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The Formation, Structure, and Properties of the Extracomplexes of Porphyrins

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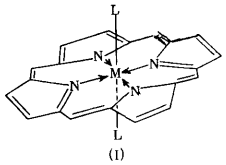
The results of studies on the extracomplexes of metalloporphyrins namely the conditions of their formation, structure, spectroscopy, kinetics, and thermodynamics, are considered.
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I. INTRODUCTION

Extracoordination in metalloporphyrins is one of the most important properties of compounds of this class[1]. Extracoordination is understood as additional coordination by a stable planar complex species (for example, a metalloporphyrin) or ligands occupying the fifth, sixth, etc. coordination sites in the inner coordination sphere of the metal and located above and below the plane of the initial stable complex; this results in the formation of the extracomplex (I)



(I)

If the extraligands in (I), i.e. the additional ligands, add to the fifth and sixth coordination sites along the z axis perpendicular to the plane of the molecule of the complex, the resulting complex has come to be referred to in coordination chemistry as an axial complex and the ligands are referred to as axial ligands. Numerous extracomplexes of porphyrins in which the ligands are not axial have now been obtained; consequently, the concepts of the "extracomplex" and "extracoordination" are wider than those of the "axial complex" and "axial coordination".

Depending on the nature of the metalloporphyrin (MP) and the nature and concentration of the extraligand, monoligand (LMP) or biligand (L_2MP) extracomplexes of metalloporphyrins are formed as a rule:

$$MP + L \rightleftharpoons LMP + L \rightleftharpoons L_2MP. \quad (1)$$

The molecules of water, organic solvents, nitrogen-containing heterocycles, aliphatic and aromatic amines, polypeptides, and proteins are most frequently used as the extraligands, while the acido-ligands are halide, acetate and other carboxylate, CN^-, OH^-, O^{2-}, HO_2^-, etc. ions.

Much attention is being devoted nowadays to experimental and theoretical studies to extracomplexes and the phenomenon of extracoordination to metalloporphyrins. The great interest in the extracomplexes of porphyrins is due to the fact that the most important biological functions of metalloporphyrins such as photosynthesis, the fixation and transport of oxygen by blood haemoglobin, and other enzymatic processes are associated primarily with the extracoordination of H_2O, O_2, H_2O_2, nitrogen-containing heterocycles, proteins, and other molecules. It is most likely that the catalytic activity of MP in both enzyme and chemical catalysis is due to the possibility of the formation of mono- and bi-ligand extracomplexes. Extracoordination ensures that the reacting molecules in the extracomplex are linked to one another. The ready reversibility of the formation of the extracomplex, and the possibility of chemical and photochemical oxidation-reduction reactions involving the complex.

It has been established[2] that chlorophyll strongly coordinates one water molecule to form an aquo-extracomplex. In combination with a protein molecule, which can also be part of the extracomplex, this complex is involved in the first (photophysical) stage of photosynthesis (and possibly also in the photochemical water oxidation stage).

The physical chemistry of extracoordination has been investigated for a long time, starting with the first studies by Williams[3]. However, until the 1970's the majority of the investigations were not systematic. From the 1970's the number of investigations of the extracomplexes of porphyrins (of their structure, spectroscopy, the thermodynamics of their formation, etc.) increased sharply. This review represents an attempt to survey the extensive data on extracomplexes which have accumulated hitherto: the conditions of their formation, structure, spectroscopy, kinetics, and thermodynamics; it deals only with the most fundamental studies.

II. GENERAL PRINCIPLES OF THE FORMATION OF EXTRACOMPLEXES OF METALLOPORPHYRINS

Depending on the strength of the metal–porphyrin coordination interaction, which is determined by the degree of covalence of the N–N dative bonds, i.e. the electronic structure of the porphyrin, the structure and charge of the cation, as well as steric factors, metalloporphyrins can be divided into coordination-saturated and coordination-unsaturated[1]. The former have a 2+ charge on the metal ion and form extremely stable covalent dsp^2-hybrid complexes (Cu^{2+}, Pt^{2+}, Pd^{2+}). Ions forming part of the coordination-saturated MP do not have low-energy non-bonding orbitals; their effective charge is low and they show little tendency to combine with extraligands regardless of the nature of the porphyrin molecule and the solvent. Naturally in the gas phase

the addition of extraligands to them takes place nevertheless[4], because the absolute coordination saturation of atomic-molecular species is virtually impossible. There are data[5] indicating the formation of very unstable monoligand extracomplexes by the porphyrin complexes of copper and nickel in solution.

Coordination-unsaturated porphyrin complexes contain ions which, having a formal 2+ charge, do not tend to undergo dsp^2-hybridisation (Zn^{2+}, Fe^{2+}, Cr^{2+}, Mn^{2+}), have unstable oxidation states (Co^{2+}, Re^{2+}), form predominantly ionic complexes with a weakly neutralised charge (Be^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+}, Ca^{2+}, Ga^{2+}), and all have a formal charge greater than two (Co^{3+}, Ru^{3+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Mn^{3+}, Os^{4+}, Sn^{4+}, Ti^{4+}, VO_2^{2+}, UO_2^{2+}).[1] The subdivision of the central atoms in the MP into two groups—with coordination numbers of 5 and 6—of the kind carried out by Falk[6] cannot be regarded as desirable. The point is that, as a result of the strong saturation of the chemical affinity of the metal by the porphyrin molecule in the case of Mn^{2+} and in addition by the counterion in the case of Mn^{3+} the energy of subsequent coordination of extraligands usually proves to be so low that the degree of the overall extrainteraction cannot be measured and assessed quantitatively by the existing spectroscopic and thermodynamic methods. The nature of the extraligand plays a considerable role in the coordination of extracomplexes; extraligands containing N, O, P, and S atoms, and, as already mentioned, acido-ligands as the electron-donating species are mainly investigated nowadays. The formation of extracomplexes is naturally regulated by the thermodynamics of their formation.

1. Synthesis of Extracomplexes

The synthesis of extracomplexes of porphyrins and phthalocyanines has been described in many studies. The formation of extracomplexes of iron[7-31], cobalt[32-38], manganese[39,40], rhenium and technetium[41-43], rhodium[43-46], ruthenium[43,47,48], iridium[43], osmium[49], chromium[37], yttrium, lutetium, and thorium[50,51], and almost all the lanthanides except cerium and promethium[52] has been studied. Fairly detailed information about the extracomplexes synthesised and isolated in a crystalline state has been given in a review[53].

The formation of anionic extracomplexes of porphyrins, incorporating cations with a charge greater than two, takes place spontaneously in the synthesis of metalloporphyrins from porphyrin (H_2P) and a salt:

$$H_2P + MX_{(n+2)} \rightarrow (X)_nMP + 2HX \qquad (2)$$

($n = 1,2,3,4$; X = any singly charged anion). The anion X can then be substituted by any other anion on treatment of the extracomplex $(X)_nMP$ with solutions of salts or acids[20,36,37,54]. In the presence of water there is a possibility of hydrolysis:

$$MP \quad MP \qquad (3)$$

In many instances there is a possibility of the formation of a μ-oxo-dimer:

$$2OHMP \rightleftharpoons MPO\text{-}MP + H_2O \qquad (4)$$

or an oxo-extracomplex:

$$(OH)_2MP \rightleftharpoons O = MP + H_2O. \qquad (5)$$

Complexes of Al^{3+}, Ga^{3+}, Cr^{3+}, Sn^{4+}, Si^{4+}, and Ge^{4+} are formed readily in reaction (3).[53] Reaction (4) is preferred for Sc^{3+}, Fe^{3+}, and In^{3+}, which is attributed[55] to the ease of displacement of the metal atom from the plane of the porphyrin molecule (see Section III), but the metals in the first list are also capable of forming μ-oxo-dimers. Complexes of Ti^{4+}, V^{4+}, Nb^{5+}, Mo^{5+}, W^{5+}, Re^{5+}, and Os^{6+} are formed via reaction (5).[53]

If a coordination-unsaturated MP and an extraligand are the initial reactants, the extracomplex is formed in a homogeneous phase when solutions of the metalloporphyrin and the extraligand in a weakly coordinating solvent are mixed; the concentration of the extraligand should usually greatly exceed that of the MP. Depending on the nature of the MP and the extraligand, the equilibration time varies from several minutes to several days. The extracomplexes of metalloporphyrins containing a readily oxidisable metal atom are obtained in an inert gas; the solvent is slowly evaporated in order to obtain solid complexes—in some cases *in vacuo*[23,24]. Thus, in order to obtain $L_2Fe^{+}PP$ (H_2PP = protoporphyrin) with a series of substituted imidazoles as the extraligands L, a suspension of protohaemin in a solution of the extraligand is shaken for 50 h.[10] The extracomplexes of iron-phthalocyanine FePc with amines[13], LCoPc, and L_2CoPc (L = pyridine or 4-methylpyridine) have been obtained similarly[32,33].

The extraligand can also be introduced into the complex in a chromatographic process. The presence of water in chromatography on Al_2O_3 or silica gel frequently leads to the substitution of the extraligand or to hydrolysis with subsequent reactions (3), (4), and (5).[53]

The extraligands and solvents employed must be carefully purified. It has been noted[53] that the most suitable solvents are methylene chloride and chloroform, which should be freed from alcohols and hydrochloric acid (otherwise alkoxo- and chloro-extracomplexes are formed). It has been observed[56,57] that *ortho*-substituted pyridines form extracomplexes only in the presence of negligible amounts of sterically unhindered pyridines as impurities.

