(R) cannot be made until more quantitative information becomes available from other sources such as electronic and ESR spectra and rigorous MO calculations.

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Registry No. $Ni(S_2C_2H_2)_2$, 19042-52-5; $N(C_2H_5)_4[Ni(S_2C_2H_2)_2]$, 15528-35-5; $Ni(S_2C_2(CF_3)_2)_2$, 18820-78-5; $N(C_2H_5)_4[Ni(S_2C_2(CF_3)_2)_2]$, 15225-60-2; $[N(C_2H_5)_4]_2[Ni(S_2C_2(CF_3)_2)_2]$, 15613-49-7; $Ni(S_2C_2(C_6H_5)_2)_2$, 28984-20-5; $N(C_2H_5)_4[Ni(S_2C_2(C_6H_5)_2)_2]$, 38930-10-8; $(N_2H_5)_2[Ni(S_2C_2(C_6H_5)_2)_2]$, 38883-74-8; $N(C_2H_5)_4[Ni(S_2C_2(CN)_2)_2]$, 15077-50-6; $[N(C_2H_5)_4]_2[Ni(S_2C_2(CN)_2)_2]$, 15665-90-4.

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Infrared Spectra of Metal Complexes of Octaethylchlorine Analogs of Chlorophyll and Heme d

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The infrared spectra of *trans*-octaethylchlorine (OEC) and its divalent metal complexes of the types M(OEC) (M = Zn, Cu, Ni) and $Mg(OEC)(py)_2$ and ferric complexes Fe(OEC)X (X^- = F^-, Cl^-, Br^-, I^-) have been measured from 4000 to 100 cm^{-1}. The M–N(OEC) and Mg–N(py) stretching bands have been assigned based on metal isotope substitution. The similarity of the spectra of OEC complexes and of chlorophylls has been discussed.

Introduction

It has been generally recognized that knowledge of the coordination behavior of the magnesium ion in chlorophyll is important in the understanding of the photosynthetic process. Unfortunately, X-ray analysis has not been carried out because of the difficulty in preparing sufficiently large single crystals of chlorophyll.[1] Thus far, infrared and NMR spectroscopy has provided valuable information about the structural chemistry of chlorophyll.[2,3] For example, Katz and his coworkers have provided spectral evidence to show that the chlorophylls are aggregated in nonpolar solvents and in the solid state.[3] It is of special interest that they have made an empirical assignment of two magnesium–nitrogen stretching vibrations in addition to a peak characteristic of aggregation.[5] Their assignment, however, seems to require more reliable evidence. To this end, we have performed a systematic study on the infrared spectra of *trans*-octaethylchlorine (OEC) complexes.

In this paper, we report definitive assignments of metal–nitrogen stretching frequencies of the divalent metal chlorines based on metal isotope experiments. The infrared spectra of the halide complexes of ferric octaethylchlorine have also been reported and the iron–nitrogen stretching frequencies assigned based on a comparison with the spectra of ferric octaethylporphyrin for which isotope experiments were performed.[6] The iron complex of chlorine (heme d) is also found in some hemoprotein enzymes (cytochrome *cd*) such as "ferrocytochrome:nitrite oxidoreductase", the structure and function of which has not been fully understood as yet.[7] The molecular structure of OEC metal complexes is closely related to chlorophyll except for the fifth isocyclic ring (Figure 1).

Experimental Section

Preparation of Compounds. *trans*-Octaethylchlorine ($OECH_2$) was stereoselectively prepared according to the method of Whitlock et al.[8] The spectral data (visible and NMR) were in good agreement with those reported.[8-12]

$Mg(OEC)(py)_2$. A pyridine solution of $OECH_2$ (100 mg) and anhydrous magnesium perchlorate (200 mg) was sealed in a glass tube and subsequently heated on an oil bath at 100° for 24 hr. The solution was deaerated in a glass tube by a repeated freeze–thaw process under vacuum before sealing. The resulting solution of Mg(OEC) was concentrated to a small volume under vacuum and then poured into 300 ml of ether containing a small amount of pyridine. The ether solution was successively washed several times with equal volumes

