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Synthesis, structure and properties of coordination compounds of iron phthalocyanines and their analogues

V N Nemykin, I N Tret'yakova, S V Volkov, V D Li, N G Mekhryakova, O L Kaliya, E A Luk'yanets

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Abstract. Methods for the synthesis of various coordination compounds of iron phthalocyanines and their closest structural analogues, *viz*., iron porphyrazines and naphthalocyanines, their structures, properties and applications are surveyed. The bibliography includes 230 references.

I. Introduction

Haem-containing biological systems play a unique role in living nature. These systems are involved in oxygen binding and transport (haemoglobin and myoglobin) and in catalysis of vital reactions (oxygenases, catalases, peroxidases and cytochromes).[1,2]

The closest synthetic analogues of porphyrins, *viz*., phthalocyanines (tetraazatetrabenzoporphins) and related compounds, find wide applications primarily as dyes, pigments and catalysts of oxidative desulfurisation of hydrocarbons.[3,4] In recent years, these compounds have also been examined and used as components of gas sensors, electrochromic materials, passive laser valves and isolators for amplifying stages of solid-state and chemical lasers. These compounds have also found use as antimicrobial agents and photosensitisers in the photodynamic therapy of cancer.[5] In the last decades, catalysts exhibiting high oxidase and peroxidase activities have been constructed based on phthalocyanines.[3] Iron-containing complexes have particular promise. Increased scientific and practical interest in these complexes stems from the fact that they are characterised by a great diversity of coordination and redox forms.[6–11] In spite of the fact that different aspects of chemistry and applications of iron phthalocyanines and their analogues have been considered in a great number of publications and patents, many questions about the structures and the valent and spin states of the major coordination forms of these compounds remain as the subjects of discussion.

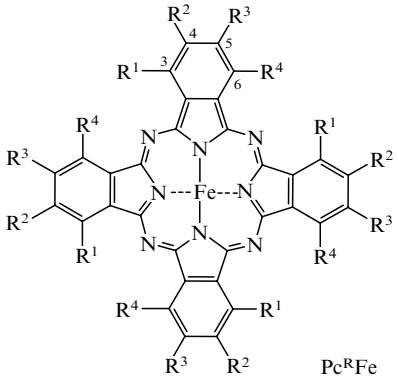
The properties and applications of selected coordination forms of complexes of iron phthalocyanines and their analogues have been surveyed in several fundamental reviews.[3,4,9–11] However, the systematic analysis of a wide range of these compounds is lacking in the literature. In the present review, modern data on the synthesis and coordination chemistry of iron phthalocyanines and their analogues are considered and analysed.

V N Nemykin, I N Tret'yakova, S V Volkov V I Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, prosp. Palladina 32/34, 252680 Kiev, Ukraine.
Fax (38-044) 444 30 70. Tel. (38-044) 444 32 70
E-mail: victor_nemykin@yahoo.com (V N Nemykin),
(38-044) 444 10 11 (S V Volkov)
V D Li, N G Mekhryakova, O L Kaliya, E A Luk'yanets State Scientific Centre of the Russian Federation 'NIOPIK', ul. Bol'shaya Sadovaya 1/4, 103787 Moscow, Russian Federation. Fax (7-095) 254 12 00.
Tel. (7-095) 408 59 47 (N G Mekhryakova), (7-095) 254 98 66
E-mail: jerrik@cityline.ru (O L Kaliya), rmeluk@cityline.ru
(E A Luk'yanets)

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II. Synthesis and properties of iron phthalocyanines and their analogues

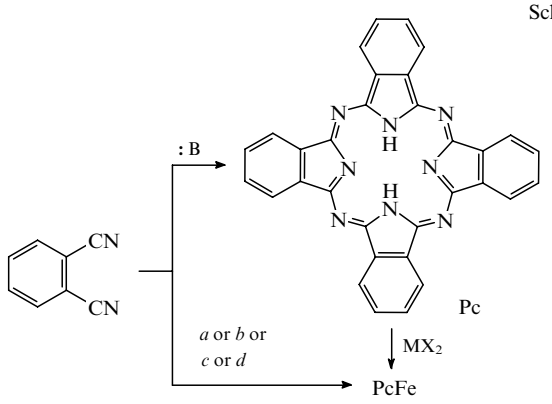
In 1928, chemists from the 'Scottish Dyes Ltd.' found a dark-blue compound deposited on the walls of a reactor in the synthesis of phthalimide from phthalic anhydride and ammonia. This compound was extremely stable with respect to acids and alkalis, and it was suggested that it has the structure of PcFe (Pc^RFe, where $R^1 = R^2 = R^3 = R^4 = H$) based on the results of a detailed study of its properties and structure.