The addition of gaseous NO as extraligand to ClFeTPP (H_2TPP = tetraphenylporphin) has been described[9,12]. A convenient method has been developed for the synthesis of porphyrin extracomplexes from metal acetylacetonates and octaethylporphin in quinoline and in imidazole and phenol melts[37]. The yield of extracomplexes varies from 55 to 85%, phenol constituting the most favourable reaction medium. The synthesis of Cr^{3+} complexes in diethylene glycol led to the formation of extracomplexes with unidentified extraligands, which forced the authors[37] to recrystallise the extracomplex. We may note that crystallisation is sometimes used as a method of obtaining extracomplexes[58].

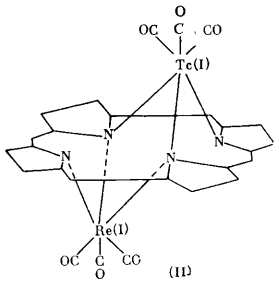
Complexes with tetra-arylporphyrins in which β-diketones serve as the extraligands have been obtained from lanthanide β-diketonates[52].

Metal carbonyls were used for the first time to synthesise extracomplexes of metalloporphyrins by Tsutsui et al.[59] The development of these methods is an important achievement in the synthetic chemistry of MP and their extracomplexes. New metalloporphyrins with chromium, molybdenum, technetium, ruthenium, rhodium, rhenium, and iridium have been obtained by the reaction of metal carbonyls and metal carbonyl halides with porphyrins[42,46,48,49,60-77]. With the exception of chromium and molybdenum complexes, the carbonyl groups used as extraligands are firmly retained at the central atom[43] and the number of carbonyl groups located on one side of the plane of the MP molecule varies from one for Ru and Ir to two for Rh [44,45] and three for Tc and Re.

Unusual extracomplexes of metalloporphyrins have been obtained[41] by heating $Re_2(CO)_{10}$ and $Tc_2(CO)_{10}$ in decalin†;[41]

† The term "axial complexes" cannot be applied to these complexes of metalloporphyrins as well as many others.

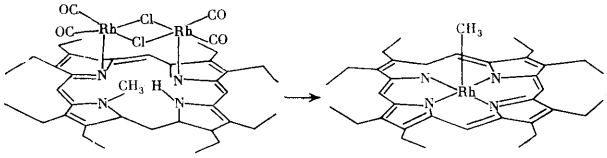
they have the structure



(II)

Formally these MP cannot be called extracomplexes. Their structure resembles that of the intermediate formed in many instances in the coordination of porphyrins to certain metal salts[78].

The synthesis of compound (III) from *N*-methyloctaethylporphin and $[Rh(CO_2)Cl]$, the product being converted on slight heating in chloroform or in the course of chromatography on silica gel into methylrhodium-octaethylporphin (IV),



(III) (IV)

i.e. a compound which is not an extracomplex of rhodium but combines the properties of a complex and an organometallic compound, has been described[46]. Numerous similar instances are now known. In conclusion we should note that the extracomplexes of iron- and cobalt-porphyrins merits particular attention in view of their catalytic activity, which is undoubtedly associated with extracoordination. These complexes have been examined in fair detail[53].

III. STEREOCHEMISTRY OF THE EXTRACOMPLEXES OF METALLOPORPHYRINS

The influence of the nature of the central atom as well as the structure of the porphyrin molecule and the extraligand on the M–extraligand bond length and on the position of the metal atom relative to the plane of the coordinating nitrogen atoms of the porphyrin molecule is examined below. These structural factors determine the physicochemical properties of the extracomplexes of metalloporphyrins.

The structure of many complexes has been determined by X-ray diffraction (Table 1). Table 1 lists the M–extraligand bond lengths for certain monoligand (tetragonal pyramid) and biligand (distorted octahedron) extracomplexes of porphyrins (Fig. 1).

It is known that the central atoms in MP capable of existing without an extraligand are located in the plane of the molecule (for example, Ni, Cu, and Pd). On the other hand, the formation of monoligand extracomplexes[33,39,79–94] leads to the displacement of the metal atoms from the plane of the porphyrin molecule, the deformation of the porphyrin skeleton, and in many instances the non-equivalence of the $M-N_{porph}$ bonds (where N_{porph} is a porphyrin nitrogen atom) in the solid phase. Depending on the nature of the complex, the metal atom is displaced from the plane of the porphyrin ring by 0.2–0.6 Å. It is noteworthy that, despite the apparent abundance of the results listed in Table 2, the dependence of the displacement of the metal atom from the molecular plane on the nature of the porphyrin, the central atom, and the extraligand virtually cannot be described in general terms in view of the lack of data in which only one of the above factors is varied.

Table 1. The metal–extraligand bond lengths in the extracomplexes of porphyrins.

Extracomplex	$M-L_1$ bond	$M-L_1$ bond length, A	$M-L_2$ bond	$M-L_2$ bond length, A	δ**, A	Refs.
(NO)FeTPP	Fe-NO	1.717	–	–	0.211	79
(N)FeTPP	Fe-N	1.661	–	–	0.32	80
$(SC_6H_4NO_2)$FePP	Fe-S	2.32	–	–	0.43	81
$(SC_6H_4$-*p*-$NO_2)$FePP	Fe-S	2.324	–	–	0.448	82
(Cl)FePP	Fe-Cl	2.218	–	–	0.575	83
(OCH_3)FeMP	Fe-O	1.842	–	–	0.456	84
$O(FeTPP)_2$	Fe-O	1.763	–	–	0.50	85
$(2\text{-}CH_3\text{-im})$FeTPP	Fe-N	2.136	–	–	0.42	86
$(pip)_2$FeTPP	Fe-N	2.127	Fe-N	2.127	–	101
(py)(CO)FeTPP	Fe-CO	1.777	Fe-N	2.10	0.02	27
$(N\text{-}CH_3\text{-im})$(NO)FeTPP	Fe-NO	1.734	Fe-N	2.180	0.07	96
$(im)_2$FeTPP	Fe-N	1.957	Fe-N	1.991	0.009	97
$(im)_2$FeOAEP	Fe-N	2.01	Fe-N	2.01	–	102
$(1\text{-}CH_3\text{-im})_2$FePP	Fe-N	1.966	Fe-N	1.988	–	8
$(1\text{-}CH_3\text{-im})[(CH_3)_3COO^-]$.(CO)FePP	Fe-N	2.05	–	–	-0.03	100
(Cl)CoTPP	Co-Cl	2.149	–	–	0.05	33
$(1\text{-}CH_3\text{-im})$CoTPP	Co-N	2.157	–	–	0.13	87
$(1\text{-}CH_3\text{-im})$CoOAEP	Co-N	2.150	–	–	0.13	88
$(im)_2$CoTPP	Co-N	1.906	Co-N	1.945	–	30
$(pip)_2$CoTPP	Co-N	2.060	Co-N	2.060	–	103
$[1,2\text{-}(CH_3)_2\text{-im}]$CoTPP	Co-N	2.216	–	–	0.15	89
(Cl)Co(N-CH_3TPP)	Co-Cl	2.242	–	–	0.558	90
(NO_2)(3,5-lut)CoTPP	Co-NO_2	1.948	Co-N	2.036	–	104
(Cl)(py)CoTPP	Co-py	1.978	Co-Cl	2.251	0	105
$(pip)_2$CoTPP	Co-N	1.987	Co-N	1.987	0	106
$(3\text{-}CH_3\text{-py})_2$CoOAEP	Co-N	2.386	Co-N	2.386	0	111
$(3,5\text{-}CH_3\text{-py})$CoTPP	Co-N	2.161	–	–	0.14	100
$(im)_2$ClCoOAEP	Co-im	1.99				
(Cl)MnTPP	Mn-Cl	2.363	–	–	0.27	100
$(1\text{-}CH_3\text{-im})$MnTPP	Mn-N	2.192	–	–	0.5	95
(py)ClMnTPP	Mn-N	2.444	Mn-Cl	2.467	0.12	39
$(N_3)(CH_3OH)$MnTPP	Mn-N_3	2.176	Mn-O	2.329	–	98
(py)ZnTpyP	Zn-N	2.143	–	–	0.33	107,108
(py)ZnOAEP	Zn-N	2.200	–	–	0.31	93
$(im)_2$Ni(4-N-CH_3py TPP)	Ni-N	2.160	Ni-N	2.160	–	100
$(py)_2$RuOAEP	Ru-N	2.089	Ru-N	2.100	–	109
(CO)(py)RuTPP	Ru-N	2.193	–	–	-0.08	47
(H_2O)MgTPP	Mg-O	2.099	–	–	0.27	99
$(py)_2$MgAEP	Mg-N	2.34			0.31	94
(O_2)TiOAEP	Ti-O	1.829	Ti-O	1.822	–	100
$[(CO)_3Re]_2$TPP	Re-CO	1.855	Re-CO_3	1.855	–	94
$[(CO)_3Tc]_2$TPP	Tc-CO	1.892	Tc-CO_3	1.892	–	41

* Abbreviations: H_2MP = mesoporphyrin; H_2TpyP = tetrapyridylporphyrin; lut = lutidine; pip = piperidine; py = pyridine [TPP = tetraphenylporphyrins; PP = protoporphyrin IX; OAEP = octoethylporphyrin].

