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THE INFRARED SPECTRA OF METALLOTETRANAPHTYLPORPHYRINS

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ABSTRACT

The infrared spectra of some metallic complexes of tetranaphtylporphyrins [Me(II) TNP (Me(II) = Mg, Zn, Co, Cu, Cd, Pb, Pd, Ni) and Me(III) TNP X(X2).(Me(III)=Fe,Mn,Co,Al; X=Cl, Imidazole)], have been studied over the range 4000-200 cm^{-1}. The main bands have been assigned in this paper. The correlation between the metal-nitrogen or metal-axial ligand frequencies and the photostability for all these porphyrins hase also been analysed in this paper.

RESUMO

O espectro de alguns complexos metálicos de tetranaftil-porfirinas (Me(II) TNP, (Me(II) = Mg, Zn, Co, Cu, Cd, Pb, Pd, Ni) e Me(III) TNP $X(X_2)$, Me(III) = Fe, Mn, Co, Al; X = Cl, Imidazol) foi estudada na região infravermelha entre 4000 cm^{-1} 200 cm^{-1}. As bandas importamtes foram atribuidas. As correlações entre as frêquencias metal-nitrogênio e metal-ligante axial e a foto-estabilidade de estas porfirinas foram analisadas.

Keywords : Porphyrins, metalloporphyrins, IR spectra, tetranaphtylporphyrins

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INTRODUCTION

The metalloporphyrins are one of the most important biological class of compounds [1]. The wide range of biological activity is due, in part, to the nature of the interaction of the central atom with the porphyrin nucleus.

The IR spectroscopy can provide some information about the nature of metal-ligand interactions [2-8].

In this paper, the infrared frequencies for some metallo-tetranaphtylporphyrins, prepared and studied for the first time in the literature, are presented.

It is anticipated that low frequency infrared spectra will provide valuable information about the structure of the complex, the strength of the metal-ligand bonds and the photostability of the metallotetranaphtylporphyrins analysed.

EXPERIMENTAL PROCEDURE

1.Materials

The preparation and the purification of TNP and TNP-Zn(II), have been reported in the literature [9]. The other metallic complexes of TNP, have been prepared for the first time in the literature and have been reported elsewhere [5, 10-12].

2.Spectral Measurements

Infrared spectra were measured on a Specord M 80, Carl Zeiss Jena type spectrophotometer, using either the KBr pellets technique (for the 4000-300 cm^{-1} region) or CCl4 solution technique (for the 4000-200 cm^{-1} region) or the Nujoll pellets technique (for the 400-200 cm^{-1} region).

UV-Vis spectra for the porphyrins were measured on a Specord M 400, Carl Zeiss Jena spectrophotometer, in benzene solutions.

RESULTS AND DISCUSSION.

A typical absorption spectrum in the IR region ,e.g.for tetranaphtylporphyrine, (TNP), is given in Figure 1.

As we know, for free base porphyrins,the main frecquency is located in 3400-3600 cm^{-1} region and it is atributed to inner N-H bond vibrations[25].

The main absorption frequencies in the IR domain of free TNP and of its metallic complexes are given in Table 1.

The spectra of free porphyrin bases and metalloporphyrins of the same ligand differ considerably, the latter generally exhibiting less and sharper infrared absorptions due to their higher symmetry [13]. The differences are more pronounced for the vibrations of the porphyrin skeleton than fot the inner vibrations of the peripheral substituents. They are most obvious in the far infrared where the M-N vibrations of metalloporphyrins are located. These cannot be considered to be isolated, since they are coupled with skeletal bending modes (Table 1).

All the TNP complexes show three weak absorptions above 3000 cm $^{-1}$ which can be assigned to the C-H methine stretching vibrations.

Porphyrins exhibit only weak infrared absorptions between 1700 and 1470 cm^{-1} . The low infrared intensity of these vibrations is obviously due to the highly symmetrical macrocycle of metal complex than that of the free ligand, [13-20].

Hydrogenation of the pyrole ring (⇨chlorins) causes the appearance of a strong infrared absorption close to 1600 cm $^{-1}$ (chlorine band). These absorptions arise from the activation of a porphyrin vibration which is forbidden or weak in the infrared under D4h symmetry, [21-28].

Chlorine bands are of particular analytical value. Table 2 summarizes some experimental data.