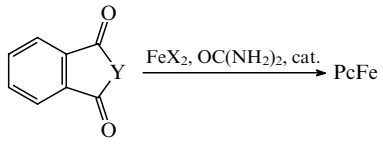
Pc^RFe

As a result, a new class of macrocyclic tetrapyrrole compounds, *viz*., phthalocyanines, has been discovered.[15–17] The synthesis of PcFe was described in detail for the first time in the classical papers of Linstead.[16,17] Presently, PcFe and its numerous R-substituted derivatives (Pc^RFe) are prepared by reactions of various derivatives of phthalic acid with iron or its compounds, which are often performed in the presence of catalysts (Scheme 1). In all cases, the reactions are carried out either in a melt of the reagents (the sintering method) or in high-boiling organic sol-

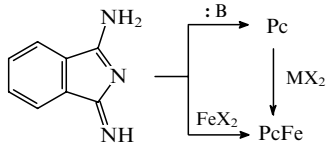
Scheme 1



(*a*) FeX_2; (*b*) $Fe(CO)_5$; (*c*) $FePy_4Cl_2$; (*d*) Fe.



Y = O, NH.



vents.[3,4,10,11] Thus heating of phthalonitrile with iron(II) hydroxide in trichlorobenzene containing 10% of quinoline afforded PcFe in 73% yield.[18] Boiling of phthalonitrile with iron pentacarbonyl in 1-chloronaphthalene gave PcFe in 50% yield. In the latter case, there was virtually no need for further purification of the product.[19,20] The syntheses of PcFe from phthalonitrile and $FePy_4Cl_2$ (in yields of up to 70%)[21] or from phthalic anhydride, urea and powdered iron (or its compounds) in the presence of different catalysts (boric acid, ammonium molybdate or titanium chloride) (in yields of up to 65%) were described; however, the purities of the final product were often not reported.[22–24] Iron phthalocyanine can also be synthesised by metallation of metal-free phthalocyanine (Pc) prepared from the diimino derivative of isoindolinedione or phthalonitrile in the presence of a base (**:B**). A convenient procedure for the preparation of PcFe and its derivatives by heating the reagents with the use of microwave radiation was proposed.[25] The latter procedure afforded the highly pure (up to 97%) target product in high yields (up to 80%). Iron phthalocyanine was also formed as a result of macrocycle contraction in the reaction of the so-called uranyl superphthalocyanine, which is a pentadentate analogue of phthalocyanine, with iron salts.[26] Substituted iron phthalocyanines are synthesised according to procedures virtually identical to those used for the preparation of PcFe. Complexes Pc^RFe containing different numbers of substituents R, where R is the halogen atom or the alkyl, aryl, nitro, alkoxy, aryloxy, alkylthio, arylthio, arylsulfonyl, polyfluoroalkoxy, polyfluorosulfamoyloxy, carboxy, sulfo, *etc*. groups, were described in the literature.[4,6–8,27–36]

Final purification of complexes was carried out by high-temperature sublimation *in vacuo* or by removal of ligands (L) from bisaxially coordinated complexes of the general formula Pc^RFeL_2 on heating *in vacuo* or under a stream of an inert gas.[6–14]

Polymeric compounds containing the PcFe fragments can be prepared in a way analogous to that for the preparation of substituted iron phthalocyanines.[37–40] The formation of polymeric PcFe by the reaction of pyromellitic acid, an iron salt and urea in the presence of a catalyst was studied in detail.[40] The Mössbauer spectra of the resulting polymer contain four doublets belonging to polymeric and monomeric complexes as well as to oxidation products containing the phthalocyanine fragments. After purification of the polymer by gel permeation chromatography and its heating to 300 °C, the Mössbauer spectra exhibit only one doublet with the parameters characteristic of the $[PcFe^{II}]_n$ complex.

Like the majority of phthalocyanine complexes with other metals, PcFe can occur in different crystal modifications.[4,12,14] According to the data from X-ray diffraction analysis, the environment about the iron ion in one of these modifications, *viz*., in the β-modification of PcFe, is a pseudooctahedron formed by four isoindole nitrogen atoms of the virtually planar phthalocyanine ligand and two *meso*-nitrogen atoms of the adjacent PcFe molecules (Table 1).[41] The magnetic moments (μ_{eff}) for different specimens of PcFe at room temperature are in the range of 3.7–4.5 μ_B.[51–53] The Mössbauer spectra of a series of Pc^RFe complexes in which the σ-donor and π-acceptor properties of the peripheral substituents vary over a rather wide range were examined (Table 2). The parameters of the Mössbauer spectra δ and ΔE_Q for these complexes, which reflect the character of the Pc–Fe interaction, should correlate with the Hammett constants (σ). However, with the aim of giving an adequate account of the effect of substituents in the phthalocyanine macrocycle on the Mössbauer parameters, the authors[27,28] had to introduce two arbitrary additional parameters describing the σ-donor and π-acceptor properties of the substituents (Σ and Π, respectively).