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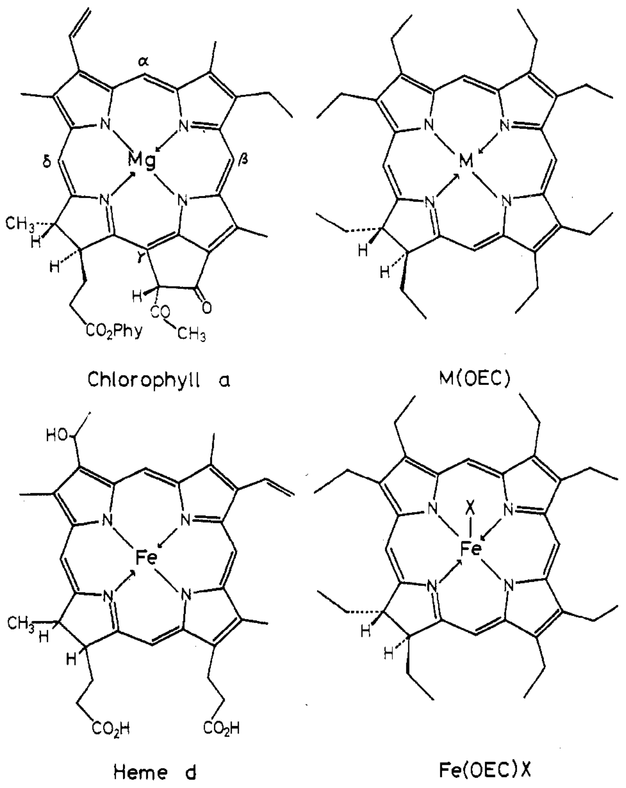
of aqueous K_2CO_3 solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was recrystallized from pyridine–petroleum ether which yielded deep blue microcrystals of $Mg(OEC)(py)_2$ (30 mg). Earlier investigators[12,13] have reported isolations of hydrated magnesium complexes and dipyridinated complexes for related macrocyclic systems. However their structures have been determined based mainly on their microanalysis (C, H, and N). Crystallographic studies have been reported for $Mg(Pc)(py)\cdot H_2O$,[14] $Mg(TPP)\cdot H_2O$,[15] and ethyl chlorophyllide a–2-water.[1] Although accurate analysis of oxygen could not be performed due to the presence of magnesium, we have concluded that the deep blue crystals formulated as $C_{46}H_{56}N_6Mg$ are completely free from water on the basis of the following reasons. (1) No absorption was observed in the OH stretching region either in hexachlorobutadiene mull as is shown in Figure 2 or in chloroform solution. On the contrary, the monohydrated complex $Mg(OEC)\cdot H_2O$[16] showed clearly a medium sharp band at 3505 cm^{-1} with an overlapping broad band at 3510–3200 cm^{-1}, closely similar to those reported for the hydrated chlorophylls.[4] (2) The absorption region and relative intensity of the infrared peaks due to pyridine are quite similar to those observed for $Mg(OEP)(py)_2$[13c] (see Figure 2). The peaks are found at 3120 (3110), 3030 (3050), — (1600), 1487 (1486), 1442 (1442), 1036 (1035), 698 (698), and 627 (627) cm^{-1} (the frequencies in the parentheses indicate those for $Mg(OEP)(py)_2$). (3) In chloroform, this blue Mg–OEC complex was converted completely to $Mg(OEP)(py)_2$ on exposure to air and light. (4) Finally, no signal associated with water protons could be detected in the 220-MHz NMR spectrum in hexadeuteriobenzene as is shown in Figure 3. The spectrum supports our proposed structure $Mg(OEC)(py)_2$: τ 0.02 (s, =CH–, 2 H), 1.16 (s, =CH–, 2 H), 4.75 (m, pyridine γ-H, 2 H), 5.35 (m, $CH_3CH_2C\mathit{H}$, 2 H), 5.65 (m, pyridine β-H, 4 H), 6.07 (m, $CH_3C\mathit{H}_2C$=, 8 H), 6.15 (q, $CH_3C\mathit{H}_2C$=, 4 H), 6.46 (m, pyridine α-H, 4 H), 7.5–8.0 (m, $CH_3C\mathit{H}_2CH$, 4 H), [8.12 (t), 8.14 (t), 8.16 (t) ($C\mathit{H}_3CH_2C$=, 18 H)], 9.12 (t, $C\mathit{H}_3CH_2CH$–, 6 H). The presence of two molecules of pyridine per Mg(OEC) has been confirmed by counting the intensities of pyridine proton peaks. The pyridine protons are shifted to higher field due to the ring current of the aromatic chlorine ring. Their chemical shifts are quite similar to those observed for pyridine-



Chlorophyll a M(OEC)

Heme d Fe(OEC)X

Figure 1. Structures of metallochlorines.