** Here δ is the degree of displacement of the metal atom from the plane of the four nitrogen atoms.

The displacement of the central atom from the molecular plane has been attributed[91,94] to the considerable resistance of the porphyrin ligand to external deforming influences, the incomplete charge transfer from the porphyrin to the central atom, and the repulsion of the electron shells of the extraligands and the nitrogen atoms of the macroring.

From the standpoint of the chemistry of coordination compounds, the displacement of the central atom in the extracomplexes of metalloporphyrins under the influence of the extraligand can be due to three main causes: (1) the stepwise nature of the complex formation, (2) the interaction of the force fields of the metal and the first extraligand entering the complex, and (3) the repulsion of the electron shells of the extraligand and the π-electron cloud of the porphyrin macroring. The contributions of these individual factors to the geometry of the extracomplex can vary markedly as a function of the configuration of the porphyrin molecule and the nature of charge of the metal and the extraligand.

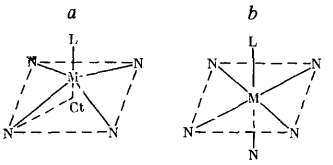


Figure 1. a) Monoligand extracomplex; b) biligand extracomplex.

Table 2. Magnetic properties of certain metalloporphyrins.

Electronic configuration of metal ion	Complex*	Coordination number	μ_{eff}, μ_B	Temp. range**	No. of unpaired electrons	Refs.
d^8	Ni	4	0	*N*	0	240
d^8	$(py)_2$Ni(diac)DP	6	3.45	*R* (*S*)	2	241
d^7	CoMP	4	2.89	*N*	1	240
d^6	(H_2O)(Cl)CoHP	6	0.23	*N*	0	240
d^6	(H_2O)(Cl)RhMP	6	0.05	*R*	0	74
d^6	$(H_2O)_2$FePP	6	4.83—5.02	*R* (*S*)	4	242
d^6	(py)(CO)FePP	6	0	*R* (*S*)	0	243
d^6	(CO)(Cl)IrHP	6	0	*R*	0	74
d^5	(Cl)FePP	5	5.88	*N*	5	244
d^5	$(im)_2$(Cl)FeTPP	6	2.36	*H*	1	245
d^5	$(py)_2$MnHP	6	5.9	*R* (*S*)	5	182
d^5	(C_6H_5Cl)phTPP	6	1.95	*R*	1	74
d^4	(H_2O)(Cl)MnHP	6	4.88	*N*	4	182
d^3	(H_2O)MnHP	6	2.0	*R* (*S*)	1	182

* Abbreviations: HP = haematoporphyrin; (diac)DP = diacetyldeuteroporphyrin.

** Here *R* = room temperature, *N* = temperature range 80 to 300 K, *H* = temperature range 4.2–50 K, and *S* = solution.

It has been suggested[91] that large extraligands, resembling the chloride ion, always cause a marked breakdown of the planarity of the coordination unit of the metalloporphyrin; small extraligands may not distort significantly the planar configuration of the MP. This postulate is valid for ClMnTPP and ClFePP, but it does not hold for ClCoTPP, in which the displacement of Co from the molecular plane is very slight. The latter can be explained by the fact that the cobalt ion in the complex is of the low-spin type and therefore has a comparatively small effective radius. On the other hand, the iron complex is of the high-spin type; its antibonding molecular orbitals, formed with participation of the d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal, are filled, which leads to an increase of the effective radius and to the displacement of the central atom from the plane of the porphyrin[95].

The most significant displacement from the molecular plane is caused by the entry (substitution) of the first extraligand. The entry (substitution) of the second extraligand either diminishes the displacement from the molecular plane[27,96-99] or, as a rule, reduces it to zero[8,41,47,100,101-111] when both extraligands are of the same type (Table 2).

On the basis of ideas concerning the radius of the central cavity of the porphyrin, which determines the distance between each nitrogen atom and the centre of the molecule (Ct) (Fig. 1), Hoard[112] concluded that the metal can be located in the plane formed by the four nitrogen atoms, provided that the metal–nitrogen bond length is equal to the Ct–N distance (it amounts to ≤2.015 ± 0.007 Å). For example, according to Rifkind[113], the high-spin iron complexes (the Fe–N bond length is 2.061 ± 0.012 Å) cannot be planar, while the low-spin complexes (Fe–N = 1.91 Å) can be planar. However, the Fe–N bond length in the complex $Cl(pip)_2$FeTPP is 2.127 Å (Table 2), which does not lead to the displacement of the Fe from the plane of the ring[96].

Data for complexes of iron-containing porphyrins with proteins and other bioligands have been analysed in two reviews[113,114].

IV. PHYSICAL PROPERTIES OF THE EXTRACOMPLEXES

The typical electronic absorption spectra of porphyrins and metallo-porphyrins are their most important characteristics. Absorption spectroscopy is most widely used in the study of processes associated with extracoordination[5,9,14,25,45,47,81,82,91,114-137], due to the considerable possibilities of the method. Absorption spectroscopy is most frequently used to follow the formation of extracomplexes in solutions, to determine the number of extraligands combined, and to measure the stability of the extracomplexes.

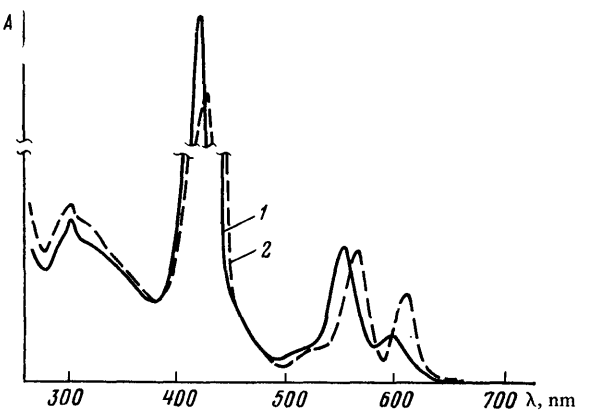


Figure 2. Electronic absorption spectra of ZnTPP (curve *1*) and its extracomplex (DMSO)ZnTPP (curve *2*) in CCl_4 at 25 °C.

A theoretical discussion of the absorption spectra of porphyrins and metalloporphyrins has been described in a monograph[138] and partially by Berezin[1]. However, the spectroscopy of the extracomplexes of porphyrins have been hardly discussed in the above publications. There have been a number of studies specially devoted to the electronic spectra

of the extracomplexes of porphyrins and phthalocyanines[14,36,91,139,140]. The positions and intensities of the absorption bands have been published[37,114] for a large number of extracomplexes of octaethylporphin.

The absorption spectra of metalloporphyrins in the range 350–750 nm consists as a rule of three bands[138]: the Soret band located in the near ultraviolet and two bands in the visible part of the spectrum (Fig. 2). The absorption bands of the MP are due to the $\pi-\pi^*$ transitions in the porphyrin molecule, which are described satisfactorily in terms of the four-orbital Simpson–Platt–Gouterman model[141,142]. The addition of extraligands is accompanied by a 5–35 nm shift of the absorption bands (Fig. 2). The magnitude of the shift and its direction (bathochromic or hypsochromic) depend on the nature of the central atom of the MP, the extraligand, and the structure of the porphyrin.

It is interesting to reproduce the essential feature of a brief analysis of the bathochromic and hypsochromic shifts of the absorption bands of the extracomplexes based on Berezin's data[1]. The extracomplexes of metalloporphyrins constitute one of the groups of mixed complexes. The characteristics of the formation of complexes with a mixed coordination sphere and the characteristics of the compatibility of the ligands in these complexes have been analysed in detail[143]. In the inner coordination sphere ligands of a similar electronic type (for example, σ-donor, π-acceptor, and electrostatic) are most compatible. It is therefore to be expected that π-ligands such as pyridine, imidazole, CN^-, dimethyl sulphoxide (DMSO), CO, O_2, and others of a similar type with both σ-donor and π-acceptor properties will enter more readily the coordination spheres of porphyrin complexes.

Allowance for only the electronic interaction of the extraligand with the MP makes it possible to use the concept of the electronic effects of coordination in planar macrocyclic complexes developed by Berezin[1,144] and to achieve a simpler treatment of the changes in the properties of MP on extracoordination of ligands; this approach is justified in many instances. According to it, for metals with an unfilled d shell the extraligands with suitable π orbitals can enter into a competitive interaction with the dxy, dxz, and dyz orbitals of the metals. As a result, the $d_\pi-p_\pi$ metal–porphyrin interaction is weakened due to the $d_\pi-p_\pi$ interaction of the metal with the extraligands and the role of the metal–porphyrin σ-interaction increases. The coordination of π-acceptor ligands should therefore result in a hypsochromic shift of the first band in the electronic spectra of MP, provided that the extraligands are indeed involved in the π-interaction with the metal atom[3]. The changes in the electronic spectra show that there is not only an electrostatic MP–ligand interaction but also a donor–acceptor interaction between the ligand and the metal atom[138].

In those cases where the central metal atom in the porphyrin complex has closed stable electronic orbitals (the overall orbital moment and the spin are zero), the formation of dative metal–ligand π-bonds becomes virtually impossible. Such cases occur in the metalloporphyrins of Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, etc., where the interaction is limited to the σ-binding of the extraligand by the d^2sp^3 orbitals or ion–dipole attraction. In both cases the extraligand increases the electron density at the metal atom and decreases the degree of its σ-interaction with the porphyrin, so that one should expect a bathochromic shift of the first band in the electronic absorption spectrum of the complex.