Table 1. Structures of iron phthalocyanine, its biaxially coordinated complexes and their analogues established by X-ray diffraction studies.

Complex	Oxidation state of iron	Coordination polyhedron	Bond lengths /Å		Ref.
			Fe–N(Pc)	Fe–L	
PcFe	+2	N_4	1.926, 1.927		41
$[PcFe]^-$	+1/+2	N_4	1.910		42
$[PcFe]^{2-}$	+1/+2	N_4	1.910		42
$PcFe(DMSO)_2$	+2	N_4S_2	1.931, 1.951	2.308	43
$PcFe(4\text{-}MeC_5H_4N)_2$	+2	N_6	1.932, 1.937	2.040	44
$PcFe(MeIm)_2$	+2	N_6	1.926, 1.955	1.946	45
$PcFe(4\text{-}MeC_5H_{10}N)_2$	+2	N_6	1.929, 1.930	2.119	46
PcFe(CO)(DMF)	+2	N_4OC	1.889	1.72 (CO), 2.07 (O)	47
$1,2\text{-}NcFe(cyclo\text{-}C_6H_{11}NC)_2$	+2	N_4C_2	1.936, 1.949	1.911	48
$1,2\text{-}Nc^tFe(Bu^tNC)_2$	+2	N_4C_2	–	1.913	49
PNP[PcFe(CN)$_2$]	+3	N_4C_2	1.939, 1.957	1.976	50

Note. MeIm is *N*-methylimidazole, 1,2-NcFe is iron 1,2-naphthalocyanine, $1,2\text{-}Nc^tFe$ is tetrakis(7-*tert*-butyl)-substituted 1,2-NcFe, PNP is the triphenylphosphineimmonium cation.

Table 2. Parameters of Mössbauer spectra of the Pc^RFe complexes.

R^1	R^2	R^3	R^4	T/K	δ [a] /mm s^{-1}	ΔE_Q /mm s^{-1}	Ref.
H	H	H	H	4.2	0.48	2.70	28
				111	0.736 [b]	2.601	54
				163	0.691 [b]	2.609	
				203	0.667 [b]	2.604	
				298	0.634 [b]	2.581	
H	$CO_2C_{10}H_{21}$	H	H	4.3	0.29	2.78	28
				78.8	0.29	2.71	
				298	0.22	2.61	
H	$CO_2C_{10}H_{21}$	$CO_2C_{10}H_{21}$	H	4.2	0.23	2.48	28
				79.3	0.20	2.50	
				298	0.17	2.48	
H	$C(O)N(C_{10}H_{21})C(O)$		H	4.3	0.30	1.96	28
				79.3	0.27	1.96	
				298	0.16	1.96	
H	NO_2	H	H	4.3	0.22	1.99	28
				78.5	0.22	1.99	
				298	0.15	2.00	
Cl	Cl	Cl	Cl	4.5	0.32	1.72	28
				78.7	0.32	1.65	
				291	0.25	1.69	
H	CN	CN	H	4.3	0.27	1.56	28
				79.0	0.27	1.56	
				298	0.20	1.56	
H	Me	Me	H	5.1	0.49	2.66	27
				79	0.48	2.67	
				297	0.38	2.58	
H	OCH_2O		H	4.6	0.47	2.88	27
				79	0.47	2.80	
				292	0.37	2.61	
H	OMe	OMe	H	4.2	0.48	2.54	27
				79	0.46	2.53	
				297	0.33	2.49	
H	Bu^t	H	H	79	0.43	2.42	27
H	OBu^i	H	H	4.2	0.28	2.91	27
				79	0.28	2.91	
				299	0.20	2.53	
H	SPh	H	H	4.4	0.24	1.38	27
				79	0.23	1.37	
				296	0.14	1.36	
H	CO_2H	CO_2H	H	77	0.238	2.554	9
				293	0.137	2.498	
H	CO_2H	H	H	77	0.297	2.923	9
H	$(CH_2)_4$		H	4.3	0.47	2.36	27
				79	0.46	2.31	
				299	0.37	2.28	
				293	0.36	2.21	55

[a] Relative to metallic iron; [b] relative to sodium nitroprusside.