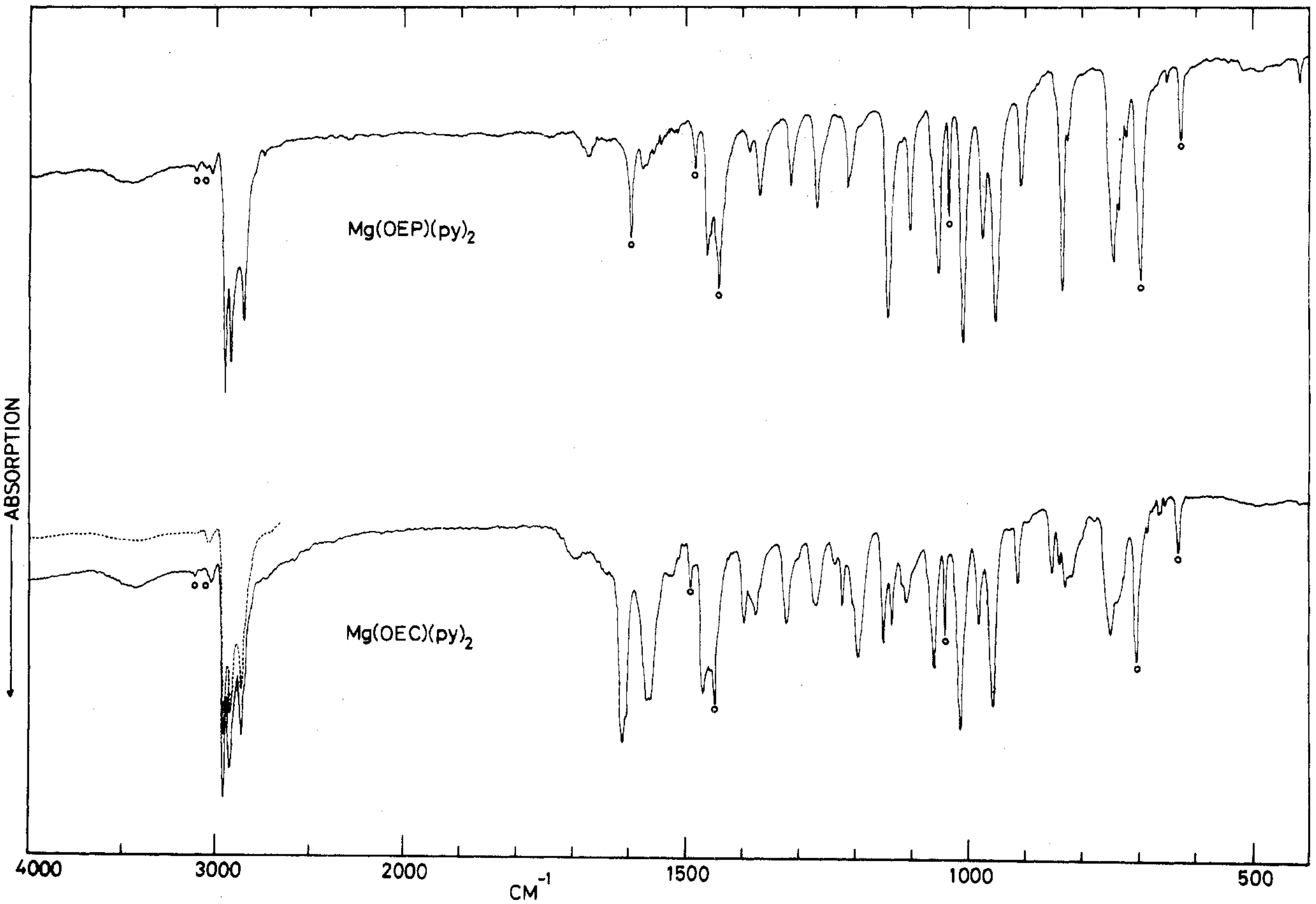


Figure 2. Infrared spectra of $Mg(OEP)(py)_2$ and $Mg(OEC)(py)_2$ (4000–400 cm^{-1}): solid line, in a KBr disk; dashed line, in hexachlorobutadiene mull. The tiny circles indicate the absorptions due to pyridine.

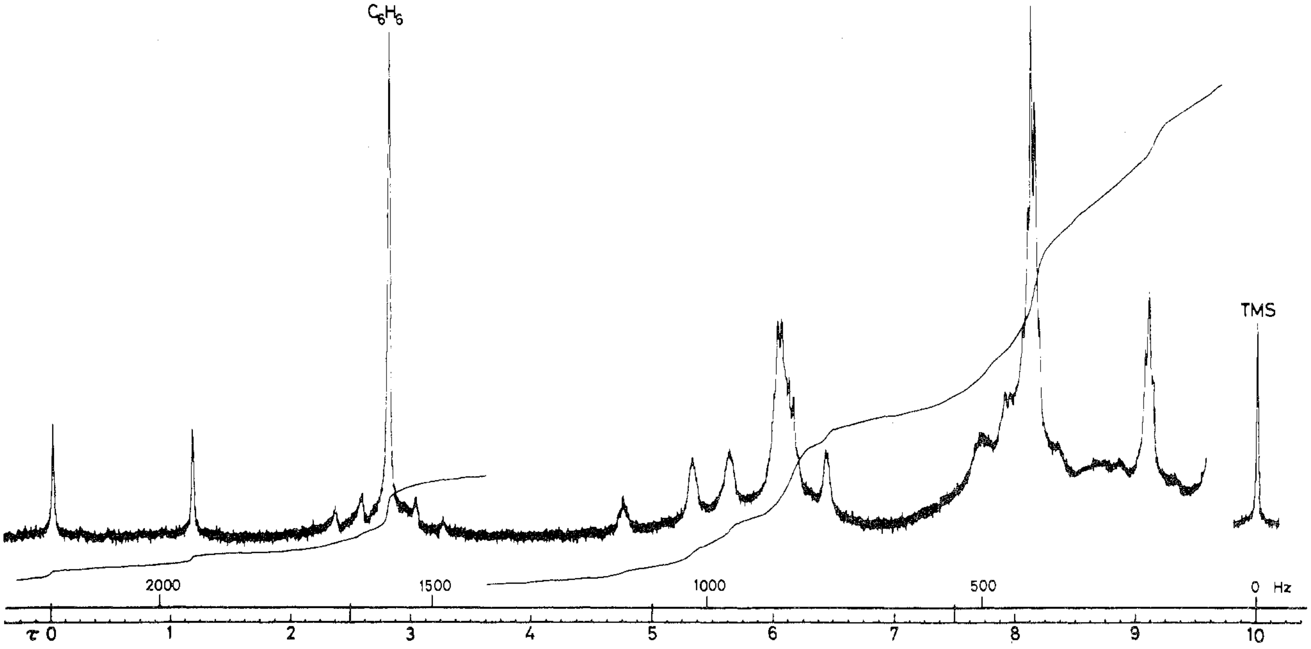


Figure 3. The 220-MHz NMR spectrum of Mg(OEC)$(py)_2$ in hexadeuteriobenzene.

Table I. Results of Microanalysis

Compd	Formula	% C		% H		% N		% X	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Mg(OEC)$(py)_2$	$C_{46}H_{56}N_6Mg$	77.02	77.13	7.87	7.66	11.72	11.42		
Ni(OEC)	$C_{36}H_{46}N_4Ni$	72.85	72.56	7.81	7.94	9.44	9.22		
Cu(OEC)	$C_{36}H_{46}N_4Cu$	72.27	72.22	7.75	7.85	9.36	9.33		
Zn(OEC)	$C_{36}H_{46}N_4Zn$	72.04	72.00	7.73	7.94	9.34	9.09		
$[Fe(OEC)]_2O$	$C_{72}H_{92}N_8OFe_2$	72.22	71.76	7.74	7.74	9.36	9.23		
Fe(OEC)F	$C_{36}H_{46}N_4FFe$	70.94	70.68	7.61	7.32	9.19	8.92	3.12	2.82
Fe(OEC)Br	$C_{36}H_{46}N_4BrFe$	64.58	64.81	6.93	7.18	8.37	8.10	11.94	12.20
Fe(OEC)I	$C_{36}H_{46}N_4IFe$	60.26	60.05	6.46	6.49	7.81	7.76	17.69	17.92

coordinated Mg(Etio II) and Mg(TPP) complexes.[17] From these NMR data and comparison of the ir spectra between Mg(OEC)$(py)_2$ and Mg(OEP)$(py)_2$, it seems most likely that two pyridine molecules coordinate to the Mg atom above and below the chlorinato plane in the solid state. This is confirmed by the presence of a Mg–N(py) stretching band in the far-infrared region (for details, see Discussion).

