N)$ $\nu(C_p{-}C_m)$	Pyrrole, some $(C_p'{-}N)$
1031 w	1050 vw			
1019 vw	1020 m	C–H rock pyrrole	$\delta(C_p{-}H)$, $\nu(C_p{-}C_p)$	Metal sensitive, not much $(C_p'{-}N)$
1005 vs	1005 vs			
999 vs	997 s		$\nu(C_p{-}C_p')$, $\nu(C_p'{-}N)$	
987 s				Also $\nu(C_p{-}C_p')$, $\nu(C_p'{-}N)$
863 vw				Some $(C_p'{-}N)$
756 s	751 s	Monosubstituted phenyl	π(ring deformation)	Ring deformation

[a] Complete listing is available as supplementary information. [b] Reference 10. [c] Reference 9, for porphine complexes, not TPP complexes.

material. The peaks for the values listed for CoTPP in Table II were obtained by Thomas and Martell,[10] who based assignments on simpler chelates, changes of TPP bands on complexation, and comparisons with other meso-substituted porphyrin complexes. The entries from the study of Ogoshi, Saito, and Nakamoto[9] are assignments based on a normal-coordinate analysis of highly symmetric (D_{4h}) porphyrin complexes. The structure of the porphyrin ring system is disturbed very little by phenyl substituents at the meso positions,[14] so that the assignments by Ogoshi et al., except for bands involving significant participation at the meso carbons, may carry over to planar TPP complexes such as CoTPP. The ClCo-*N*-CH$_3$TPP complex has much lower symmetry, possessing only a mirror plane;[6] hence a number of new bands would be expected. Most of the bands found for CoTPP are shifted only slightly in the ClCo-*N*-CH$_3$TPP spectrum.

Assignments for the new peaks (vide infra) are based on the assignments for peaks of similar energy by Ogoshi et al.[9] and the information provided by the spectrum of ClCo-*N*-CD$_3$TPP. Table III lists the peaks which are found in the *N*-methyl complexes but not in CoTPP or which are noticeably shifted and indicates the effect of deuteration of the *N*-methyl group. Using the nomenclature of Ogoshi et al., C_p is the β carbon of the pyrrole, C_p' the α carbon and C_m the meso position carbon which bridges the α-carbon atom of adjacent pyrrole units.

Discussion

Despite the great interest in the structural aspects of metalloporphyrin chemistry,[14,16] few systematic studies of infrared spectra of metalloporphyrin complexes have been reported. In part, this has been due to the complexity of the ligand structure and the resulting difficulty of accurately assigning the infrared absorption bands. In this report of the infrared spectra of *N*-methyltetraphenylporphyrin complexes, the empirical assignments from studies of complexes of porphyrin,[9,17] tetraphenylporphyrin,[10,18] octaethylporphyrin,[9,19,20] protoporphyrin IX dimethyl ester,[21] and hematoporphyrin IX dimethyl ester,[21] as well as the results of the normal-coordinate analysis,[9] will be used for comparison.

Table III. Comparison of Infrared Spectra of ClCo-*N*-CH$_3$TPP and ClCo-*N*-CD$_3$TPP

ClCo-*N*-CH$_3$-TPP	ClCo-*N*-CD$_3$-TPP	Tentative assignment	Comments
1484	1483	$(C_p{-}C_p)$, unique pyrrole	$C_p{-}C_p$ is longer in unique pyrrole[1]
1468	1466	$\nu(C_p'{-}N)$, $\delta(CCN)$	Some effect of substitution, some $(C_p'{-}N)$ included
1416	1408	Some $(C_p'{-}N)$	Large effect of substitution
1406	1406	$\delta(C_p'{-}H)$	Near region calcd by Ogoshi et al.,[9] unaffected by substitution
1329	1329		
1252	1247	Some $(C_p'{-}N)$	Substitution effect
1186	1186	$\delta(C_p{-}H)$, unique pyrrole	In correct region–no substitution effect
1082	1083	Little $(C_p'{-}N)$, probably $(C_p'{-}C_m)$	As above
1072	1062	Some $(C_p'{-}N)$	Large effect of substitution
987	985	Some $(C_p'{-}N)$, $(C_p{-}C_p')$	In agreement with Ogoshi et al.[9]
863	857	Some $(C_p'{-}N)$	Large effect of substitution
756	754	Pyrrole ring def	In agreement with Ogoshi et al., [9] some dependence on substitution
669	647	N–CH$_3$	Only peak with shift close to prediction of mass change

