The Infrared Spectra of Metallooctaethylporphyrins[1]

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The infrared spectra of the Mg(II), Co(II), Cu(II), Zn(II), Pd(II), Ni(II), and Ge(IV)Cl_2 complexes of octaethylporphyrins have been studied over the range 4000—100 cm^{-1}. Metal sensitive bands have been observed at about 980, 920, 340, 230, and 130 cm^{-1}.

The metalloporphyrins constitute a large number of biologically important compounds. The wide range of biological activity is due in part to the nature of the interaction of the central metal atom with the porphyrine nucleus. Infrared spectroscopy provides one means by which the nature of metal-ligand interactions can be studied. Previous investigators have reported the infrared spectra of a number of naturally occurring porphyrins and chlorophylls.[2,3] We report here the results of an infrared investigation of the metal complexes of the symmetrical porphyrin, octaethylporphyrin (OEP).

Experimental

The preparation of the OEP complexes of Mg(II), Ni(II), Zn(II), Pd(II), Co(II), and Cu(II) have already been reported in the literature.[4,5] However, no micro analyses have been given for the Ni(II) and Pd(II) complexes.

Ni(II)-OEP. The Ni(II) complex was prepared by the treatment of OEP[6] with nickel acetate in glacial acetic acid.[7] Chromatography on alumina (neutral, activity II—III, Brockman) gave dark red crystals. Found: C, 73.78; H, 7,74; N, 8.91%. Calcd for $C_{36}H_{44}N_4Ni$: C, 73.10; H, 7.50; N, 9.47%.

Pd(II)-OED. The Pd(II) complex was prepared from 101 mg of OEP and 103 mg of $PdCl_2$ using the method of Theorell.[8] The NMR gave $\tau=8.08$ (24H, triplet, $-CH_2\underline{CH_3}$, $J=8.0$), $\tau=5.82$ (16H, quartet, $-\underline{CH_2}CH_3$, $J=7.2$) $\tau=-0.20$ (4H, singlet, -CH=).

Found: C, 66.29; H, 6.87; N, 8.32%. Calcd for $C_{36}H_{44}N_4Pd$: C, 67.65; H, 6.94; N, 8.77%.

Ge(IV)-OEP Dichloride. This complex was prepared from OEP and $GeCl_4$ in quinoline.[9] Purification was accomplished by chromatography of alumina using 3 : 1 benzene-chloroform mixture.

Found: C, 63.81; H, 6.56; N, 8.08%. Calcd for $C_{36}H_{44}N_4GeCl_2$: C, 63.94; H, 6.56; N, 8.28%.

Spectral Measurement. The infrared spectra were recorded on a Beckman IR 12 (4000—400 cm^{-1}, KBr pellet) and a Hitachi-Perkin-Elmer FIS-3 (400—100 cm^{-1}, Nujol mull). The UV spectra and NMR spectra were obtained by using a Hitachi EPS-3T spectrophotometer and a Jeolco JNM SH-60 spectrometer, respectively.

Results and Discussion

The observed frequencies of free OEP and its metal complexes are given in Table 1. All the OEP complexes show three weak absorptions above 3000 cm^{-1} which can be assigned to the C–H methine streching vibrations.[10,11] The three strong bands at about 2960, 2940 and 2870 cm^{-1} can be assigned to the C–H stretching vibrations of the ethyl group. Since the strong band at 2960 was very weak in the octamethylporphyrin complexes,[12] it can be attributed to the CH_2 stretching vibration. Free OEP also shows a medium band at 3320 cm^{-1} which is assigned to the N–H strecthing mode. This band disappears in the porphyrin complexes.[2,10]

As has been reported for etioporphyrin II[2,11] three medium to weak bands were observed at about 1670, 1600 and 1560 cm^{-1} and are assigned to the C=C and C=N stretching modes. The four bands at 1470, 1450, 1380, and 1370 cm^{-1} are probably due to the CH_2 asymmetric deformation and the CH_3 asymmetric and symmetric deformation vibrations. In general, the spectra of metal complexes are simpler than those of the free ligand in the region from 1500 to 1000 cm^{-1}. This is probably due to the fact that the symmetry of a metal complex is higher than that of the free ligand. For example, a weak band at 1412 cm^{-1} of OEP disappears on coordination to a metal. The two strong absorptions at 1268 and 1147 cm^{-1} are assigned tentatively to in-plane ring vibrations.[2,13] The latter is much stronger in the metal complex than in the free ligand. The two medium peaks at *ca.* 1150 and 1110 cm^{-1} are probably due to the ring deformation and CH in-plane bending mode of the pyrrole hydrogen, respectively. The bands at 1065 and 1057 cm^{-1} seem to be associated with the in-plane deformation of the porphyrin ring. The strong