Ni(OEC). A mixture of $OECH_2$ (200 mg), $Ni(acac)_2 \cdot 4H_2O$ (390 mg), and water-free imidazole (300 mg) was heated at 250° for 10 min under an N_2 stream. After cooling of the mixture to room temperature, the residue was extracted with chloroform and then evaporated to dryness to give crude Ni(OEC). The crude product was chromatographed on Al_2O_3 (Brockman II-III) with benzene. After the solvent was removed, recrystallization from benzene gave a green amorphous solid of Ni(OEC) (75 mg).

Cu(OEC). To 90 mg of $OECH_2$ in boiling benzene was added 50 ml of a methanol solution of copper acetate (100 mg), and the reaction mixture was refluxed for 2 min under N_2. After cooling of the mixture to room temperature, the solution was washed with aqueous ammonia and then successively with small portions of water. The solvent was removed under reduced pressure and the residue was recrystallized from benzene to give small purple crystals of Cu(OEC) (85 mg).

Zn(OEC). To a chloroform solution of $OECH_2$ (100 mg) was added a methanol solution of zinc acetate (110 mg). The solution was stirred at room temperature for 10 min under a nitrogen atmosphere and then evaporated. Recrystallization from methanol afforded purple crystals of Zn(OEC) (60 mg).

$[Fe(OEC)]_2O$. A benzene solution of Fe(OEC)Cl[8] (100 mg) was added to a 15% aqueous solution of NaOH. The reaction mixture was vigorously stirred at room temperature for 2 hr under a stream of nitrogen. The benzene layer was separated, washed with several portions of water, dried over anhydrous sodium sulfate, and evaporated to dryness on a steam bath under reduced pressure. Recrystallization from petroleum ether–methanol gave 70 mg of deep purple crystals. The preparative method is analogous to that reported for the μ-oxo dimers $[Fe(TPP)]_2O$[18] and $[Fe(OEP)]_2O$.[19] The effective magnetic moment per iron is 2.04 BM at 291°K, similar to those reported for $[Fe(salen)(py)]_2O$,[20] $[Fe(salen)]_2O$,[20] and $[Fe(TPP)H_2O]_2O$.[21] A broad Fe–O–Fe stretching band was observed at 855 cm^{-1} in a KBr disk, while a sharp band at 855 cm^{-1} with a shoulder at 870 cm^{-1} of medium intensity was observed in CS_2 solution. These bands are characteristic of the oxo-bridged dimers.[18,21,22]

Fe(OEC)X (X = F, Br, I). A benzene solution of $[Fe(OEC)]_2O$ (100 mg) was added to a saturated aqueous solution of the corresponding potassium halide weakly acidified with sulfuric acid. The reaction mixture was vigorously stirred at room temperature under a nitrogen atmosphere until the μ-oxo complex was converted to Fe(OEC)X. The process of the reaction was monitored by measuring the visible spectrum. The subsequent procedures for purification are the same as described in $[Fe(OEC)]_2O$. Yields of the complexes are 40, 30, and 25 mg for the halide F^-, Br^-, and I^-, respectively. Nearly all the metallochlorines obtained here are unstable in some solvents toward light-induced oxidations as has been reported in the case of tetraphenylchlorine complexes.[9] Among the metallochlorines, the magnesium complex is most unstable. Therefore, care must be taken in handling the complex to protect it from light.

A summary of the analytical data for the metallochlorines is given in Table I. All the complexes show the visible spectra typical of metallochlorines as is shown in Table II.

Complexes Containing Metal Isotopes. Metal isotopes (^{24}Mg, ^{26}Mg, ^{64}Zn, ^{68}Zn, ^{63}Cu, ^{65}Cu) were purchased from Oak Ridge National Laboratory in the form of metal oxides. The purity of each isotope was as follows: ^{24}Mg, 99%; ^{26}Mg, 95%; ^{64}Zn, 99.66%; ^{68}Zn, 98.50%; ^{63}Cu, 99.62%; ^{65}Cu, 99.70%. Anhydrous magnesium perchlorate was obtained by treatment of magnesium oxide with an equimolar amount of 10% perchloric acid and dehydration by heating at 250° under vacuum for 2 hr. Zinc and copper acetates were prepared by the usual procedures. The corresponding metal isotope complexes were prepared by the same procedures described above.

Deuteration of γ and δ Positions of $OECH_2$. γ,δ-Deuterated $OECH_2$ was obtained by treating $OECH_2$ in THF with D_2SO_4–D_2O

Table II. Visible Spectra of the Metallooctaethylchlorine Complexes in Chloroform

Compd	λ_{max}, nm (log ϵ_{max})						
	I	II	III	IV	V	VI	VII
$Mg(OEC)(py)_2$	410 (5.39)	502 (3.59)	544 (3.93)	580 (3.97)	621 (4.33)		
Cu(OEC)	401 (5.31)	496 (3.76)	532 (3.70)	574 (3.94)	617 (4.76)		
Ni(OEC)	399 (4.93)	492 (3.63)	525 (3.60)	576 (3.85)	618 (4.54)		
Zn(OEC)	401 (5.21)	503 (3.70)	537 (3.68)	572 (3.91)	623 (4.47)		
$[Fe(OEC)]_2O$[a]	383 (4.73)	530 (3.67)	571 (3.64)	604 (3.75)	658 (4.04)		
Fe(OEC)F	388 (4.85)	466 (3.88)	500 (3.76)		583 (4.08)	647 (3.49)	725 (3.51)
Fe(OEC)Cl	379 (4.97)	474 (3.88)	507 (3.85)	543 (3.78)	604 (4.18)	700 (3.06)	766 (3.25)
Fe(OEC)Br	381 (4.97)	472 (3.93)	509 (3.87)	564 (3.84)	607 (4.34)	700 (3.14)	772 (3.38)
Fe(OEC)I	382 (4.89)	474 (3.94)	515 (3.89)	567 (3.22)	610 (4.22)	708 (3.10)	800 (3.27)

[a] log ϵ_{max} (per Fe(OEC)) values are listed.