The above interpretation of the spectra does not conflict with experiment, provided that the geometrical parameters of the coordination centre of the MP, particularly the coordinates of the metal and the nitrogen atoms linked to it, are not altered. If a displacement of the metal from the plane of the N atoms or the opposite movement is observed in extracoordination, an unambiguous solution of the problem of the nature of the spectroscopic changes in the extracoordination is still difficult. Thus examples of both hypsochromic[125] and bathochormic[122] shifts of the first band in the spectra of cobalt complexes of porphyrin are known. A hypsochromic shift of the first band has been observed for the iron complexes[137].

Despite numerous studies devoted to extracoordination to porphyrins, there are still no systematic studies of the dependence of the absorption spectra of extracomplexes on the nature of the central atom, the extraligand, and the porphyrin under comparable conditions. It is therefore at present difficult to establish rigorous correlations between the M–N bond lengths, the band shifts in the electronic absorption spectra, and the thermodynamic parameters of the extracoordination reaction.

A number of studies by other spectroscopic methods have appeared recently in the literature. EPR has been used for the extracomplexes of cobalt-, iron-, and manganese-porphyrins. Problems associated with the determination of the stoichiometry of the mono- or bi-ligand complexes formed[32,145] and of the spin state of the central atom[82,146–148] have been solved mainly by EPR, which also proved to be an effective method for the detection of cobalt-oxygen complexes[32,121,145,147].

It has been shown by EPR [121] that at −45 °C in air in the presence of imidazole or benzimidazole, CoPP forms a 1:1 complex of the type $(L)(O_2)(CoPP)$, which rapidly decomposes at room temperature with formation of $(L)CoP(O_2)PCo(L)$. It is believed[121] that bridged complexes should be characteristic of cobalt extracomplexes. On the basis of a study of the EPR spectra of CoPP in dimethylformamide (DMF), Stynes and Ibers[149] concluded that the greater the basicity of the extraligand the smaller the capacity of cobalt for oxidation. This conclusion is probably not general[145].

NMR has been used to determine the thermodynamic and kinetic parameters of the extracoordination reaction (see Sections V and VI), to determine the structure of the extracomplex[41,47,150], and to investigate the exchange of extraligands[151]. It has been correctly stated[152,153] that the calculation of K_{st} from NMR data is complicated by the solvent–solute interaction. In general a change in the nature of the extraligands is reflected to a greater extent in the chemical shifts of the protons of the methyl and α-methylene groups and of the meso-protons of the paramagnetic complexes. These data do not allow a distinction to be made between contact and pseudocontact shifts, which hinders the estimation of the effects of extracoordination and association[114]. It has been suggested[114] that the resulting contact shifts depend on the degree of type of interaction between iron and the nitrogen atoms of porphyrins, which depend in their turn on the differences in the binding of the central atom to the extraligands.

Infrared spectra have been used mainly to identify extracomplexes and extraligands. Analysis of the infrared spectra of haemins have led to the conclusion[114] that the nitrogen atom is displaced from the plane of the porphyrin ring by 0.5 Å or more.

Lack of space precludes a detailed examination of all the spectroscopic data for the extracomplexes of porphyrins. Numerous EPR [32,35,82,121,131,135,146–149,154–160], NMR [20,23,38,41,47–49,52,114,150,151,161–171], infrared spectroscopic[9–13,137,172–177], Raman spectroscopic[178–180], and Mössbauer spectroscopic[21,30,82,114,181–186] studies as well as studies based on magnetic circular dichroism spectra[187–189] have been made on porphyrin extracomplexes. The spectroscopic methods yield much useful information about porphyrins, but the lack of

systematic specific investigations hinders a general survey of these data.

The magnetic properties of metalloporphyrins and their extracomplexes are of considerable interest, since they make it possible to determine directly the oxidation state of the central metal atom. Magnetic properties depend significantly on the presence of extraligands in the molecule. Table 2 lists the magnetic properties of certain metalloporphyrins. The results of magnetic measurements have been discussed in detail in the literature[152,153].

V. KINETICS OF THE FORMATION OF THE EXTRACOMPLEXES

Information about the state of extraligands and the nature of their bonds with the metal atom in the extracomplex can be obtained by studying the kinetics of the formation and dissociation of these complexes. Several tens of studies on the kinetics of the formation of extracomplexes of metalloporphyrins and phthalocyanines have been published recently.

Blyumenfel'd[190] established for the first time (on the basis of the rate of substitution of one protein by another in a *gem*-protein complex saturated with O_2 and CO) that the rate of elimination of globin from the oxygenated protohaem (O_2). .FePP is limited by the rate of elimination of O_2, i.e. by the rate of the reaction

$$(O_2)\text{FePP} \rightleftharpoons O_2 + \text{FePP}. \qquad (6)$$

The rate constant for the reaction proved to be $k_V = (5 \pm 2) \times 10^5\ s^{-1}$; such a high rate is evidence for a low strength of the Fe–O_2 covalent bond. The activation energy for the reaction

$$(\text{globin})\text{FePP} + O_2 \rightarrow (\text{globin})O_2\text{FePP} \qquad (7)$$

is close to zero.

On the other hand, for the reverse reaction, it is 21 ± 1.5 kcal mol^{-1}, which is due to the simultaneous abstraction of O_2 and protein imidazole residue from the Fe atom. The considerable possibilities of the kinetic method for the investigation of phenomena based on extracoordination were demonstrated in the same study[190].

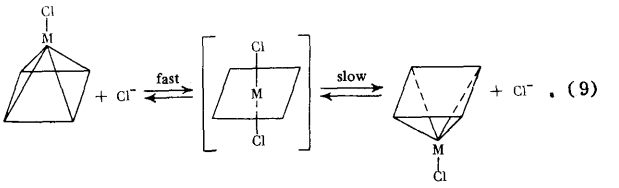
The imidazole exchange in low-spin iron(II) complexes of porphyrins (tetraphenylporphyrin, octaethylporphyrin, and protoporphyrin) has been studied[151] by ^1H NMR. Depending on the nature of the porphyrin, the rate of the exchange reaction

$$(\text{N—CH}_3\text{im})_2\text{FeTPP} + \text{N—CH}_3\text{im}^* \underset{\tau_{-1}}{\overset{\tau_1}{\rightleftarrows}} (\text{N—CH}_3\text{im})^*(\text{N—CH}_3\text{im})^*\text{FeTPP} + \text{N—CH}_3\text{im} \qquad (8)$$

can vary by an order of magnitude, which proves that the binding of imidazole to FePP is covalent.

It has been observed[191] that, under the influence of the extraligand, the metalloporphyrins ClFeTPP(p-CH_3)$_4$ and ClFeOEP undergo inversion with the rate constants of 15×10^2 and 60 s^{-1} respectively. It follows from these data that the rate of inversion determines the strength of the extracoordination of the second extraligand: as a result of the reduced effective charge on FeOEP compared with FeTPP, the strength of the binding of Cl^- to the former is smaller, the fraction of $(Cl)_2$FeOEP is small, and the rate of inversion is low.

An S_N2 mechanism has been proposed for the process



(9)

The rate of inversion was investigated later[20] and the activation parameters were calculated for a series of porphyrins; the data presented in Table 3 indicate the presence of solution of mono- and bi-ligand extracomplexes and show that their stabilities are different. Evidently the inversion reactions are virtually isentropic and the differences between their rates are caused mainly by the differences between the activation enthalpies for the inversion process, i.e. are associated with the stability of the extracomplexes. It is noteworthy that studies similar to that described above[20] can prove useful for the understanding of the detailed mechanisms of the formation and dissociation of porphyrin complexes, particularly with metals such as iron, cobalt, and manganese.

Table 3. Activation parameters for the inversion reaction (6).[20]

Extracomplex	extra-ligand	k^{298}, $m^{-1}\ s^{-4}$	$\Delta G^{\neq}$, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$-\Delta S^{\neq}$, e.u.
(Cl)FeTPP(p-CH_3)$_4$	Cl	$(5.6\pm1.4)\cdot10^2$	14.2±1.2	9.1±0.8	17±4
(I)FeTPP(p-CH_3)$_4$	I	$(5.9\pm1.2)\cdot10^3$	12.2±0.6	6.5±0.3	19±2
(Cl)FeOAEP	Cl	$(5.8\pm1.2)\cdot10$	15.0±1.0	8.8±0.5	21±2
(I)FeOAEP	I	$(9.0\pm1.6)\cdot10^2$	13.2±0.4	7.2±0.2	20±2

The self-reduction of Fe^{3+} to Fe^{2+} has been observed in the interaction with ClFeTPP with piperidine in $CDCl_3$.[192] In the presence of the cyanide ion and oxygen, continuous oxidation-reduction of iron takes place.

The kinetics and thermodynamics of the substitution of O_2 as an extraligand by an excess of the main extraligand in $(L)(O_2)$FeTPP, where L = pyridine piperidine, or 1-methylimidazole, have been investigated[193]:

$$(L)(O_2)\,\text{FeTPP} \xrightarrow[k_V]{\text{slow}} (L)\,\text{FeTPP} + O_2\,, \qquad (10)$$

$$(L)\text{FeTPP} + L \xrightarrow{\text{fast}} (L)_2\text{FeTPP}. \qquad (11)$$

For the extraligands enumerated, reaction (10) is characterised by the following rate constants respectively: $k_V = 4.3 \times 10^{-3}$, 2.3×10^{-3}, and $0.17 \times 10^{-3}\ s^{-1}$. The corresponding sequence based on the variation of the rate constants for the elimination of O_2 is due to the decrease of the π-donor activity of the central Fe(II) atom, which takes place under the influence of the change in the type and strength of the Fe–L bond and the effective charge on the iron atom. It also follows from the above data[193] that the strength of the binding of O_2 is determined not only by the π-acceptor but also by the σ-donor properties of extraligands.