The Σ value is larger for stronger σ-donors, whereas the Π value is larger for stronger π-donor and weaker π-acceptor. The Mössbauer parameters are related to the Σ and Π constants by the following equations:

$$\delta = -\Sigma + \Pi,$$

$$\Delta E_Q = a\Sigma - b\Pi + c,$$

where a, b and c are constants and $a > b > 0$. The Mössbauer spectra of all the Pc^RFe complexes studied are characterised by high and virtually temperature-independent quadrupole splitting (see Table 2) typical of iron(II) complexes with the intermediate ($S = 1$) spin state.[27, 28, 41, 51]

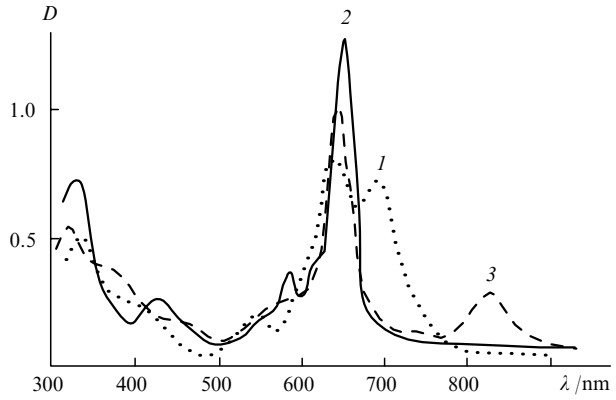
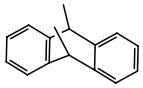


Figure 1. Electronic absorption spectra of iron(II) tetrakis(4-*tert*-butyl)phthalocyanine (Pc^tFe) in dry degassed benzene (*1*), Pc^tFePy_2 in benzene with an admixture of pyridine (*2*) and HPc^tFeCl in benzene (*3*) ($c \approx 10^{-3}$ mol litre^{-1}, $l = 0.01$ cm).

The electronic absorption spectra of PcFe in the gas phase and in noncoordinating solvents depend on the procedure for the preparation and the purity of the specimen. In our opinion, the most reliable data were obtained for sublimed specimens of PcFe dissolved in naphthalene at 110 °C in an atmosphere of helium.[56] Bands similar in shape and position were observed in the electronic absorption spectra of benzene solutions of Pc^RFe under an inert atmosphere (Table 3, Fig. 1)[6, 7] The spectra of Pc^RFe both in the gas phase[61] and in noncoordinating solvents[6, 7, 56] are untypical of the Pc^RM complexes (M is metal).[61, 62] For example, the electronic absorption spectra of iron(II) tetrakis(4-*tert*-butyl)phthalocyanine (Pc^tFe) always have several overlapping bands with approximately equal intensities in the long-wavelength region (580 – 750 nm), whereas this region in the spectrum of its bisaxially coordinated adduct Pc^tFePy_2 is typical of the Pc^RM complexes (Fig. 1). (It should be noted that axial coordination in the Pc^RM complexes of other metals affects rather slightly the electronic absorption spectral patterns.) Originally, this anomaly was attributed to the fact that the Pc^RFe complexes are strongly aggregated in noncoordinating solvents.[29] However, more recent studies of Pc^RFe complexes containing bulky substituents at the α position of the phthalocyanine macrocycle did not confirm this suggestion. Thus the spectral patterns of both sterically unhindered complexes and complexes containing bulky substituents, which prevent intermolecular aggregation (for example, the 2,4,6-trimethylphenyl substituents), are approximately identical.[7] In this connection and taking into account that the planar-square environment is untypical of iron(II) complexes, it was suggested[7] that Pc^RFe complexes have a tetrahedrally distorted geometry, which leads to a change in the electronic absorption spectra.

The configuration of the ground electronic state of Pc^RFe has been discussed in the literature over a long period. In the late 1960s, based on the results of Mössbauer spectroscopy (including the data obtained in magnetic fields), Dale postulated that the ground electronic state of the iron ion in PcFe has the $^3E_g[(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1]$ configuration.[51, 63] Using the data on magnetic susceptibility of PcFe, Lever[53] postulated another configuration of the iron ion, *viz.*, $^3A_{2g}[(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^2]$. Subsequent quantum-chemical calculations[64, 65] and studies of the Mössbauer spectra of a wide range of substituted iron phthalocyanines[27, 28] made it possible to state reliably that the ground electronic state of the iron ion in the compounds under study has the $^3E_g[(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1]$ configuration. Apparently, the sole exception is iron terakis(4-phenylthio)phthalocyanine, which has anomalous Mössbauer parameters (see Table 2). As a consequence, the configuration of the ground electronic state of

Table 3. Electronic absorption spectra of the Pc^RFe and TAP^RFe complexes in benzene.