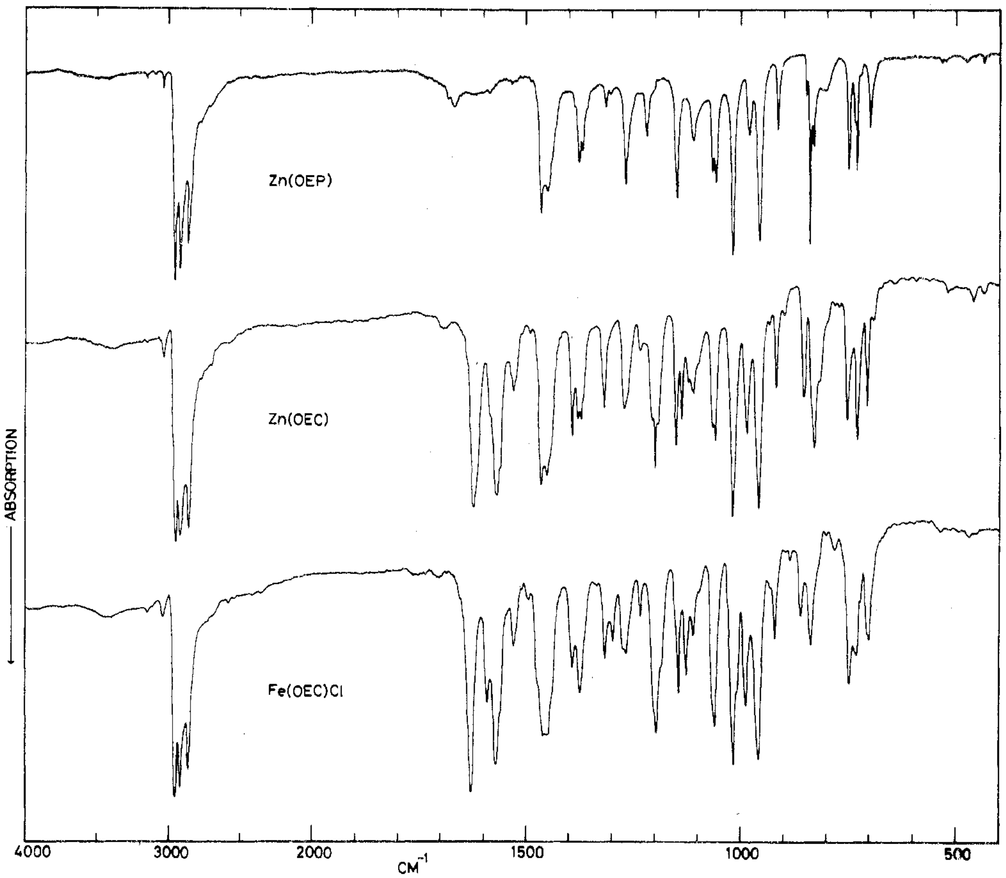


Figure 4. Infrared spectra of OEC–metal complexes (4000–400 cm^{-1}).

(2:1) under a nitrogen atmosphere. Of the two NMR peaks due to meso hydrogens at τ 1.14 (γ-H, δ-H) and 0.13 (α-H, β-H) in the spectrum in $CDCl_3$, the former signal had completely disappeared, indicating that only δ and γ positions were deuterated. This result is in good agreement with that of rhodochlorine dimethyl ester.[23] The ir bands of $OECH_2$ at 3055, 1400, 1300, 1190, 1169, 827, and 815 cm^{-1} are shifted to lower frequencies upon γ and δ deuteration. The bands appearing at 3027, 1392, 1318, 1200, 1190, 829, and 815 cm^{-1} for Zn(OEC) are shifted to lower frequencies by the same deuteration.

Spectral Measurements. The methods employed for the measurements of infrared and far-infrared spectra were identical with those reported previously.[6] Visible spectra were obtained in chloroform using a Hitachi EPS-3T spectrophotometer, and NMR spectra were determined with Varian T 60 and HR 220 instruments. A usual Gouy balance was used for the measurement of magnetic moments.

Results and Discussion

High-Frequency Region (4000–400 cm^{-1}). Representative spectra of metallooctaethylchlorines in KBr together with Zn(OEP) are shown in Figure 4. The infrared spectra of the metallochlorines are similar to those of the corresponding metalloporphyrins except for the appearance of fairly strong absorptions in the 1700–1500-cm^{-1} region.[24] The reduction of one pyrrolic ring of a metalloporphyrin lowers the molecular symmetry from D_{4h} to C_{2v}. Consequently, one expects more infrared bands for metallochlorines than for metalloporphyrins. It is noted that a series of chlorophyll derivatives[2,25] exhibit similar bands in the same region. These bands may be assigned to skeletal (C=C and C=N) vibrations characteristic of the chlorine macrocyclic system. Chlorophyll a, for instance, exhibits these bands at 1597, 1553, 1536, and 1494 cm^{-1}. Corresponding bands for $Mg(OEC)(py)_2$ are observed at 1610, 1575, and 1563 cm^{-1} as are shown in Figure 2. Although these absorptions are essentially due to the chlorine core deformations, they are significantly metal sensitive in the OEC complexes; their frequencies are shifted in the order Zn < Cu < Ni. Several metal-sensitive vibrations with the same order have been reported for the synthetic[24,26–29] and naturally occurring porphyrin complexes[30] and are directly related to the strengths of metal–ligand bonds. Such metal-dependent absorptions appearing in the high-frequency region have never been reported for metallochlorines. If similar arguments are applicable to the chlorine complex, the results indicate that the nature of the inner coordination sphere has a significant

Table III. Far-Infrared Frequencies, Metal Isotope Shifts, and Band Assignments of the Divalent Metal–OEC Complexes (cm^{-1})^a