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TABLE 1. OBSERVED FREQUENCIES OF METAL OEP COMPLEXES (cm^{-1})

Mg	Zn	Cu	Co	Ni	Pd	$GeCl_2$	OEP	Assignment
							3320	ν (N–H)
3132vw	3157vw	3195vw	3215vw	3185w	3185vw	3192w		
3175vw	3095vw	3123vw			3120vw	3150vw		ν (C–H)$_m$
3038vw	3045vw	3055w	3060w	3075w	3055w	3060w		
						3040w		
2965s	2962s	2965s	2955s	2965s	2965s	2965s	2970s	
2932s	2930s	2935s	2920s	2935s	2932s	2932s	2938s	ν (C–H)$_e$
2868s	2872s	2875s	2855s	2872s	2870s	2977s	2875s	
1708m		1720w	1715w					
1670m	1676w	1675w	1677m	1670w	1682m	1680m	1685w	
1604w		1602w	1615w	1618w	1608w	1621w	1675m	ν (C=C)
1580w	1580vw	1550w	1565w	1570w	1550m	1597w	1607m	ν (C=N)
	1532vw					1570w		
1467s	1467s	1478w	1465s	1467s	1469s	1501m	1503w	
		1465s				1480m	1469s	
1453s	1454s	1452s	1451s	1453s	1448s	1467s	1450s	δ (CH_2)
						1451s	1412w	δ (CH_3)
1390w	1378m	1381m	1381m	1385m	1382m	1386w	1397w	
1372m	1370m	1370m	1370m	1372m	1371m	1375m	1370m	
1317w	1317w	1317w	1316w	1318w	1318m	1320m	1317m	
	1303vw	1308vw	1306w	1309vw	1306w			
1268m	1268s	1271s	1271s	1272s	1273s	1272m	1277w	
							1260w	ring def.
1217m	1220m	1223m	1228m	1229m	1229m	1223m	1232w	
							1218m	
							1187m	
1148s	1147s	1148s	1147m	1147m	1152s	1152s	1147m	ring def.
							1140m	
1109m	1110m	1113m	1112m	1113m	1113m	1113m	1113s	δ (C–H)$_p$
1063sh	1064m	1066m	1064m	1064m	1064sh	1070s		
1057s	1057s	1058s	1057s	1054m	1055s	1057s	1057s	ring def.
1014s	1016s	1018s	1019s	1018s	1019s	1022s	1014s	ρ_t (C_2H_5)
							1003m	
977m	980m	985m	990m	992m	993m	990s	975w	ring. edf.
955s	953s	954s	955s	954s	958s	962	950s	ρ_r (C_2H_5)
911m	912m	919m	921w	923w	923w	920m		
	847w	846w	847sh	845sh		869w	892m	ν (C–C)$_e$
834s	836s	837s	837s	837s	839s	843m		π (C–H)$_m$
827s	827m	830s	830s	830s	835sh	809m	820m	ν (C–C)$_e$
746s	748m	750m	753m	754m	745s	787m	745s	π (ring)
						751m		
731m	730sh	730m	733m	732m	734m	730m		
	728m	717w	715w	713w	720m	707m	720m	π (ring)
703m	700m	697m	697m	700m	700w		698m	
						676m	675m	
						630m	667sh	
						613m	615w	
						607m	572	
	530w	535w				525w	512w	
	515w	520w					490w	
495vw	475vw	475vw	477vw	475wv	487w	480m	475w	
	400	443					447w	
347sh						375w		
336s	334s	336s	351s	355s	348s	348s	328m	ν (M–N)+ligand
	310w	313w			320w		320—310	
						306s	(w,br)	ν (Ge–Cl)
214s	203m	234m	264m	287w	275vw	245w		ν (M–N)
129s,b	121s	152w	157w			131w	159w	

(C–H)$_m$, methine hydrogen; (C–H)$_e$, ethyl hydrogen; (C–H)$_p$, pyrrole hydrogen; ν, stretching; δ; in-plane bending; π, out-of-plane bending; ρ_t, twisting; ρ_r, rocking