In a study of the kinetics and thermodynamics of the binding of CO and O_2 to $(L)_2$FeTPP, Weschler et al.[19] used the same extraligands as in the previous study[193]. The reaction

proceeds in accordance with the equations

$$(L)_2FeTPP \rightleftharpoons (L)FeTPP + L; \quad (12)$$

$$(L)FeTPP + O_2 \rightleftharpoons (L)(O_2)FeTPP; \quad (13)$$

$$(L)FeTPP + CO \rightleftharpoons (L)(CO)FeTPP. \quad (14)$$

The study of the rate of the process as a function of the O_2 and CO concentrations Weschler et al.[19] to suggest a dissociative mechanism with formation of the extracomplex L(Fe). TPP. The rate of formation of the complexes with O_2 and CO decreases in the sequence pyridine > piperidine > 1-methylimidazole due to the increasing strength of σ- and π-binding of the extraligands.

It follows from the above data[19,193] that the strengthening of the π-donor properties of the extraligand in processes similar to reactions (10)–(14) leads to a decrease of the strength of the M–O_2 bond in the extracomplex. However, in a study of the interaction of O_2 with FePP in the presence of 2-picoline, 2-methylimidazole, and t-butyl alcohol, Wagner and Kassner[116] concluded that the coordinating properties of the extraligands are insignificant for the binding of O_2 and that ligands of the type of imidazole are not unique extraligands in this process. This conclusion is probably erroneous, since it has been shown in a number of studies[1,194] that π-binding determines the competition between the extraligands for *d* electrons (the *trans*-influence discovered by Chernyaev[195] plays a significant role here).

The electronic nature of the *trans*-influence, examined from modern standpoints in a number of studies, for example by Bersuker[196], can serve as the basis of the treatment of extracoordination to iron-porphyrins[1]. Comparison of the properties of imidazole with those of other nitrogen-containing protein residues led to the conclusion[194] that none of the latter creates more favourable conditions for the addition of O_2 than imidazole.

The reaction of $(pip)_2FePP$ with CO has also been studied by other workers[197,198], but fundamentally new information was not obtained. The substitution of water in diaquoiron(III)- and diaquocobalt(II)-haematoporphyrins by CN^- and SCN^- ions has been described[151,153,199]. The kinetics of the binding of CN^- and imidazole by haemin in micelles have been investigated[200]. A polarographic study has been made[201] of ClFePP in the presence of nitrogen-containing bases (4-cyanopyridine, 4-acetylpyridine, pyridine, 4-phenylpyridine, 4-aminopyridine, piperidine, pyrazole, benzimidazole, 5,6-dimethylimidazole, and imidazole). This study is interesting in connection with the observed linear relation between the pK_B of the nitrogen-containing bases and the rate of electron transfer. The correlation has been explained by the change of ligand environment and the spin state of iron.

Several interesting studies have been made on iron-phthalocyanines[202–206]. The kinetics of the reaction

$$(DMSO)_2FePc + 2im \rightleftharpoons (im)_2FePc + 2DMSO \quad (15)$$

have been studied. It was observed that the substitution of the first DMSO molecule is the rate-limiting stage and that even at a high imidazole concentration the reaction is of second order[205].

The reactions of FePc with tri-n-butyl phosphite [$P(OBu)_3$] and tri-n-butylphosphine (PBu_3) have been reported[206]. The reaction products are low-spin bi-ligand extracomplexes. The kinetics of the substitution reaction

$$[\{P(OBu)_3\}_2FePc] + 2PBu_3 \rightarrow (PBu_3)_2FePc + 2P(OBu)_3 \quad (16)$$

have been investigated. The rate of elimination of $P(OBu)_3$ from $[P(OBu)_3]_2FePc$ is 5000 times greater than the rate of elimination of imidazole from $(im)_2FePc$. Schweigart[206] attributes this finding to the greater *trans*-effect of $P(OBu)_3$ compared with imidazole on the grounds that the substitution of $P(OBu)_3$ by imidazole leads to $[P(OBu)_3](im)FePc$.

The kinetics of the substitution of chlorine by the OH^- group in dichlorosilicon-phthalocyanine have been investigated[207]:

$$Cl_2SiPc(solid) + 2OH^- \rightarrow (HO)_2SiPc(solid). \quad (17)$$

The rate constant for the substitution reaction in 0.1M NaOH solution is 6×10^{-6} s^{-1}, $E = 15.6$ kcal mol^{-1}, and $\Delta S = -19$ e.u. It is suggested that the low rates of substitution of chlorine in the extracomplex of silicon-phthalocyanine are due to the sharp decrease of the positive charge on the silicon atom owing to the strong coordinate σ-bond and the reverse dative Si ← N π-bond. The latter is formed by filling the vacant d_π orbital of silicon with the p_z electrons of chlorine, which reduces sharply the tendency of the Si atom towards nucleophilic substitution reactions.

There have been several studies on the kinetics of the substitution of extraligands in extracomplexes of cobalt[124,208,209]. The conclusions reached do not differ fundamentally from those described above. Reactions involving the substitution of extraligands in extracomplexes of manganese have been described in detail in Boucher's review[210].

Thus the above data show that numerous studies, usually isolated and scattered, have been devoted to the kinetics of the substitution of extraligands in extracomplexes of porphyrins. Large-scale systematic investigations are as yet lacking; the need for such investigations is entirely evident.

VI. THERMODYNAMICS OF THE EXTRACOORDINATION REACTION

The extracoordination reaction in solution

$$MP + L_n \rightleftarrows (L)_n MP \quad (18)$$

is as a rule investigated by electronic absorption and emission spectroscopy. It is readily reversible, which makes it possible to displace the equilibrium in the required direction by a moderate alteration of the concentration of the extraligand, the nature of the solvent, and temperature. Studies on stability are usually carried out by the isothermal saturation method. There have been investigations[211,212] in which the thermodynamic parameters of reaction (18) were determined calorimetrically.

The methods for the calculation of the constants do not differ from those generally adopted for the determination of the stepwise stability constants of the usual complexes[213]. The method proposed by Miller and Dorough[130] is most frequently used. The number of added ligands is found as described by Bent and French[214] and from the decrease of weight on heating the extracomplex *in vacuo*[129]. The latter method is suitable only for porphyrin molecules resistant to thermal degradation. There exist data for the thermodynamic parameters of reaction (18) for the Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, and VO^{2+} complexes of porphyrins with a large number of extraligands of different types.

One of the first studies[130] was devoted to pyridine complexes in benzene. The stability of pyridine complexes of metalloporphyrins is due to a number of factors, which have been examined[1]. According to the published[130] stability constants K_S, the monoligand extracomplexes of porphyrins can be arranged in the sequence Zn > Cd > Hg > VO. The pyridine complex of VO-porphyrin with H_2TPP has also been

included in this sequence[153], but we were unable to find its stability constant K_S in the literature. It follows from the above data[130] that the hydrogenation of the porphyrin ring leads to appreciable stabilisation of the pyridine complexes of Mg- and Zn-porphyrins; only Mg-porphyrins form a relatively stable dipyridine complex[130]. It has been shown that zinc also forms bi-ligand extracomplexes of a similar type with certain extraligands[215,216]. Baker et al.[5] observed the formation of a dipiperidine complex of Ni-mesoporphyrin and a monopiperidine copper complex. The influence of the nature of the extraligand on the stability of the extracomplexes has been examined in several studies[6,125,129,217-218].

Table 4 presents the logarithms of the stability constants of the monoligand extracomplex of chlorophyll a (MgChl) in benzene[6]. The constants were estimated from the fluorescence intensity, which increases as the extraligand is added to the chlorophyll solution in absolutely dry benzene. The stability of the extracomplexes is associated with the increase of the electron-donating capacity of the ligand. It is noteworthy that the data in Table 4 do not reflect the true stability constants, since the development of fluorescence need not be caused solely by the deaggregation of the associated chlorophyll species due to extracoordination. However, these data do reflect correctly the sequence in the variation of stability. The complexity of the phenomenon may be caused by the operation of several mechanisms of the formation and decomposition of the MgChl associated species[1]. Table 6 shows that the Mg atom in MgChl coordinates oxygen and nitrogen-containing ligands equally effectively.

Table 4. The stability constants of monoligand extracomplexes of chlorophyll *a* in benzene (6).

Extraligand	$\lg K_S$	Extraligand	$\lg K_S$
Dimethylaniline	1.0	Quinoline	4.1
Phenol	1.2	Benzylamine	4.4
Aniline	1.7	Water	4.5
n-Octyl alcohol	3.7	n-Heptylamine	5.2
Benzyl alcohol	3.5		

The formation of complexes of various substituted pyridines with Fe-porphyrins has been investigated[6]. It has been pointed out[129] that the stability constants K_S vary in inverse proportion to the basicity of the extraligand. It has been observed that there is only a tendency towards an increase of stability with decrease of the basicity of the extraligand, but a rigorous correlation has not been found. This complex dependence reflects the fact that the stability of the extracomplexes of iron-porphyrins is determined both by σ- and π-binding of the ligands. The data obtained have been discussed by Falk[6], who notes, in particular, the influence of steric factors on the binding of certain substituted pyridines by the central atom, which may be non-axial.