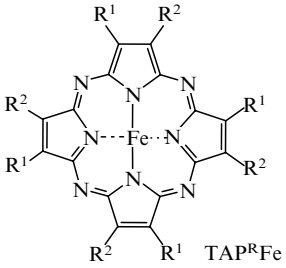
R^1	R^2	R^3	R^4	Positions of bands in electronic absorption spectra/nm ($10^{-5}\varepsilon$)	Ref.
Pc^RFe					
H	Bu^t	H	H	690 sh, 647, 550, 350	6
2,4,6-$Me_3C_6H_2$	H	H	H	690 sh, 647(0.60), 550(0.18), 460 sh, 410 sh, 352(0.46)	7
2,4,6-$Me_3C_6H_2$	H	Bu^t	H	710 sh, 653, 550, 490 sh, 450 sh, 354	7
H	Bu^i	Bu^i	H	710 sh, 660(0.72), 562(0.16), 470 sh, 420 sh, 345(0.55)	7
TAP^RFe					
Et	Et			659 sh, 590, 561 sh, 537 sh, 489, 474 sh, 427, 339	57
Ph	Ph			626, 443, 330 (see[a])	58
				648(1), 550(0.34), 386(1.24), 322(1.93)	59
4-$Bu^tC_6H_4$	4-$Bu^tC_6H_4$			635(4.41), 595(4.30), 455(4.38), 345(4.85)	60

[a] The parameters of Mössbauer spectra at 300 K relative to metallic iron: $\delta = 0.05$ mm s^{-1}, $\Delta E_Q = 2.53$ mm s^{-1}.[58]

the iron ion in this compound was described as $^3A_{2g}[(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^2]$.[27]

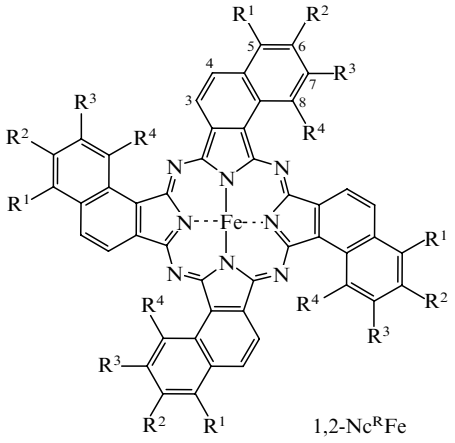
The reaction of PcFe with potassium *tert*-butylthiolate in the presence of 2,2,2-cryptand (C⊂222) afforded the one-electron-reduced complex $[C\subset222]^+[PcFe]^-$.[42] The reaction of PcFe with $LiAlH_4$ and 18-crown-6 (18-C-6) in a THF solution yielded the two-electron-reduced complex $[Li_2(THF)(18\text{-}C\text{-}6)_2]^{2+}[PcFe]^{2-}$.[42] In both cases, the central iron atom is coordinated by four nitrogen atoms of the isoindole fragments of the planar phthalocyanine ligand (see Table 1). Based on the results of spectral studies, the following two schemes of the equilibrium of isoelectronic forms of the one- and two-electron-reduced complexes were proposed: $[Fe^IPc^{2-}] \rightleftharpoons [Fe^{II}Pc^{3-}]$ and $[Fe^IPc^{3-}] \rightleftharpoons [Fe^{II}Pc^{4-}]$.

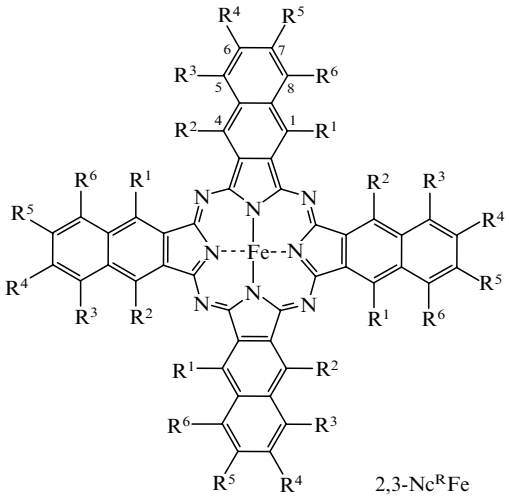
Complexes of iron tetraazaporphin (TAP^RFe) have been poorly studied.[6, 57–60, 66]



Presently, only octaphenyl-[58, 60] octaethyl-,[57] dibenzobarrelene-[59, 66] and octakis(4-*tert*-butylphenyl)-containing[60] complexes (see Table 3 and notes therein) are reliably characterised by electronic absorption spectra, Mössbauer spectra and magnetic susceptibility data. On the basis of the data from magnetic susceptibility (3.8[58] and 3.82 μ_B[57] for octaphenyl- and octaethylporphyrazine iron complexes, respectively) and Mössbauer spectroscopy, all TAP^RFe complexes were assigned to iron(II) compounds characterised by the intermediate ($S = 1$) spin state.