^{24}Mg(OEC)(py)$_2$	^{64}Zn(OEC)	^{63}Cu(OEC)	Ni(OEC)	Assignment
343.7 (0.8)	334.0 (0.0)	340.5 (0.0)	358	δ(CCN) + ν(CC, CN) + ν(M–N)
326.0 (0.0)	312.5 (0.0)	317.0 (0.0)		
	281.5 (0.0)	290.0 (1.0)	298	
277.0 (2.5)	267.0 (0.0)	276.0 (0.5)	284	
256.0 (0.0)	254.0 (0.0)			
227.5 (5.5)				ν(Mg–N$_{py}$)
176.5 (4.0)	212.0 (1.0)	233.0 (1.6)	256	ν(M–N)
142.0 (3.0)	168.0 (0.5)	168.0 (0.0)		π(ring)

[a] Numbers in parentheses indicate the metal isotope shift: $\tilde{\nu}(^{24}\mathrm{Mg}) - \tilde{\nu}(^{26}\mathrm{Mg})$, $\tilde{\nu}(^{64}\mathrm{Zn}) - \tilde{\nu}(^{68}\mathrm{Zn})$, or $\tilde{\nu}(^{63}\mathrm{Cu}) - \tilde{\nu}(^{65}\mathrm{Cu})$.

effect upon the C=N and C=C bonds in the aromatic chlorine ring. In addition, metal-independent absorptions at 1200, 1190, 829, and 815 cm^{-1} for Zn(OEC) can be assigned to the meso C–H (γ and δ positions) in-plane and out-of-plane bending modes based on our deuteration experiments. In the case of metalloporphyrins, these vibrations are known to be slightly metal dependent.[27]

Magnetic susceptibility measurements were made on the solid Fe(OEC)Cl at 12°. The effective magnetic moment is 5.80 BM which corresponds to the spin-only value for five unpaired electrons, 5.92 BM, and agrees well with the expected value for the spin-free d^5 ferric complex.[31] It is concluded that the remaining halide complexes are also of high spin and the halide is weakly coordinated to iron on the basis of the following reasons. (i) All of the ferric complexes except [Fe(OEC)]$_2$O exhibit two strongly halide-dependent near-infrared transitions of modest intensity (VI and VII in Table II), while the divalent metal complexes do not show these absorptions. Furthermore, these bands disappear completely on addition of an excess of free imidazole. This indicates that imidazole molecules coordinate to iron as a fifth and sixth ligand to form a low-spin ferric complex ($S = 1/2$). It is, therefore, most likely that the bands VI and VII arise from intramolecular CT transitions between the chlorine ligand and ferric ion, characteristic of the high-spin ferric complex. A similar phenomenon has been observed and well characterized for the ferric porphyrin complexes.[32] (ii) The iron–halogen stretching frequencies of Fe(OEC)X are almost the same as those of Fe(OEP)X[6] (vide infra).

The infrared spectra of the Fe(OEC)X complexes in the NaCl region show intense skeletal vibrations as did the Fe(OEP)X complexes. It is of interest to note that these bands did not show any halide dependency in contrast to their metal dependency. Consequently the effect of the axial halide on the chlorine macrocycle via ferric ion seems to be weak. A similar conclusion is reached from visible spectra whose absorption maxima due to the ligand π–π^* transitions do not vary markedly with the axial halide except for the fluoro complex (Table II).

Low-Frequency Region (400–100 cm^{-1}). Divalent Metal Complexes. Figure 5 illustrates the far-infrared spectra of the divalent metal complexes together with those of the free base, Zn(OEP) and Mg(OEP)(py)$_2$. The observed frequencies and their assignments are given in Table III. The spectra show a prominent band common to all the complexes and the free base at around 340 cm^{-1} with a weak satellite in a somewhat lower region. These bands are shifted to higher frequencies upon metal coordination. These bands can be assigned to the chlorine core in-plane CCN$_p$ bending coupled with metal–nitrogen stretching modes in agreement with the results of the normal-coordinate analysis of metalloporphines.[28]

Several bands are observed at 300–250 cm^{-1} which are completely absent in the spectra of the OEP complexes and OEPH$_2$. In the Zn, Cu, and Ni complexes, these absorptions are shifted to higher frequencies (Zn < Cu < Ni) with a decrease in intensity. It seems reasonable to assign these bands to the in-plane core CCN$_p$ bending modes involving the saturated pyrrolic ring. Finally, there is a medium band near 200 cm^{-1} which exhibits significant isotope sensitivity ($\Delta\nu$ = 1–3 cm^{-1}). This band is shifted to higher frequencies with a marked decrease in intensity in the order Zn < Cu < Ni, as has been observed for the porphyrin complexes.[24,28] Thus, these isotope-sensitive bands are assigned to the metal–nitrogen (OEC) stretching coupled with a core in-plane bending mode. For Mg(OEC)(py)$_2$, the isotope-sensitive peaks of moderate intensity at 229 and 180 cm^{-1} are safely assigned to magnesium–nitrogen (pyridine) and magnesium–nitrogen (OEC) stretching modes, respectively. The assignment of the former at the higher frequency is in agreement with the trend observed in a series of six-coordinate Fe(III) complexes of octaethylporphyrin in which the iron–nitrogen (imidazole, benzimidazole, etc.) stretching occurred at a higher frequency than the iron–nitrogen (OEP) stretching vibration.[6] Furthermore, the six-coordinate magnesium species would be expected to exhibit a metal–nitrogen (OEC) stretch at a lower frequency than the four-coordinate Zn(OEC). The presence of a single metal–nitrogen stretching band in the spectra of all divalent metal complexes can be accounted for by assuming an approximately planar MN$_4$ skeleton. It is noted that recent X-ray analyses have shown a marked difference in the diagonal N···N distance in the case of the macrocyclic compounds with an isocyclic ring such as MePPb,[33] VO–DPEP,[34] and Ni–DPE.[35] (Abbreviations: MePPb, methyl pheorphorbide a; DPEP, deoxophylloerythroetioporphyrin; DPE, deoxophylloerythrin methyl ester.) This difference has been attributed to the added strain of the fifth isocyclic ring. For OEC complexes, the saturated bond in the pyrrole ring is possibly another cause of deformation of the chlorine central core. However, the difference in the four M–N distances, even if it exists, would be too small to be distinguished in the far-infrared spectra.