The stability constants K_S of 4-substituted pyridine complexes of MgDP have been published[129] and a correlation has been observed between the basicity of the substituted pyridine and the stability of the extracomplex. Analogous relations have been observed for ZnTPP, CdTPP, and HgTPP [217] as well as ZnTPP and NiTPP in $CHCl_3$ and benzene[218]. A correlation was observed in the above studies between K_S and the Hammett constants. This type of correlation has also been established for CoPP.[125]

An attempt has been made[129] to find a relation between the stability of the pyridine extracomplexes of Mg-porphyrin and the structure of the porphyrin molecule (Table 5). Table 5 lists the thermodynamic parameters of the reaction

$$(py)MgP + py \rightleftharpoons (py)_2MgP. \quad (19)$$

A difference has been observed between the equilibrium constants, but nothing definite has been established concerning the problem of the influence of the structure of the porphyrin molecule on extracoordination. The estimate of the error of the thermodynamic parameters obtained, quoted by Storm et al.[129], shows that the values of ΔH and ΔS for reaction (19), involving different porphyrins, are probably within the limits of experimental error. The influence of the porphyrin structure on the addition of the second extraligand is slight, owing to the weakness of the LMP—L coordination interaction. It is seen in relation to 2,4-dinitrodeuteroporphyrin[129] that even the introduction of two nitro-groups causes little change in K_2 and ΔH.

Table 5. Thermodynamic parameters of reaction (9) in 2,6-lutidine.

P	K_2	ΔG, kcal mol^{-1}	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, e.u
Mesoporphyrin IX d.m.e.*	0.070	1.60	3.98	18
Actioporphyrin II (H_2AEP)	0.068	1.62	2.92	15
Protoporphyrin IX d.m.e.	0.242	0.84	4.25	17
Deoxophylloerythrin m.m.e.	0.074	1.56	2.55	14
Dinitrodeuteroporphyrin IX d.m.e.	0.326	0.68	3.99	15
Mesoporphyrin IX dicholesteryl ether	0.142	1.16	3.77	16
Tetraphenylporphin	0.161	1.08	2.37	11
Dichlorodeuteroporphyrin IX d.m.e.	0.282	0.76	3.90	15
Deuteroporphyrin IX d.m.e.	0.228	0.85	3.89	16

* Here d.m.e. = dimethyl ester [and m.m.e. = monomethyl ester].

A weak dependence of the thermodynamic parameters of extracoordination to zinc-porphyrins on the porphyrin structure has been observed in a study of the equilibrium in the extracoordination of DMSO [215,216,219]. The addition of DMSO to the zinc complexes takes place stepwise:

$$ZnP + DMSO \rightleftharpoons (DMSO)ZnP; \quad (20)$$

$$(DMSO)ZnP + DMSO \rightleftharpoons (DMSO)_2ZnP. \quad (21)$$

The nature of the plots of the absorbance A against c_0^L (the concentration of the extraligand) (Fig.3) is the same for all the complexes investigated. The first DMSO molecule adds in the DMSO concentration range up to 1.3×10^{-3} M and the second molecule adds on further increase of the ligand concentration. The number of added extraligands (n) in solution has been determined by the Bent—French method[214].

However, one should note that $n = 1$ has been found in a series of studies[130,218,220-221] of the extracoordination to Zn-porphyrins using several extraligands; this is probably due to the inadequate number of experimental points over a wide range of concentrations.

The influence of the structure of the porphyrin molecule on the thermodynamic parameters of the extracoordination reaction has been investigated by Walker et al.[222], who published data for a series of Ni^{2+} and VO^{2+} complexes of *p*- and

m-derivatives of tetraphenylporphin; unfortunately, complete thermodynamic characteristics have been published only for two porphyrins. The second equilibrium constants in the reaction of piperidine with nickel-tetraphenylporphyrin[222] indicate a significant influence of the substituents in the phenyl residues of tetraphenylporphin on the K_S for the extracomplexes of the Ni^{2+} compound. The authors[222] note that the extent of this influence depends on the d_π electrons in the central atom: it is greater for $Ni^{2+}(d^8)$ than for $VO^{2+}(d^1)$. The observation of a correlation between K_S and the Hammett and Taft constants led the authors[222] to the conclusion that there exists a moderate conjugation between the phenyl residues and the macroring. They believe that the roles of the conjugation and inductive effects for *para*-substituted tetraphenylporphins are approximately the same; for *meta*-substituted tetraphenylporphins, the inductive effect predominates.

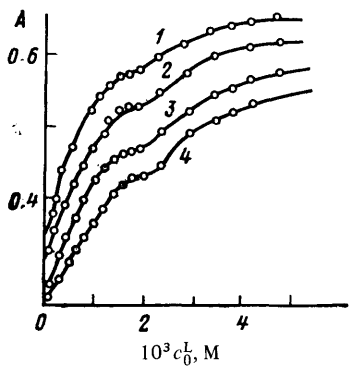


Figure 3. Dependence of A on c_0^L for (DMSO)ZnTPP at different temperatures (°C): *1*) 15; *2*) 25; *3*) 35; *4*) 45.

It is noteworthy that the conclusion that there is conjugation between the macroring and the benzene rings in tetraphenylporphyrins is based on shaky foundations. It can be regarded as premature, since it has not been confirmed by either spectroscopic or kinetic data[1]. The increase of the equilibrium constant K_2 for the binding of piperidine by nickel-tetraphenylporphyrins with enhancement of the electron-accepting properties of *para*-substituents ($NO_2 > CN > OCOCH_3 > Cl$—Table 10) can be readily accounted for by the increase of the effective charge on the nickel atom as a result of the weakening of the σ-donor properties of the corresponding tetraphenylporphin derivatives, which is caused by the inductive effect of the $-C_6H_4X$ groups in the molecule.

One must note that well-founded conclusions concerning the influence of the molecular structure of metalloporphyrins on the nature of their interaction with extraligands and other types of mutual influence of atoms in metalloporphyrins cannot be reached on the basis of the constants for the addition (particularly the second constants!) of extraligands in the absence of reliable numerical data for the entropies and enthalpies of extracoordination.

In their reaction with piperidine, the VO^{2+} complexes are less sensitive to the nature of the substituent in the benzene ring of the tetraphenylporphin[222]. They form only "monoligand" extracomplexes. The location of the vanadium atom outside the molecular plane leads to a change in the degree of overlap of its *d* orbitals with the π orbitals of the porphyrin, which the authors[223] believe to cause a decrease of the "sensitivity" of vanadium-porphyrins to the nature of the substituents in the benzene rings. Furthermore, nickel is capable of back π-bonding (interaction of d_π orbitals with the π^* orbitals of the porphyrin). On the other hand, in the case of V^{4+} its single *d* electron is located in the d_{xy} orbital[224,225] and cannot form a stable bond with the π^* orbitals of the porphyrin ring.

The hypothesis of the authors of an interesting and on the whole useful study[222] concerning the identical degrees of solvation of the complex in the extracoordination process appears doubtful; for example, the quantitative data obtained in our laboratory reveal a significant dependent of ΔH_{solv} on the structure of the porphyrin[219].

The thermodynamic parameters of the formation of extracomplexes of ZnTPP with tetramethylthiourea, tetramethylurea, and triphenylphosphine in benzene have been determined[221]. The increase of ΔH (kcal mol^{-1}) has been observed in the sequence S (−5.6) > O(−6.5) > P(−7.7). The methods of calculation of the equilibrium constant for the extracoordination reaction were critically analysed in the same study[221] and preference was given to the method of Rose and Drago[226].

The equilibrium constants for the coordination of the vanadyl group VO to porphyrins of different structure have been published[223,227,228] (Table 6). Unfortunately the lack of thermodynamic parameters hinders the analysis of the data obtained, which are of considerable interest.

Table 6. The stability constants of monopyridine extracomplexes at 25 °C in $CHCl_3$.

MP	10^2K_S	Refs.	MP	10^2K_S	Refs.
VOAEP*	1.99	227	VOHP	1100	223
VOMP	5.21	228	VOTpyP	1120	228
VODP	7.30	228	$VODP(Br)_2$	1125	228
VOPP	9.13	228	$VODP(CH_3CO)_2$	3330	228

* Solvent—dioxan.

The use of vanadyl complexes of porphyrins is of interest in connection with the presence of the =O group in a single extraposition and also in connection with the possibility of the formation of the "monoligand" complex only. The dependence of K_S on the nature of functional substituents can be clearly traced in a series of porphyrins (Table 6). Electron-donating substituents (in H_2AEP and H_2MP) increase the electron density of the vanadyl ion and K_S is reduced compared with H_2DP. Electron-accepting substituents (in H_2PP, H_2HP, H_2TpyP, $H_2DP(Br)_2$, etc.) lead to an increase of K_S owing to the decrease of the electron density at the vanadyl ion.

Several studies have been published in recent years on the thermodynamics of extracoordination (Table 7) to various Co-porphyrins[121,123,125,161,209,229-231]. A sharp increase of the number of similar studies is apparently to be expected in the immediate future in connection with the extremely interesting ability of the cobalt complexes to combine reversibly with oxygen when the molecule contains another, particularly polymeric, extraligand. The main difficulty arising in the joint examination of these studies is in the first place the different reaction conditions. The marked dependence of the results of the measurements on the nature of the solvent

observed in a number of investigations[117,149,211,218] necessitates caution in comparing data obtained in different solvents.