Due to the low stability of iron 1,2-naphthalocyanine complexes (1,2-Nc^RFe) and, particularly, iron 2,3-naphthalocyanine complexes (2,3-Nc^RFe), which are prone to oxidation, reliable data on their properties in solutions are lacking. However, these complexes are stable in the solid state, which made it possible to measure their Mössbauer spectra. According to the available results, 2,3-NcFe belongs to iron(II) compounds with the intermediate ($S = 1$) spin.[27]





Fused aza analogues of PcFe, *viz*., complexes of tetrakis(2,3-quinoxalino- and -quinolino)porphyrazines, were also synthesised and their thermal stabilities have been examined.[67]

III. Bisaxially coordinated complexes of iron phthalocyanine and its analogues

1. Iron(II) complexes

Coordinatively unsaturated compounds Pc^RFe readily form axially coordinated diamagnetic low-spin ($S = 0$) complexes of

the general formula Pc^RFeL_2 with nitrogen-,[15,17,46,68–73] phosphorus-,[74] sulfur-[47] and carbon-containing[75,76] σ-donor and (or) π-acceptor ligands (L). In addition, mixed complexes with different axial ligands of the general formula $Pc^RFeL^1L^2$ can be formed.[76–78]

The formation of bisaxially coordinated $PcFeL_2$ complexes, where L are nitrogen bases, was investigated in detail by kinetic methods.[77–84] According to concepts developed in these studies, the stepwise successive coordination of two ligand molecules proceeds by a dissociation mechanism

$$(solv)_2PcFe \rightleftharpoons (solv)PcFe \overset{L}{\rightleftharpoons} (solv)PcFeL \rightleftharpoons PcFeL \overset{L}{\rightleftharpoons} PcFeL_2.$$

Among complexes of the Pc^RFeL_2 type, compounds containing nitrogen bases of the heteroaromatic or aliphatic series as axial ligands were studied in most detail.[46,68,69,71,72] Complexes with ligands containing the pyridine nitrogen atoms (which act simultaneously as σ-donors and π-acceptors) are more stable compared to complexes containing aliphatic amines (pure σ-donors).[46,71,73] Stynes[78] studied the kinetics of replacement of the axial ligand in $PcFeL_2$, where L is methylimidazole, pyridine or piperidine, by benzyl isocyanide. The direct replacement of one axial ligand was observed only in the dark. When illuminated in the presence of L, the resulting complex PcFeL(BnNC) reverted to $PcFeL_2$.[78]

Pyridine derivatives containing substituents at the β and γ positions enter into the reaction of axial coordination, whereas substituents at the α position inhibit this reaction.[69] Iron phthalocyanine also readily reacts with primary aliphatic amines, including such sterically hindered compounds as *tert*-butylamine.[71] The range of dialkylamines, which can be axially coordinated to Pc^RFe, is narrower. Branching of the carbon skeleton at the α-carbon atom [Pr^i_2NH, (cyclo-$C_6H_{11})_2NH$] prevents the preparation of axially coordinated complexes of the $PcFeL_2$ type.[46,71] In other words, as in the case of pyridine-type ligands, the choice of dialkylamines which can be axially coordinated is limited by steric factors. It is even more difficult to prepare axially coordinated complexes of this type with trialkylamines. Thus an unstable complex with quinuclidine is the only compound of this type, which was isolated and characterised by spectroscopic methods.[72]

Unlike tertiary amines, trisubstituted phosphines and phosphites readily form complexes with PcFe.[74,85,86] Compounds of the Pc^RFeL_2 type, where L are aliphatic or aromatic isocyanides,[75] carbon monoxide[47,76–78] or the cyanide ion,[68,87,88] are also well studied. Of complexes containing the Fe–S bond, only those with tetrahydrothiophene and DMSO have been described.[43,47] Data on analogous complexes containing the Fe–O bonds are lacking in the literature. Among mixed-ligand complexes of the $Pc^RFeL^1L^2$ type, compounds PcFe(CO)L (where L is nitrogen-, sulfur- or oxygen-containing ligands),[47,76,78,87] $Pc^RFe(CN)L$ (where L is a nitrogen-containing ligand)[50] and $PcFeL^1L^2$ (where L^1 and L^2 are either two different nitrogen-containing ligands[77] or isocyanide and nitrogen-containing ligands[78]) were studied.