The complexes of *N*-methylporphyrins have been studied for the purpose of elucidating the properties of nonmethylated porphyrins[5,8,22–24] as well as for their intrinsically interesting properties.[2–4,6,7,11,25,26] There are two features of *N*-methyltetraphenylporphyrin complexes which are investigated herein by the use of infrared spectroscopy. The first of these is the comparison of the similarities within a series of *N*-methyltetraphenylporphyrin complexes relative to a series of nonalkylated TPP complexes, with special attention to the "metal-sensitive" bands. In making this comparison, the new peaks found in the spectra of *N*-CH$_3$TPP complexes are assigned and empirical assignments for TPP complexes[10,18] are discussed. Comparison is also made between isotopic shifts of ^{64}Zn and ^{68}Zn complexes of *N*-CH$_3$TPP and TPP. The second feature involves the metal–halide stretching frequencies.

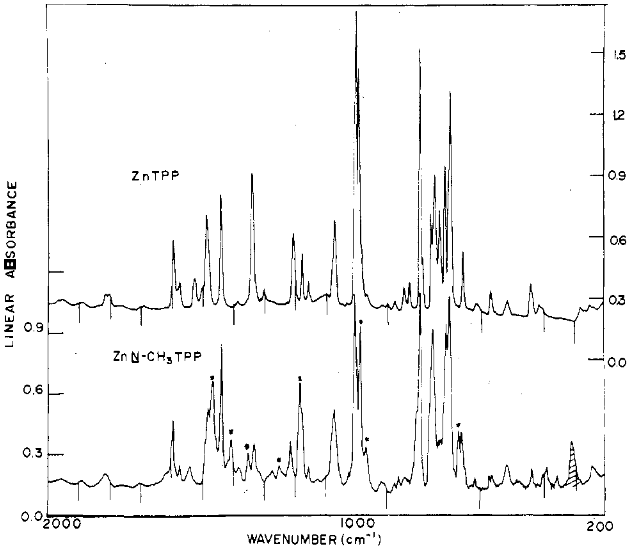

Figure 1. Infrared spectra of tetraphenylporphinatozinc(II) (1.0% in CsI) and chloro-*N*-methyltetraphenylporphinatozinc(II) (1.25% in CsI). The starred peaks on the spectrum of $ClZnNCH_3TPP$ are the new peaks. Shifts in these peaks upon deuteration of the *N*-CH_3 group and tentative assignments are given in Table III.

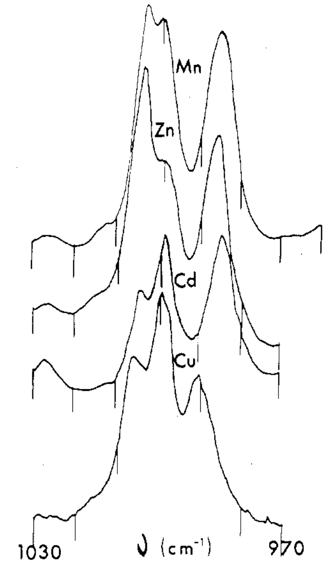

Figure 2. Spectra of several *N*-methyltetraphenylporphyrin complexes in the "metal-sensitive region" near 1000 cm^{-1}. Note the difference in intensity of the peaks near 1005 and 990 cm^{-1} relative to the peak at 999 cm^{-1}.

In this regard, it is interesting that for chloronickel and chlorocopper complexes of *N*-CH_3TPP ion-pair formation between Cl^- and $MNCH_3TPP^+$ has been indicated in demethylation reactions.[11,27]

Assignments. The assignments for new bands found in complexes of *N*-CH_3TPP but not TPP (Figure 1, starred peaks) were aided by deuteration of the *N*-methyl group. Since the effect of deuteration is a mass effect, the greatest shift would be expected for the *N*-CH_3 stretch followed by shifts in bands with a significant component from C_p'–N modes, then perhaps deformation of the unique pyrrole ring. A second general consideration in these assignments is the position of the band. Since large bond length changes in the N-alkylated porphyrin complexes are not found,[6,7,28] the bands should be close in energy to corresponding bands in nonmethylated porphyrin complexes. It should be noted that the best assignment scheme presently available for nonmethylated porphyrins is based on infrared data only[9] and may require some modification to accommodate results of Raman experiments.