The results of a study of cobalt-protoporphyrin are of considerable interest[121,125]. The extracoordination of eight extraligands to CoPP was investigated[125] (Table 12). It was established that there is no simple correlation between any thermodynamic parameter and the basicity of the ligand. The thermodynamic parameters of the addition of the second extraligand were not obtained, because the authors[125] were quite rightly afraid of introducing large amounts of extraligand capable of altering the structure of the solvent; the accompanying effects can lead to an erroneous interpretation of the results. The data obtained[125] showed that DMF is a "poore" extraligand for Co-porphyrins and can be used as a "neutral" solvent for the investigation of the extracoordination. The substitution of an alkyl in pyridine has only a slight influence on the complex-forming capacity of the latter, while the CN group causes a sharp decrease of this capacity. A similar behaviour was observed for imidazole, which is a somewhat weaker extraligand for the cobalt complex than pyridine. The identical complex-forming properties of pyridine and piperidine clearly indicate a major role of both σ- and π-binding in extracoordination to cobalt-porphyrins.

The interaction of CoTPP(p-CH_3)$_4$ with a series of π-acceptors and π-donors has been investigated by NMR in $CDCl_3$ (Table 7).[161] Thermodynamic parameters have been found for trinitrobenzene as an extraligand. The virtually complete identity of the K_S for acceptors and donors indicates, according to La Mar and Viscio[150], the ability of the metalloporphyrin to exhibit the properties of a π-acceptor or a π-donor, depending on the conditions. However, this claim does not appear convincing in the absence of fundamental thermodynamic characteristics of the extracoordination reaction.

It has been found[123] for phosphorus-, sulphur-, and arsenic-containing extraligands that the coordinating capacity diminishes in the sequence (Table 11) $P(C_4H_9)_3 \gg P(OCH_3)_3 > P(C_6H_5)_3 > S(CH_3)_2 > As(C_6H_5)_3$, while the K_S are correlated with the pK_B of the ligands. These results led the authors to the conclusion that σ-binding plays a dominant role for the above extraligands, i.e. the role of the d_π–d_π interaction between cobalt and the above ligands is small.

The formation of complexes by CoTPP and CoTPP(p-OCH_3)$_4$ with DMSO in CCl_4 has been investigated by a spectroscopic method[230]. It was established that two DMSO molecules are added in steps (Table 7). CoTPP and CoTPP(p-OCH_3)$_4$ were found to exhibit a significant difference in the extracoordination reaction with DMSO. The introduction of p-OCH_3 groups into the benzene rings alters significantly the enthalpy (increases it by 6 kcal) and entropy (increases it by 17 e.u.) of coordination. The stability constant then decreases almost by a factor of 2.5 (Table 7); the authors[230] attributed its decrease to the increase of the electron density in the porphyrin macroring and at the cobalt atom as a consequence of the greater electron-donating capacity of the $C_6H_4OCH_3$ group compared with the phenyl residue. However, this conclusion was reached without taking into account solvation and steric factors and cannot be regarded as well-founded. It is seen from the data in Table 7 how much the entropy can change in isotypical extracoordination reactions.

Interesting data on the extracoordination of nitrogen-containing heterocycles to ethoxycarbonyl derivatives of porphin (ECP complexes of Co^{2+} and Cu^{2+}) were obtained by Ginzburg et al.[231] Extracoordination is accompanied by a decrease of entropy from −7 to −12 e.u. (for pyridine), depending on the number of ethoxycarbonyl groups (Table 7). The enthalpy then decreases from −7 to −9 kcal mol^{-1}. Somewhat greater values of ΔH, ΔS, and stability constants are characteristic of the extracoordination of piperidine. Overall, the extracoordination to the ECP complexes of cobalt resembles that for CoTPP.

Table 7. Thermodynamic parameters of the extracoordination reaction involving cobalt-porphyrins in toluene.

Extraligand	K_S	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, e.u.	Method of determination of K_S	Refs.
		CoPP*			
DMF	15	7.9	21	SPT	125
4-Cyanopyridine	1 738	10	19	SPT	125
Pyridine	6 025	6.9	6	SPT	125
4-t-Butylpyridine	7 079	9	13	SPT	125
Imidazole	4 365	7.9	10	SPT	125
1-Methylimidazole	5 011	10.7	19	SPT	125
4-Aminopyridine	10 000	8.1	9	SPT	125
Piperidine	6 760	10.4	17	SPT	125
		CoTPP(p-CH_3)$_4$**			
Trinitrobenzene****	17.5	5.7	14	NMR	161
Trinitrotoluene	3.3	—	—	NMR	161
Dinitrobenzene	2.9	—	—	NMR	161
Tetramethyl-p-phenylenediamine	10.2	—	—	NMR	161
		CoMP***			
$P(C_6H_5)_3$	30.4	7.0	17	SP	123
$P(C_4H_9)_3$	12 000	13.3	27	SP	123
$P(OCH_3)_3$	45.1	6.9	15	SP	123
$S(CH_3)_2$	22.5	4.5	9	SP	123
$As(C_6H_5)_3$	3.5	5.2	15	SP	123
		CoTPP**			
DMSO*****	13 800	13.8	27	SP	230
		CoTPP(p-OCH_3)$_4$**			
DMSO*****	5900	8.0	10	SP	230
		Co1ECP***			
Pyridine	3388	6.8	7	SP	231
		Co2ECP***			
Piperidine	9549	6.0	3	SP	231
Pyridine	6456	8.8	13	SP	231
		Co3ECP***			
Piperidine	15 135	8.3	7	SP	231
Pyridine	2 457	7.5	8	SP	231
		Co4ECP***			
Piperidine	12 882	5.4	1	SP	231
Pyridine	4 677	8.5	12	SP	231

* 296 K.
** 298 K.
*** 293–299 K.
**** Solvent–$CDCl_3$.
***** Solvent–CCl_4, $K_2 = 430$ (for CoTPP) and $K_2 = 320$ [for CoTPP(p-OCH_3)$_4$]. Abbreviations: SPT = spectrophotometric titration; SP = spectrophotometric method; 1ECP = ethoxycarbonylporphyrins; 2ECP = di(ethoxycarbonyl)porphyrin; 3ECP = tri(ethoxycarbonyl)porphyrin; 4ECP = tetra(ethoxycarbonyl)porphyrin.

In contrast to the cobalt complexes, the copper complexes of ethoxycarbonylporphyrins coordinate pyridine and piperidine with greater difficulty (the values of $\lg K_S$ decrease from 0.2 to −0.8) and with smaller entropy changes ($-\Delta S$ changes from 16 to 24 e.u. for piperidine).[231] There is virtually no dependence on the number of ethoxycarbonyl groups.

The most numerous data on extracoordination have been obtained for iron-porphyrins. Studies on iron-porphyrins have been carried out for more than three decades. The first extensive investigations of the interaction of ferrous

and ferric protoporphyrins with hydroxide and cyanide ions as well as pyridine were carried out by Schak and Clark[232] in 1947.

The iron atom in porphyrin complexes has an especially high affinity of anions of the type of CN^-. The oxidation state of the initial iron atom plays a significant role in this. Thus the overall equilibrium constant for the addition of ligands in the extracomplexes $[(CN)_2FePP]^-$ is $K_{1,2} = 1.4 \times 10^{12}$, while the constant for $[(CN)_2FePP]^{2-}$ is $K_{1,2} = 8 \times 10^9$. At the same time the equilibrium constants for the dipyridine complex are $K_1 = 0.8$ and $K_2 = 5 \times 10^7$. The relative affinities of different types of ligands for Fe^{3+}-porphyrins vary in the sequence $CN^- \gg$ imidazoles $\gg$ pyridine[233], which indicates a significant role for π-binding of the extraligands by the iron-porphyrin. The accumulation of the negative charge in the porphyrin macroring then leads to destabilisation of the system. Anionic complexes are therefore more stable for Fe^{3+}-porphyrins and less stable for Fe^{2+}-porphyrins[1].

Since the mobility of *d* electrons diminishes with increase of the positive charge on the central atom, ferric porphyrins become less capable, relative to ferrous porphyrins, of the extracoordination of molecules (of the type of pyridine and oxygen) tending to form dative π-bonds. This ability is restored when one of the extraligands is a powerful electron pair donor. Mixed complexes of Fe^{3+}-porphyrins with cyano- and pyridine groups are therefore more stable than the corresponding Fe^{2+}-porphyrins {$K_{1,2} = 3.6 \times 10^{12}$ for (CN)(py)FePP and $K_{1,2} = 8 \times 10^{10}$ for $[(CN)(py)FePP]^-$ have been found}. Mixed π-ligands then entail a significant gain of the free energy ΔG compared with homogeneous ligands (2py, $2CN^-$).[1]

The central atoms in ferric and ferrous porphyrins exhibit a high affinity also in relation to other nitrogen-containing molecules as well as oxygen containing ligands (H_2O, OH^-, H_2O_2, CO, O_2). The study of the extracomplexes with H_2O and OH^- in an alkaline medium is greatly complicated by the dimerisation and greater degree of aggregation of metalloporphyrins, which makes the measurement of the thermodynamic parameters of extracoordination significantly more difficult[1]. This can probably explain the fact that only the values of K_S have been determined in the majority of studies on extracoordination equilibria[28,29,116,162,234].