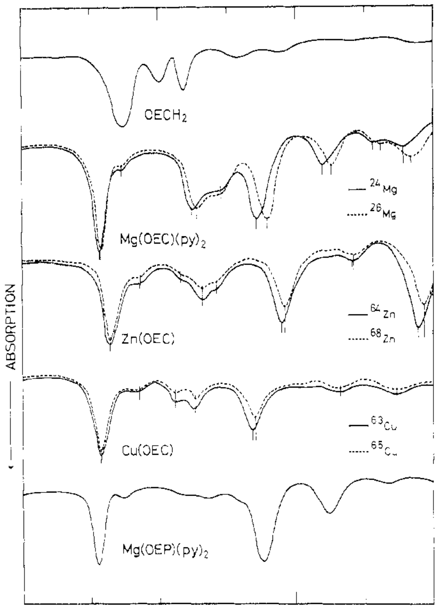


Figure 5. Far-infrared spectra of divalent metal octaethylchlorines.

Previously, Boucher et al.[5] have observed strong absorption bands at 292–296 and 195–196 cm^{-1} in the spectra of monomeric chlorophyll derivatives in pyridine–cyclohexane which were attributed to magnesium–nitrogen stretching somewhat coupled with ring vibrations. It is clear from our studies that the former band is not predominantly Mg–N(chlorine) stretching but rather a ring deformation slightly coupled with

Table IV. Far-Infrared Frequencies and Band Assignments of the Fe(OEC)X Type Complexes (cm^{-1})

Fe(OEC)F	Fe(OEC)Cl	Fe(OEC)Br	Fe(OEC)I	Assignment
589 (605.5)[a]	352 (357)[a]	270 (270)[a]	240.5 (246)[a]	ν(Fe-X)
346	*c*	354	353	δ(CCN) + ν(CC, CN) + ν(M-N)
339.5	352[b]	345	340	
327	*c*	331	330.5	
310	*c*	310	309	
268	261	270[b]	278	ν(M-N)[d]
259	*c*	*c*	268	
229	228	229	229	π(ring)
140	140	130	136	

[a] Numbers in parentheses indicate the Fe-X stretching vibration of Fe(OEP)X. [b] Overlapped band. [c] Hidden band. [d] Overlapped by ring deformation modes. For details, see Discussion.

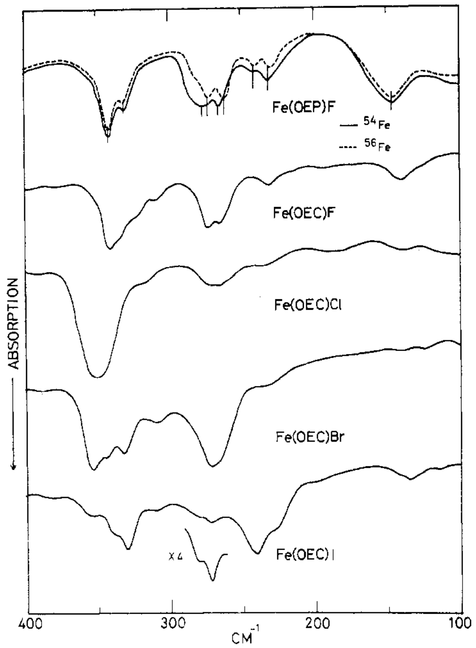


Figure 6. Far-infrared spectra of Fe(OEC)X.

Mg–N stretching, consistent with its dependency on full deuterium substitution.[5] The latter is mainly due to the Mg–N stretching vibration which corresponds to the isotope-sensitive band at 180 cm^{-1} of $\mathrm{Mg(OEC)(py)_2}$.

In addition, aggregated chlorophyll shows a new strong band at 310 cm^{-1} instead of the peak at 290 cm^{-1} of the monomeric state. This peak has been considered to involve predominantly magnesium–nitrogen and magnesium–carbonyl oxygen stretching modes. However, it seems most likely from the above results that this is an in-plane deformation of the metallochlorine rather than the Mg–N stretching vibration. The relatively large shift (ca. 20 cm^{-1}) in going from the monomeric to polymeric state may be understood in terms of the change in the central coordination sphere of the aggregated complexes. Intermolecular interaction via magnesium–oxygen bonding results in displacement of the Mg atom from the basal chlorinato plane. This out-of-plane deviation of the magnesium atom upon coordination of the axial ligand may affect the electronic structure of the chlorinato core and Mg–N bonding. Such a situation is generally inferred from X-ray studies on $\mathrm{Mg(TPP)(H_2O)}$,[15] $\mathrm{MgPc(H_2O)(py)_2}$,[14] and MePPb[33] and from MO calculations.[36] It is expected that, when the Mg atom is in a similar environment, the aggregated chlorophyll will show two ir-active Mg–N stretching modes (A_1 and E for C_{4v} geometry). It was found that the aggregated chlorophylls a and b exhibit clearly resolved doublets at ca. 190 and 205 cm^{-1}, respectively.[5]

Ferric Complexes. Figure 6 illustrates the spectra of the Fe(OEC)X series together with that of Fe(OEP)F. Table IV lists the observed frequencies and band assignments. In contrast to the nearly identical spectra in the high-frequency region, the low-frequency spectra are characteristic of each complex. The most prominent absorptions appearing in the 600–100-cm^{-1} region are listed in the first row of Table IV. These absorptions do not appear in the spectra of the divalent metal complexes. The corresponding bands of Fe(OEP)X appear at slightly higher frequencies as compared with those of Fe(OEC)X. As has been discussed in the previous section, the bands at 350–300 cm^{-1} observed for all ferric chlorine complexes can be associated with in-plane core bending modes.