The peak of CoTPP found at 1541 cm^{-1} is considerably weaker in ClCo-*N*-CH_3TPP (1542 cm^{-1}). Since the C_p–C_p bond of the unique pyrrole has been found to be somewhat longer in *N*-CH_3TPP complexes,[7] the new peak at 1484 cm^{-1} is assigned to the C_p–C_p stretch in the unique pyrrole. The peak at 1353 cm^{-1} in ClCo-*N*-CH_3TPP corresponds to the peak at 1350 cm^{-1} in CoTPP (Table II). Since this peak does not shift on deuteration, the assignment of this peak as $\delta(C_p{-}H)$ based on the study by Ogoshi et al.[9] is more reasonable than its assignment as a C–N stretch.[10] Due to (1) similar energy, (2) the lower intensity of the 1353-cm^{-1} peak relative to the 1350-cm^{-1} peak of CoTPP, and (3) lack of shift on deuteration, the peak at 1329 cm^{-1} for ClCo-*N*-CH_3TPP is assigned to $\delta(C_p{-}H)$ of the unique pyrrole. Most of the other empirical assignments made by Thomas and Martell are consistent with Ogoshi's assignments and are consistent with our results. An exception is the strong peak at 756 cm^{-1} in ClCo-*N*-CH_3TPP (751 cm^{-1} in CoTPP), which changes on deuteration and is, therefore, more consistent with ring deformation than phenyl ring vibration.

Metal-Sensitive Bands. Three regions of the infrared spectra of metalloporphyrin have been discussed as indicators of the strength of metal–ligand interactions. The first of these regions to be discussed lies near 1000 cm^{-1}. Boucher and Katz[21] reported metal-sensitive bands near this region (927–970 cm^{-1}) for protoporphyrin IX dimethyl ester and hematoporphyrin IX dimethyl ester. For complexes more closely related to *N*-CH_3TPP, namely those of TPP, Thomas and Martell noted that the strong band near 1000 cm^{-1} is found at progressively higher energies in a series of metal complexes which are increasingly more stable to metal ion removal (the porphyrin stability order).[29] The values determined for chloro complexes of *N*-CH_3TPP (in cm^{-1}) are the following: 1005 (Co(II)), 1006 (Zn(II)), 1005 (Cd(II)), 1004 (Mn(II)), 1007 (Ni(II)), 1007 (Cu(II)), 1002 (Fe(II)), and 1005 for the phenylmercury(II) complex. The BrCo-*N*-CH_3TPP and ClCo-*N*-CH_3TPP peaks are also at 1005 cm^{-1}. This region is shown for several of these complexes in Figure 2. For TPP complexes, the values are 1005 (Co(II)),[10] 998 (Zn(II)), 996 (Cd(II)), 1007 (Mn(II)), 1007 (Ni(II)),[10] 1004 (Cu(II)),[10] 1014 (Pd(II)),[10] and 1019 (Pt(II)).[10] This band was assigned as the C–H rock (pyrrole) by Thomas and Martell and a strong band of similar energy in porphine complexes was assigned as a combination of the C–H rock and C_p–C_p stretch by Ogoshi et al. Since this band for the *N*-CH_3TPP complexes is not shifted by deuteration, little C_p–N contribution is evidenced. Hence, this band should indicate the differences caused by various metal ions in an indirect way—by their effect on the periphery of the pyrrole units. Various metal ions cause very little change in this band of *N*-CH_3TPP complexes. The changes noted by Thomas and Martell for TPP complexes are much more significant but still correspond to bond length changes that would be too small for verification by crystal structure determination (see ref 9 for a diagram of force constants vs. C–C bond lengths). An indication of the degree of interaction of the metal ion and the porphyrin is available, however, from a consideration of the overall structures of these complexes. Those with the lowest frequency (CdTPP and ZnTPP) are out of plane while those with the highest frequency (PdTPP and PtTPP) are strictly planar. We expect that the structures of the *N*-CH_3TPP complexes are more similar to one another, since the coordination site is less constricted.[6,7,16] Consistent with this notion are the smaller changes in the vibrational spectrum of the porphyrin ligand, as indicated in Table I. It is also interesting that the values for the *N*-CH_3TPP complexes (1005 ± 1 cm^{-1}) are very similar