TABLE 2. METAL SENSITIVE BANDS AND ELECTRONIC SPECTRA

Metal	Frequency (cm^{-1})					$\lambda_{\max}$ (mμ) (log $\varepsilon_{\max}$)[c]		
						α	β	Soret
Mg	977[a]	911[a]	336[b]	214[b]	129[b]	582 (4.01),	544 (4.11),	410 (5.45)
Zn	980	912	334	203	121	570 (4.18),	533 (4.05),	402 (5.32)
Cu	985	919	336	234	152	562 (4.40),	526 (4.11),	399 (5.88)
Co	990	921	351	264	157	554 (4.29),	521 (3.99),	392 (5.14)
Ni	992	923	355	287	—	554 (4.39),	519 (3.99),	394 (5.24)
Pd	993	923	348	275	—	547 (4.48),	511 (4.00),	394 (5.19)

a) KBr pellet, b) Nujol mull, c) in $CHCl_3$

band at 1016 cm^{-1} is probably due to the CH_2 twisting vibration of the ethyl group which is slightly sensitive to the metal ion. In fact, it is absent in the spectra of Cu(II)-porphin[10] The increase in absorption intensity of 1016 cm^{-1} may be attributed to the coupling with the in-plane ring deformation vibration at 980 cm^{-1}.

Metal sensitive bands are usually observed near 1000 cm^{-1} in various types of metalloporphyrins.[2,14] OEP complexes show three bands at about 980, 955, and 912 cm^{-1}; the 980 and 912 bands are dependent on the nature of the metal (see Table 2). This metal ion dependence is not as large as that observed for proto- and hematoporphyrin dimethyl esters[2] and is of a comparable magnitude to that observed for tetraphenylporphyrin complexes.[14] The 955 and 912 cm^{-1} bands do not appear in the spectra of Cu(II)-porphyrin.[10] These two bands may therefore be assigned to the rocking vibrations of the ethyl groups. The 980 and 912 cm^{-1} bands shift to higher frequencies in the order Pd$\approx$Ni$>$Co$>$Cu$>$Zn$>$Mg which is the same order as observed for the hypsochromic shift of the α, β, and soret bands in the electronic spectra (Table 2). Free OEP also shows bands in this region at 975, 950, and 892 cm^{-1}. The 980 cm^{-1} band may be due to a ring deformation vibration involving the motion of a metal atom. The metal dependence of the 912 cm^{-1} band may indicate that this ethyl rocking mode couples strongly with the in-plane deformation vibration of the porphyrin ring.

The strong bands at about 835 cm^{-1} are assigned to the CH out-of-plane deformation vibration of the methine group.[15] The bands at about 848 and 830 cm^{-1} are possibly assigned to the C–C streching of the ethyl group. Several strong bands are observed at about 750, 730, and 700 cm^{-1}. A similar set of bands has been observed for Cu-porphyrin.[10] Consequently, these bands may be assigned to the out-of-plane deformation of the porphyrin ring. The weak bands which occur in the 650—400 cm^{-1} range are difficult to assign empirically.

Far-Infrared Spectra. The metal nitrogen streching vibrations in metalloporphyrins are expected to appear in the far-infrared region. Free OEP shows weak bands at 328 and 320—310 cm^{-1}. The former band shifts to higher frequencies and becomes stronger by complex formation. It may be due to a ligand vibration coupled slightly with a metal-nitrogen stretching mode. The Ni, Co, and Pd complexes exhibit the highest frequencies at 355, 351, and 348 cm^{-1}, respectively, (Table 2), indicating that the metal-nitrogen bond is stronger in the Ni, Co, and Pd than in the Mg and Zn complexes.

In the 300—200 cm^{-1} region, medium to weak bands have been observed for metal complexes but not for free OEP ligand. The frequency of this band is most sensitive to the nature of the metal and increases in the order Zn$<$Mg$<$Cu$<$Co$<$Pd$<$Ni. This band may due to a relatively pure metal-nitrogen streching vibraration. However, the exact nature of this vibration cannot be determined without normal coordinate analysis. It is interesting to note that the frequency order of these metal-sensitive bands in a series of metal ions studied is similar to that found for the electronic transitions in the UV region (Table 2). The stronger coordination in metalloporphyrins causes the shift of the α, β, and soret bands to the shorter wave length.[16] This would be attributed to the stabilization in the ground state through π-conjugative interaction between $2p\pi$-orbitals of the ligand and d-orbitals of the metal ion.[16,17]

Finally, OEP–$GeCl_2$ exhibits the Ge–Cl stretching mode at 360 cm^{-1}. This frequency is similar to that reported for the $GeCl_6^{2-}$ ion (293 cm^{-1}).[18]

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