Previously, we found it possible to distinguish high-spin from low-spin structures for the Fe–OEP complexes since the former exhibits a doublet at 270 cm^{-1} whereas the latter exhibits a single absorption at 310 cm^{-1}.[6] Unfortunately, the remaining bands in the 290–200-cm^{-1} region do not show good resolution probably because of the overlapping of the core bending of the chlorine macrocycle with the Fe–Br (ca. 270 cm^{-1}) or Fe–I (240 cm^{-1}) stretching band. However, a doublet is clearly observed at ~260 and ~270 cm^{-1} for $\mathrm{F^-}$ and $\mathrm{I^-}$, respectively. These Fe–N(porphine core) stretching frequencies are the same as those of iron–nitrogen stretching of ferric porphyrin in the high-spin state. This fact as well as magnetic susceptibility data leads us to conclude that all the halogeno–ferric–octaethylchlorine complexes are of high spin and that the iron atom is in a square-pyramidal environment as is observed for the high-spin ferric porphyrins.[37]

Registry No. $\mathrm{Mg(OEC)(py)_2}$, 54643-19-5; Cu(OEC), 54676-27-6; Ni(OEC), 54676-28-7; Zn(OEC), 54676-29-8; $\mathrm{[Fe(OEC)]_2O}$, 54643-20-8; Fe(OEC)F, 54643-21-9; Fe(OEC)Cl, 54643-22-0; Fe(OEC)Br, 54643-23-1; Fe(OEC)I, 54643-24-2; $\mathrm{Mg(OEP)(py)_2}$, 41114-30-1; Zn(OEP), 17632-18-7; $\mathrm{Mg(OEC){\cdot}H_2O}$, 54643-25-3.

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Studies on the Thermal Rearrangements of Chlorophosphacarboranes. Molecular and Crystal Structure of 9,10-Dichlorophosphacarborane

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Thermal rearrangement at 450° of 12-chloro-1,2-phosphacarborane gave almost exclusively 9(10)-chloro-1,7-phosphacarborane as the product. The molecular and crystal structure of 9,10-dichloro-1,7-phosphacarborane (9,10-Cl_2-1,7-$CHPB_{10}H_8$) has been determined. This compound crystallizes in the space group $P2_1/n$. Unit cell parameters are $a = 7.216$ (2) Å, $b = 12.468$ (4) Å, $c = 12.008$ (3) Å, and $\beta = 93.34$ (2)°, with four molecules per unit cell. Intensity data were collected on a Picker FACS-1 diffractometer. The structure was solved by the conventional heavy-atom method. The final value of $R_F = \sum|k|F_o| - |F_c||/\sum k|F_o|$ is 0.081 for 1342 independent X-ray diffraction maxima. The chlorine substitutions at the 9 and 10 positions are confirmed. As expected, the phosphorus atom is found to introduce significant distortion in the icosahedral structure. The six 1,7- and two 1,12-monochlorophosphacarborane isomers are isolated and their rearrangements at 550° studied. Identifications of these isomers are based on the above structure determination, the respective VPC retention times, point group symmetries, and ^{11}B NMR. The initial, intermediate, as well as final yields of these rearrangements suggest a marked shift from the predominantly cuboctahedral rearrangement suggested by previous experiments on halocarboranes to one which may involve the rotation of pentagonal pyramids. Other alternative but less plausible mechanisms cannot yet be excluded.

Studies on the thermal rearrangements of both mono- and dihalocarboranes[1-3] of the icosahedral type have so far quite consistently supported the original proposal of a cuboctahedral intermediate,[4] including allowance for rotation of triangular faces in the cuboctahedron.[1-3] The other two major pathways that have been proposed involve either the rotation of a triangular face[5] of the icosahedron or, as proposed by Hawthorne,[6] the mutual rotation of two pentagonal pyramids of the icosahedron (Figure 1). Neither has been found to occur to any significant extent in the rearrangements of icosahedral carboranes.

Of the numerous isoelectronic analogs of the carborane(12) family, the phosphacarborane, $CHPB_{10}H_{10}$, in which a CH group has been replaced by an unsubstituted P atom (having an external lone pair) is a close relative. Its numbering scheme is shown in Figure 2, where the C atom is in the 1 position and the P atom is at the 2, 7, and 12 positions, respectively, in the three possible isomers. The asymmetry results in the possible existence of six 1,2-, six 1,7-, and two 1,12-$CHPB_{10}H_9X$ isomers. We therefore thought it might be interesting to study internal rearrangements similar to those of halocarboranes but with the possibility of subtle to drastic changes in the preferred mechanism caused by the presence of P as a heteroatom.

Experimental Section

Synthesis and Isolation of the Isomers. The $CHPB_{10}H_9Cl$ isomers were prepared by known procedures,[7] and 1,7-$CCH_3PB_{10}H_{10}$ was made by Todd's method.[8] Isolation of individual isomers was achieved by TLC on E&M precoated silica gel plates and preparative VPC on an F&M 720 temperature-programmed gas chromatograph: a $^1/_4$ in. × 8 ft Carbowax 20-M column operating between 175 and 225° was used for the final isolation. The 9,10-Cl_2-1,7-$CHPB_{10}H_8$ was prepared both from direct electrophilic chlorination of 1,7-$CHPB_{10}H_{10}$ and from electrophilic chlorination of isomer H (vide infra). It was purified by sublimation and recrystallization from *n*-heptane.

Thermal Rearrangements. Samples of about 5 mg of each isomer were sealed under vacuum in Pyrex tubes of about 5-ml volume. These were then placed in a muffle furnace set at the desired temperature. They were removed and quickly cooled after appropriate periods. Isomerization products were analyzed on a $^1/_8$ in. × 8 ft Carbowax 20-M column operating from 125 to 225°. Due to the large number of overlapping peaks, the peak areas were estimated by weighing the