An interesting study[117] was devoted to the thermodynamics of the extracoordination of pyridine and its substituted derivatives to the Fe^{2+}-porphyrins of the protoporphyrin group in benzene:

$$FeP + 2L \rightleftharpoons (L)_2FeP. \qquad (22)$$

The authors investigated the dependence of the thermodynamic parameters obtained from spectroscopic data on the nature of the extraligand and the structure of the porphyrin.

Thermodynamic parameters for the iron(II) and iron(III) complexes of 2,4-dicysteine-substituted mesoporphyrin have been determined spectrophotometrically[235] in aqueous solutions. In contrast to other ligands, extracoordination takes place stepwise in this instance. In terms of the changes in ΔH for the Fe^{3+}- and Fe^{2+}-porphyrins, the extraligands investigated can be arranged in the following sequences: CN^- > histidine > imidazole > pyridine; CN^- > pyridine > histidine > imidazole > *N*-acetyl-DL-methionine. The thermodynamic parameters of extracoordination obtained have been attributed[235] to changes in the degree of solvation of iron-porphyrin in a hydrophobic cavity within the haemoprotein and to the influence of the conformational changes in the aminoacid residues. This hypothesis has been confirmed by the values of ΔH and ΔS obtained for ferric cytochrome *c*.[236,237]

The stability of haemin in the extracoordination of histidine and imidazole to a series of peptides has been studied[28,29]. The values of $\lg K$ varied with the nature of the atomic environment of histidine in the range from 7.41 to 8.32. The authors[28] arrived at the interesting conclusion that the stability of the extracomplexes depends to a large extent on steric factors, i.e. on the bulk of the groups adjoining histidine. It has also been established[29] that the stability of the extracomplexes and the strength of the coordinate bond depend on the nature of the porphyrin system (on the basicity of the porphyrin) and the length and degree of branching of the extraligand chain. Table 8 indicates the limits of the variation of $\lg K_S$ for Fe-porphyrins with a series of histidine-containing ligands. Regrettably, these interesting communications[28,29] do not contain complete thermodynamic data.

Table 8. The limits of variation of $\lg K_S$ for the extracoordination of histidine-containing extraligands to Fe-porphyrins in chloroform[28,29].

MP	FeAEP(III)	FeMP d.m.e.	FeDP	FePP d.m.e.	FePP
$\lg K_S$	6.0—6.68	6.2—6.84	6.70—7.10	7.08—7.32	8.25—8.54

Among studies devoted to Fe-porphyrins, mention should also be made of that of Anusiem and Lumry[212], primarily because of the choice of the method of investigation: the thermodynamic parameters of the extracoordination of the azide ion to ferric haemoglobin were determined calorimetrically in water over a wide range of pH. The electrochemical reduction of the iron(III) complexes of a series of porphyrins has been investigated by cyclic voltammetry in the presence of substituted bipyridyls[238], forming extracomplexes with $K_S = 1 \times 10^{-3}$ for FeOAEP and 1.8×10^4 for FeTPP.

The influence of trinitrobenzene as a π-acceptor on the thermodynamics of the extracoordination of *N*-methylimidazole to (Cl)FeTPP was studied by ^1H NMR;[163] the authors suggest that trinitrobenzene can interact with the central atom and can reduce the affinity of the complex for a second *N*-methylimidazole molecule. The stability constants K_{S2} for the reaction of Fe-tetra-arylporphyrins with substituted imidazole and pyridine were determined by NMR [164] and the formation of a biligand extracomplex was discovered. Comparison of the observed values with the K_S obtained previously from electronic spectra led the authors[164] to the conclusion that the NMR method is suitable (subject to some limitations) for the determination of the stability constants and the stoichiometry of the formation of extracomplexes. It is noteworthy that, in the determination of the temperature variation of K_S by NMR, a large error is introduced due to the characteristics of the method, in the first place and high concentration of the metalloporphyrin, which causes its association.

It follows from Table 9 [164] that the influence of substituents in the *para*-position of the benzene rings of FeTPP on the values of K_{S_2} is very insignificant. The nature of the halogen in the porphyrin complex has a significant influence on the values of K_{S2}; here K_{S2} varies in the sequence I > Br $\gg$ Cl. The dependence of K_{S2} on the nature of the extraligand is not correlated with pK_B. The authors[164] obtained the approximate value $\Delta H \approx -26$ kcal mol^{-1} for 1-methylimidazole and $\Delta H = -15$ kcal mol^{-1} for 1-methylbenzimidazole. The

authors explain the difference between the ΔH by steric factors preventing extracoordination, i.e.the maximum overlap of the iron and nitrogen orbitals in the case of 1-methylbenzimidazole.

Table 9. The influence of the structure of the porphyrin and of the halogen on the K_{S2} of the iron-porphyrin complexes with 1-methylimidazole in $CDCl_3$ at 25 °C.[164]

Complex	K_{S2}
(Cl)FeTPP(*p*-OCH_3)	$(4.0\pm0.6)\cdot10^3$
(Cl)FeTPP(*p*-CH_3)	$(3.0\pm0.4)\cdot10^3$
(Cl)FeTPP	$(1.4\pm0.7)\cdot10^3$
(Cl)FeTPP(*p*-Cl)	$(0.65\pm0.10)\cdot10^3$
(Br)FeTPP(*p*-CH_3)	$\gtrsim10^6$
(I)FeTPP(*p*-CH_3)	$>10^6$
(Cl)FeOAEP	$(0.66\pm0.13)\cdot10^3$
(Cl)FeTPP*	25 ± 5
(Br)FeTPP(*p*-CH_3)	$(2.4\pm0.5)\cdot10^3$

*Temperature—45 °C; extraligand—1-methylbenzimidazole.

Analysis of the thermodynamic parameters of the extracoordination reactions is frequently difficult, because the values of K_S, ΔH, and ΔS were obtained under non-standard conditions. The choice of solvent exerts an extremely powerful influence on the parameters of the extracoordination reaction, which has been shown in relation to Fe-porphyrins[211,239] and Cu-porphyrins[231].

Cole et al.[211] justly assumed that, when account is taken of the solvation, the extracoordination equation must be written as follows:

$$Fe^{2+}PP\,(solv)_{n_1} + 2\,L\,(solv)_{n_2} \rightleftarrows (L)_2Fe^{2+}PP\,(solv)_{n_3} + n\,(solv)\ . \qquad (23)$$

It follows from Eqn.(23) that the nature of the interaction of the metalloporphyrin can be significantly different in solvents of different types. It has been shown for the reaction of FePP with pyridine and its substituted derivatives in various solvents that the changes in ΔH and ΔS on changing the solvent can be significantly greater than the changes introduced by the structure of the porphyrin and the nature of the extraligand. Depending on the nature of the solvent, the entropies vary by up to 50 e.u. and the ΔH by up to 17 kcal mol^{-1}.

Cole et al.[211] examined the possible energy contributions to ΔH: (1) the formation of a π-complex; (2) the formation of a charge-transfer complex; (3) hydrophobic interaction; (4) dipole orientation forces; (5) dispersion interaction; (6) hydrogen bonding. The postulated contributions to ΔS are due to the following factors: (1) hindered rotation of the molecule owing to the attachment of a second ligand; (2) restricted rotation due to the π-bonding of iron to the extraligand; (3) the formation of a solvate complex, etc. Analogous results have been obtained[231] for copper complexes of ethoxycarbonylporphyrins in reactions with nitrogen-containing heterocycles.

In a study of the interaction of (Cl)FeTPP with imidazole, Kedderis et al.[239] obtained virtually identical values of all the thermodynamic parameters for a series of solvents (acetone, chloroform, methylene chloride, and ethyl acetate). The errors quoted for the values of ΔH are puzzling; whereas the errors in ΔS are consistent with the accuracy of the method, those for ΔH are too low (for the spectrophotometric method) at least by a factor of 10. The authors[239] were unable to explain the discrepancy with the results of Cole et al., but they attempted to relate it to the different charges on Fe in the systems investigated[211,239].

Comparison of the data in Table 9 [239] leads to the conclusion that the free energies of extracoordination reactions involving iron-porphyrins and their enthalpy and entropy components depend markedly on the structure of the porphyrin and the nature of the extraligand and the solvent. Low values of ΔH show that they include the effects of the solvation of the reactant in extracoordination to Fe-porphyrins, which can be inferred from the very low entropies. These data demonstrate clearly the important role of the π-bonding of extraligands to $Fe^{2+}P$.

The data presented for the thermodynamics of extracoordination demonstrate a series of interesting and practically important relations for the metalloporphyrins of certain metals. However, the lack of systematic studies (in which one or several variables are varied, while keeping a number of factors constant) rules out the possibility of wider generalisations and conclusions necessary for the solution of problems of technical and enzyme catalysis on metalloporphyrins.

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It follows from the data presented that there exist factors favouring the formation of stable extracomplexes of metalloporphyrins. They include the following: (1) the increase of the effective positive charge on the central metal atom; the σ-electron-donating and π-electron-accepting capacities of the ligands; the latter is important in extracoordination to low-spin metal complexes whose *d* orbital is more than half-filled; (3) the weakening of the solvation and acid–base interaction of the extraligands with the medium; (4) the decrease of the steric hindrance to extracoordination from the side of the extraligand. The last condition is particularly significant for the formation of biligand extracomplexes of porphyrins.

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