The structures of several complexes of the $PcFeL_2$ type, *viz*., $PcFe(4\text{-}MeC_5H_4N)_2$, $PcFe(MeIm)_2$, $PcFe(DMSO)_2$, $PcFe(4\text{-}MeC_5H_{10}N)_2$ and PcFe(CO)(DMF), were established by X-ray diffraction analysis (see Table 1).[43–47] It should be noted that the axial ligands in $PcFe(4\text{-}MeC_5H_4N)_2$ and $PcFe(MeIm)_2$ are located in two mutually perpendicular planes, whereas these ligands in $PcFe(4\text{-}MeC_5H_{10}N)_2$ are virtually coplanar. This suggests a substantial contribution of back π-bonding in the $PcFe(4\text{-}MeC_5H_4N)_2$ and $PcFe(MeIm)_2$ complexes. For the same reason, the Fe–CO distance in the PcFe(CO)(DMF) complex is shorter than the corresponding distances in the complexes with other axial ligands and shorter than the Fe–N(Pc) distance (see Table 1). Analogous effects were also observed in complexes with strong π-acceptors, such as isocyanide ligands (see Table 1).[48,49]

The electronic absorption spectra of $PcFeL_2$ containing axial ligands of virtually all known types were measured.[46,62,68–74,77–84,87] These spectra consist of a long-wavelength Q band at 660 nm which has vibrational structure, a charge-transfer band (CTB) at 425 nm and a B band at 330 nm. The σ-and π-acceptor properties of the axially coordinated ligands in these complexes most substantially affect the positions of the charge-transfer bands (Table 4).[68,69,71,87] The above-mentioned effect has been examined many times (see, for example, Refs 46, 68, 69 and 71). Based on the results of calculations by the extended Hückel method, Goutermann and coworkers[64] were the first to assign this band to charge transfer from the central iron ion to the unoccupied orbital of the axial ligand (CTB Fe → L). More recently, Dale[68] studied a series of $PcFeL_2$ complexes, where L is pyridine, imidazole, butylamine, piperidine, ammonia or the cyanide ion, and assigned this band to Fe → Pc charge transfer and related its position to the basicity of the axial ligand. Analogous correlations were also observed for a wide range of pyridine[69] and alkylamine[71] ligands. Ouedraogo and coworkers[69] followed Goutermann in attributing this band to Fe → L charge transfer. However, Stillman and coworkers[87] examined electronic absorption spectra as well as magnetic circular dichroism spectra of a series of $PcFeL_2$ complexes and demonstrated that the above-mentioned band belongs to a transfer in which one of the states is degenerate. The transition from the $3d_\pi$ orbitals of the central iron atom with symmetry e_g to the unoccupied π* orbital of the phthalocyanine ligand with the symmetry b_{1u} is the only allowed transition for the low-spin d^6 configuration of the Fe(II) ion in a complex with D_{4h} symmetry. The axial coordination of the purely σ-donor ligands, for example, of alkylamines, occurs primarily owing to the interaction between the d_{z^2} orbital of the central atom and the *n* orbital of the ligand. The enhancement of the σ-donor character of the axial ligand leads to an increase in the population of the d_{z^2} orbital of the iron atom and, consequently, to its destabilisation as well as to destabilisation of the d_π orbitals, which, in turn, leads to a bathochromic shift of the charge-transfer band.[71,87] The enhancement of the π-acceptor character of the axial ligands results in direct stabilisation of the d_π orbitals of the central atom and, as a consequence, in an increase in the energy of the charge-transfer band. Thus this band is observed at 450, 430, 415 and 400 nm for the $PcFeL_2$ complexes with the cyanide (σ- and π-donors),[87,88] alkylamine (pure σ-donors),[46,68,71] pyridine (σ-donors and π-acceptors)[68,69,87,90] and isocyanide (weak σ-donors and strong π-acceptors)[75,76,78] ligands, respectively, (see Table 4). To obtain an adequate correlation between the basicity of the axial ligands and the position of the charge-transfer band, the steric properties of these ligands should also be taken into account.[71] A new approach to the estimation of the positions of charge-transfer bands in the spectra of the $PcFeL^1L^2$ complexes with ligands of all types on the basis of their electronic structures and steric properties using second-order perturbation theory was proposed.[46,92] The electronic absorption spectra of the $PcFeL_2$ complexes with axial pyridine-type ligands containing acceptor substituents have an additional band at 500 nm. This band was assigned to Fe → L charge transfer.[69] It should be noted that the nature of the solvent has differing effects on the position of the charge-transfer band in Pc^RFeL_2 complexes depending on the type of axial ligand. Thus if the axial ligands can form a dative π bond (pyridine-type ligands, isocyanides, *etc*.), the position of the charge-transfer band depends only slightly on the nature of the solvent. For example, the charge-transfer band for the $PcFePy_2$ complex was observed at 415, 413.5 and 412 nm in DMSO, pyridine and dichloromethane, respectively.[68,69,79,87] In the case of alkylamines and, particularly, polyamines, which can form an intramolecular hydrogen bond, the position of this band varies over a wide range depending on the nature of the solvent.[68,69,71,87] For example, the charge-transfer band for the $PcFe(NH_3)_2$ complex is observed at 440 and 426 nm in DMSO[68] and dichloromethane,[87] respectively. Probably, this behaviour reflects a decrease in the bond energy on going to the Pc^RFeL_2 complexes with pure σ-donor ligands. However, there is no direct evidence for this suggestion.