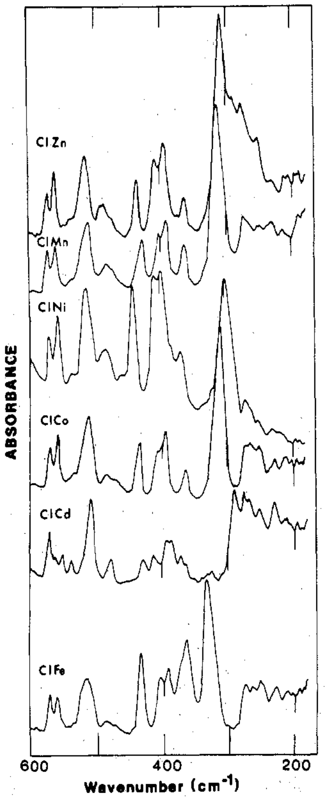

Figure 3. Spectra of several *N*-methyltetraphenylporphyrin complexes in the region 650–180 cm^{-1}. Note the striking similarity for most absorbances except the peak assigned to metal–halide stretching.

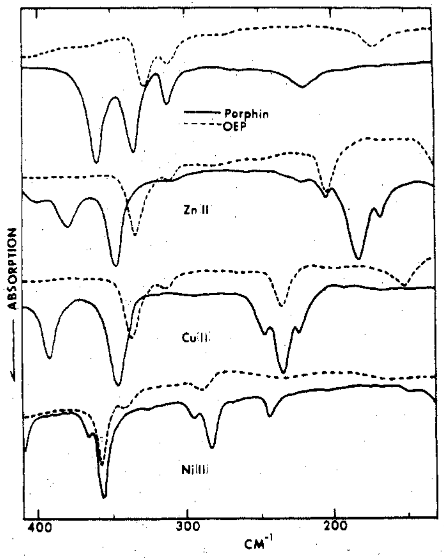

Figure 4. Spectra of complexes of unsubstituted porphine and octaethylporphyrin in the region 400–150 cm^{-1} (reproduced by permission of the *Journal of Chemical Physics*). For these species, large changes in bands associated with M–N stretching are evident.

to those of the in-plane first-row transition series complexes of TPP (Co(II), Ni(II), and Cu(II), average 1005 ± 1 cm^{-1}). The electronic structure, as evidenced from vibrational similarities, of much of the ligand would appear to be very similar for *N*-CH$_3$TPP and TPP complexes. The peak near 985 cm^{-1} that appears in *N*-CH$_3$TPP complexes shows some sensitivity to the metal ion (Table I), but again, the changes are small. There is no obvious correlation between the frequencies of this peak and the peak near 1005 cm^{-1} for the series of complexes studied.

In addition to the bands near 1000 cm^{-1}, bands in two other regions have been found to be metal ion sensitive. In complexes of protoporphyrin IX dimethyl ester and hematoporphyrin IX dimethyl ester, Boucher and Katz[21] found metal-sensitive bands in three regions: 910–920 cm^{-1} (the region noted by Thomas and Martell), the region 525–500 cm^{-1}, and a band near 350 cm^{-1}. Smaller variations occur for the second region than the first and correlation with the metalloporphyrins stability order is poorer. The third region was characterized by intensity changes rather than energy differences.

The normal-coordinate analysis of Ogoshi, Saito, and Nakamoto[9] supports the concept that some high-energy bands are sensitive to metal substitution. In porphine and octaethylporphyrin complexes, they found that bands with δ(C–H) components (1300–1320 cm^{-1}) and ν(C–N) and ν(C–C) components (1520–1550 cm^{-1}) showed metal ion sensitivity. In metal porphine complexes, no peaks appear from 650 to 430 cm^{-1} and the assignments of the 535–500-cm^{-1} peaks found by Boucher and Katz are, therefore, in doubt. Bands with significant ν(M–N) components were determined to be 200–290 and 348–366 cm^{-1} in porphine complexes and 203–287 and 334–355 cm^{-1} in octaethylporphyrin complexes.