For many types of metallo-porphyrins, there are metal sensitive bands near 1000

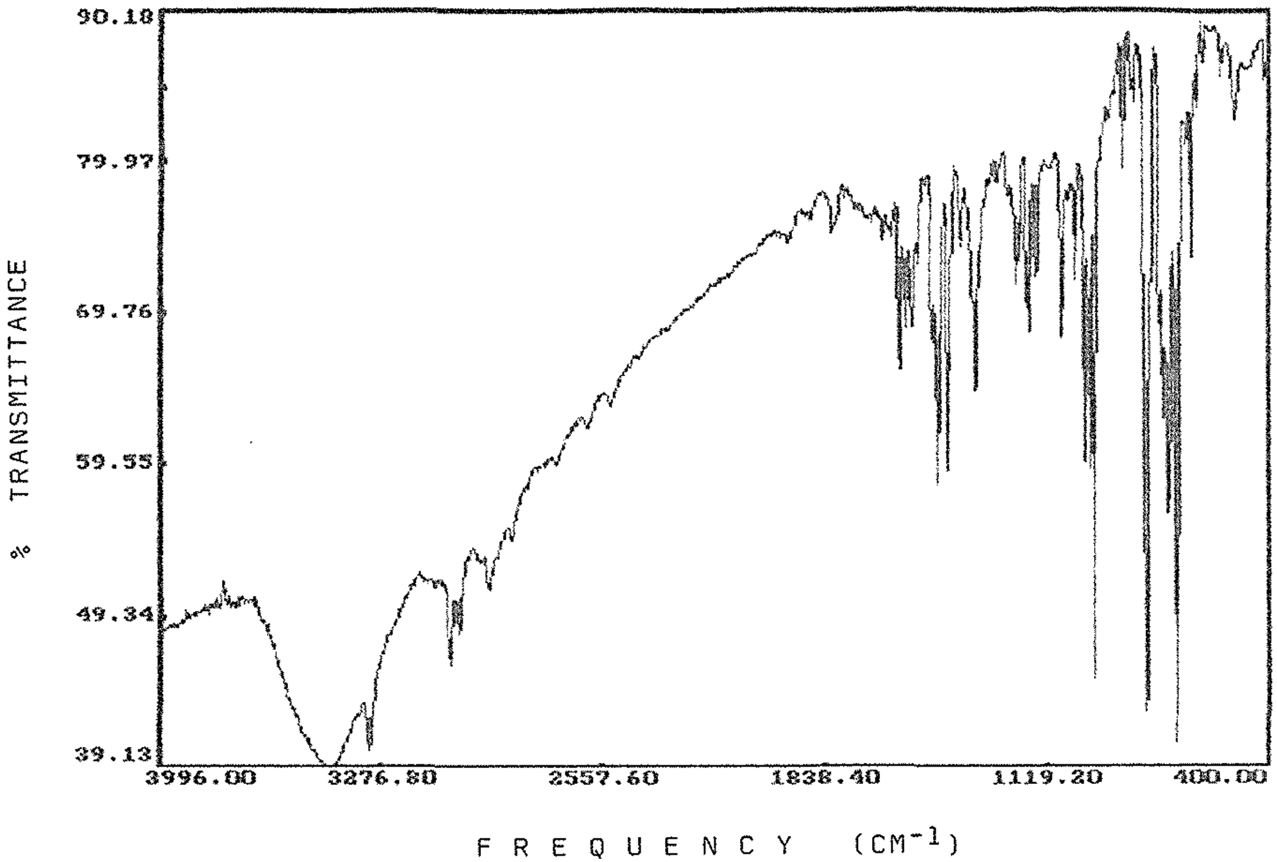

Figure 1. The IR absorption spectrum of TNP

Table 1. Observed frequencies of metallotetranaphtylporphyrins (cm^{-1}):

TNP	Mg	Zn	Pd	Pb	Cd	Co	Cu	Ni	Assignment
3320									ν (N-H)
3110	3120	3185	3160	3130	3130	3140	3150	3160	ν (C-H)methine
3030	3040	3030	3065	3062	3060	3060	3060	3062	ν (C-H)phenyl
3060	2975	2940	3015	3000	3020	2095	3010	2965	
2930	2940	2925	2935	2930	2930	2922	2925	2930	
2850	2860	2860	2860	2860	2860	2860	2850	2855	
1600	1605	1635	1675	1610	1600	1697	1670	1600	ν (C=C)
1580	1525	1575	1545	1555	1575	1550	1545	1580	ν (C=N)
-	1490	1490	1463	1485	1465	1475	1466	1470	δ (C-H)
-	1447	1450	1445	1455	1445	1430	1425	1435	
-	1160	1150	1160	1160	1155	1160	1160	1165	ring deformation
1075	1070	1068	1065	1067	1070	1070	1070	1075	
985	975	980	990	970	973	980	982	987	ν (C-H)methine
-	975	965	955	940	950	930	950	955	
840	835	830	838	835	830	834	833	837	ring deformation
765	760	780	775	770	752	750	771	772	π(ring)
730	725	710	713	712	715	716	718	716	
-	336	334	348	338	340	351	336	355	ν M-N + Ligand
-	214	223	275	287	210	264	234	275	νM-N

Table 2. The Chlorine bands are as following:

Porphyrin	Frequency[cm^{-1}]
TNP-H_2	1600
TNP-Zn	1635
TNP-Pd	1675
TNP-Ni	1675
TNP-Cu	1670
TNP-Cd	1600
TNP-Mg	1605
TNP-Pb	1610
TNP-Co	1687
TNP-MnCl	1660
TNP-FeCl	1652
TNP-CoCl	1650
TNP-AlCl	1649

cm^{-1} [29-33].

TNP complexes show two bands at about 960 and 980 cm^{-1}, which are dependent on the nature of the metal (Table 1).

We assign these two bands to the rocking vibrations of the CH group. The 960 and 980 cm^{-1} bands shift to higher frequencies in the order, (Table 3) :

$$Pd \sim Ni > Co > Cu > Zn > Pb > Mg > Cd$$

The Me-N stretching vibrations are observed among 200 and 300 cm^{-1}. These vibrations may additionally contribute to a smaller extend of vibrations among 300 and 400 cm^{-1} (see Table 4).

Table 3. The Metal bands in the IR spectra :

Metal	Frequency [cm^{-1}]	
Mg	948	975
Zn	950	980
Cu	952	982
Co	953	985
Ni	955	987
Pd	955	990
Pb	940	976
Cd	946	973
Mn	952	987
Fe	920	978
Co	930	980
Al	930	978

Axially substituted metalloporphyrins have been investigated by IR spectroscopy regarding both characteristics.

Definitely assignable inner-ligand vibrations and metal-ligand vibrations typical examples are quoted in Table 5.

All the specific IR frequencies for metallotetranaphtylporphyrins studied, varies in the same way :

Pd ~ Ni > Co > Cu > Zn > Mg > Cd ,

contrary as vary the photodegradation rate of these porphyrins, and also, the photosensitizer effect of these porphyrins [34].

Table 4. The Metal-Nitrogen vibrations:

Porphyrin	Frequency [cm^{-1}]
TNP-Zn	223
TNP-Mg	214
TNP-Cu	234
TNP-Co	264
TNP-Cd	210
TNP-Pd	275
TNP-Pb	287
TNP-Ni	275

Table 5. The frequencies of the metal- axial ligand bonding:

Porphyrin	Frequency [cm^{-1}]	
TNP-FeCl	280, 290, 305, 330	ν Fe-Cl
TNP-MnCl	310- 330	ν Mn-Cl
TNP-CoCl	300, 364, 402	ν Co-Cl
TNP-AlCl	370, 400	ν Al-C
TNP-FeIm$_2$	335, 370	ν Fe-N
TNP-MnIm$_2$	340, 390	ν Mn-N
TNP-CoIm$_2$	375, 400	ν Co-N
TNP-AlIm$_2$	360. 400	ν Al-N

Conclusions

The specific absorbance frequencies for metallotetranaphtylporphyrins studied, both in the UV-Vis (α, β and Soret bands) and in the low frequency IR spectra (metal-nitrogen and metal-axial ligand bonding) provide valuable information about the strength of the metal-ligand bonds and the photostability of the metallotetranaphtylporphyrins. All this frequencies varyy in the same way, contrary as vary the photodegradation rate and the photosensitizer effect of these copmpounds.

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