Based on these studies, variations caused by metal ions near 1550, 1300, and from 200 to 600 cm^{-1} were compared. Significant differences are evident in bands at 1535–1547 and 1341–1358 cm^{-1} but the relative orders of the energies for various metal ions in these two regions are not similar. The most direct comparison of metal–nitrogen bond strengths occurs in the low-energy regions. Figure 3 shows the infrared spectra for several *N*-CH$_3$TPP complexes in the region from 650 to 180 cm^{-1}. The *intensity* of the band near 561 cm^{-1} of the *N*-CH$_3$TPP complexes is metal sensitive, as found by Boucher and Katz for bands of protoporphyrin and hematoporphyrin complexes in this region. The changes in band positions on the lowest region (200–600 cm^{-1}) for *N*-CH$_3$TPP complexes are scarcely as striking as found by Ogoshi et al.[9] (Figure 4).

A comparison of the isotopic shifts for the ^{64}Zn and ^{68}Zn complexes of *N*-CH$_3$TPP and porphine[9] was made to aid in the assignment of M–N bands. Ogoshi et al. observed shifts of 0.5 cm^{-1} for a band at 348.0 cm^{-1} (^{64}Zn, m) and 3.5 cm^{-1} for a band at 202.8 cm^{-1} (w), both of which were assigned to combination bands including μ(M–N). We observed shifts of 0.65 cm^{-1} for a band at 253.25 cm^{-1} (^{64}Zn, m) and 0.35 cm^{-1} for a band at 205.6 cm^{-1} (w). The smaller magnitude of these shifts may indicate that the metal–nitrogen bond in *N*-CH$_3$TPP complexes is more ionic than corresponding bonds in TPP complexes. The ESR experiment is presently being undertaken with *N*-CH$_3$TPP complexes to examine this question.

Metal–Halide Vibrations. The complexes of *N*-CH$_3$TPP undergo metal ion promoted demethylation in which a nucleophile removes the methyl group.[2,8,11,27] This reaction is strongly dependent on the metal ion; for demethylation by di-*n*-butylamine,[2,8] the second-order rate constants (in M^{-1} s^{-1}) are 0.12 for Cu(II) (65 °C), 8.2 × 10^{-3} for Ni(II) (65 °C), 1.0 × 10^{-4} for Zn(II) (70 °C) and <2 × 10^{-6} for Mn(II) (70 °C). In addition, the mechanisms appear to be different, with demethylation of Cu(II) and Ni(II) complexes occurring by two-path mechanisms involving displacement of the axial ligand.[2,8] These two complexes undergo demethylation in noncoordinating solvents with the axial ligand (e.g., Cl$^-$) acting as nucleophile[11,27] whereas this reaction is suppressed in coordinating solvents,[11] implying that weaker metal–chloride bonding may be a significant feature in ClNi-*N*-CH$_3$TPP and ClCu-*N*-CH$_3$TPP complexes. For this reason, the metal–halide stretching region is of interest.

The metal–halide stretch was identified by comparison of the low-energy region for ClCo-*N*-CH$_3$TPP and BrCo-*N*-CH$_3$TPP. The medium-intensity band which is found near

315 cm^{-1} for most of the chloro complexes is absent in the spectrum of BrCo-*N*-CH_3TPP, while there is greatly increased absorbance at 257 cm^{-1}. The metal–halide stretching frequencies for ClM-*N*-CH_3TPP, in cm^{-1}, are 314 (Cl–Mn), 332 (Cl–Fe), 318 (Cl–Co), 257 (Br–Co), 300 (Cl–Ni), 264 (Br–Ni), 313 (Cl–^{64}Zn), 309 (Cl–^{68}Zn) and 292 (Cl–Cd). The frequency changes from Co–Cl to Co–Br and from Zn–Cl to Cd–Cl are in reasonable agreement with changes found for the tetrahalides[30] 284 ($MnCl_4^{2-}$), 286 ($FeCl_4^{2-}$), 297 ($CoCl_4^{2-}$), 231 ($CoBr_4^{2-}$), 289 ($NiCl_4^{2-}$), 277 ($ZnCl_4^{2-}$), and 260 cm^{-1} ($CdCl_4^{2-}$). The Fe–Cl stretch is of higher energy than the other metal–chloride stretches while the band for this complex in the "metal-sensitive" region near 1000 cm^{-1} is lower than the others. While the Cu–Cl stretches are normally very similar to Co–Cl, Zn–Cl, and Fe–Cl stretches,[30] the region near 315 cm^{-1} is vacant for ClCu-*N*-CH_3TPP for both pellet and solution spectra. Since there is no major band in the normal metal–chloride stretching region for this complex, it is likely that specific interaction between the copper and chlorine atoms is weak or nonexistent. The fact that the nickel complex shows ion-pair behavior in solution similar to that of the copper complex but exhibits a different infrared spectrum demonstrates that the nature of the metal–halide interaction of *N*-methylporphyrin complexes in the solid state can differ from that in solution.

Concerning the metal–chloride stretching frequency, it is interesting to note that the Mn–Cl stretch in ClMnTPP, in which the manganese atom is formally in the 3+ oxidation state, is 271 cm^{-1} (262 cm^{-1} in an earlier report[21]) while in ClMn-*N*-CH_3TPP the manganese atom is formally in the 2+ oxidation state, and the Mn–Cl stretch is at 314 cm^{-1}. It appears that the Mn(III) is significantly "softened" in the TPP complexes but not in the *N*-CH_3TPP complex. This "softening" may contribute to the ease of oxidation of MnTPP to $MnTPP^+$ relative to the oxidation of Mn(II) to Mn(III) in the *N*-CH_3TPP complex.[4]

There are several factors which likely contribute to the loss of the "softening" effect of the porphyrin ligand on N-alkylation. First, the coordination site of the *N*-methylporphyrin ligand is not as restrictive as that of nonalkylated porphyrins[14] allowing bond lengthing without large distortions of the porphyrin ligand. Coordination sites which are small and restricted by being rather rigid lead to a stabilization of higher oxidation states—as demonstrated by Busch et al. for macrocycles of different ring size.[32] Secondly, the metal atom in *N*-methyltetraphenylporphyrin complexes is constrained to be significantly out-of-plane[6,7] which should lead to less overlap of metal atoms and porphyrin orbitals. Third, the charge of the porphyrin ligand (−1) is less than that of the corresponding non-N-alkylated porphyrin ligand (−2), making less excess electron density available to stabilize a higher oxidation state metal atom.

Conclusions

The infrared spectra of a series of *N*-methyltetraphenylporphyrin complexes and chloro-*N*-perdeuteriomethyltetraphenylporphinatocobalt(II) allow an evaluation of empirical assignments for tetraphenylporphyrin complexes. For the most part, the empirical assignments are supported by the new data.

The spectra of *N*-CH_3TPP complexes in the "metal-sensitive" regions of the spectrum are more similar to one another than spectra of corresponding complexes of TPP, protoporphyrin IX dimethyl ester, hematoporphyrin IX dimethyl ester, octaethylporphyrin or porphine. Variation of the metal in *N*-CH_3TPP complexes, therefore, does not appear to cause effects as large as those found in other series of porphyrins. The vibrational spectra of *N*-CH_3TPP are very similar to spectra of TPP complexes with added structure mainly due to the unique pyrrole.

Metal–halide stretching energies of 2+ metal ions in *N*-CH_3TPP complexes are in the normal range of 2+ ions in classical inorganic complexes. The "softening" of the metal ion which has been proposed for TPP complexes[31] is not evident for the metal ions in the *N*-CH_3TPP complexes reported herein. The metal–halide stretch found for the chloronickel(II) complex but not for the chlorocopper(II) complex of *N*-CH_3TPP, coupled with their similar behavior in solution, indicates that the metal–halide interaction of *N*-CH_3TPP can be different in the solid state and in solution.

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Registry No. ClMn-*N*-CH_3TPP, 59765-80-9; ClZn-*N*-CH_3TPP, 59765-81-0; ClCo-*N*-CH_3TPP, 51552-52-4; ClCu-*N*-CH_3TPP, 51552-51-3; ClNi-*N*-CH_3TPP, 64813-95-2; ClCd-*N*-CH_3TPP, 64813-93-0; ClFe-*N*-CH_3TPP, 64813-94-1; ClCo-*N*-CD_3TPP, 64813-98-5; PhHg-*N*-CH_3TPP, 64813-96-3; BrCo-*N*-CH_3TPP, 64813-97-4; CoTPP, 14172-90-8.

Supplementary Material Available: Complete listings of peak positions and relative intensities for *N*-methyltetraphenylporphyrin complexes in the region 1600–200 cm^{-1} and a comparative listing of peaks for the cobalt(II) complexes of *N*-methyltetraphenylporphyrin and tetraphenylporphyrin (9 pages). Ordering information is given on any current masthead page.

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