Table 4. Electronic absorption spectra of $PcFeL_2$ complexes.

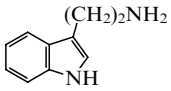
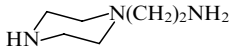
L	Solvent	Positions of bands in electronic absorption spectra/nm ($\log \varepsilon$)	Relative intensity	Ref.
NH_3	PhH – L	664, 637, 604, 425, 335	2.08 : 0.72 : 0.61 : 0.3 : 1	71
$MeNH_2$	PhH – L	664, 637, 603, 427.5, 335	2.05 : 0.56 : 0.47 : 0.31 : 1	71
Pr^nNH_2	PhH – L	664, 637, 605, 427.5, 334	1.47 : 0.81 : 0.57 : 0.28 : 1	71
Pr^iNH_2	PhH – L	663, 636, 604, 424.5, 334	1.64 : 0.7 : 0.64 : 0.28 : 1	71
Bu^nNH_2	PhH – L	664, 637, 605, 427, 334	1.58 : 0.71 : 0.6 : 0.35 : 1	71
Bu^sNH_2	PhH – L	663, 636, 604, 425, 334	2.06 : 0.8 : 0.69 : 0.32 : 1	71
Bu^iNH_2	PhH – L	663, 635, 606, 427, 332	1.37 : 0.61 : 0.52 : 0.25 : 1	71
Bu^tNH_2	PhH – L	661, 634, 600, 421.5, 331	2.23 : 0.68 : 0.57 : 0.32 : 1	71
n-$C_5H_{11}NH_2$	PhH – L	665, 636, 606, 428, 331	1.45 : 0.55 : 0.47 : 0.24 : 1	71
n-$C_6H_{13}NH_2$	PhH – L	663, 636, 604, 427.5, 333	1.75 : 0.72 : 0.51 : 0.21 : 1	71
$(EtO)_3Si(CH_2)_3NH_2$	PhH – L	664, 637, 605, 428, 334	1.65 : 0.64 : 0.55 : 0.29 : 1	71
$CF_3CH_2NH_2$	PhH – L	655, 628, 595, 416, 330	1.82 : 0.6 : 0.52 : 0.29 : 1	71
cyclo-$C_6H_{11}NH_2$	PhH – L	663, 636, 603, 425, 332	1.61 : 0.56 : 0.49 : 0.33 : 1	71
$BnCH(NH_2)Me$	PhH – L	662, 635, 602, 425, 335	1.48 : 0.57 : 0.48 : 0.27 : 1	71
	PhH – L	664, 637, 604, 427.5, 333	1.70 : 0.52 : 0.46 : 0.29 : 1	71
$Ph(CH_2)_2NH_2$	PhH – L	664, 635, 603, 426.5, 333	–	71
$BnNH_2$	PhH – L	663, 636, 604, 424, 334	1.45 : 0.65 : 0.55 : 0.29 : 1	71
	PhH – L	664, 637, 604, 426.5, 330	1.50 : 0.57 : 0.49 : 0.24 : 1	71
	PhH – L	665, 640, 607, 430, 334	1.44 : 0.66 : 0.58 : 0.29 : 1	71
cyclo-$(C_6H_{10})(NH_2)_2$	PhH – L	666, 639, 605, 432, 335	2.39 : 0.74 : 0.63 : 0.36 : 1	71
$NH_2(CH_2)_2NH_2$	CH_2Cl_2	667, 640, 606, 435, 330	–	89
$NH_2(CH_2)_3NH_2$	PhH – L	665, 639, 607, 433, 334	1.72 : 0.75 : 0.69 : 0.32 : 1	71
$NH_2(CH_2)_4NH_2$	PhH – L	666, 640, 608, 433, 334	1.84 : 0.81 : 0.71 : 0.35 : 1	71
$NH_2(CH_2)_5NH_2$	PhH – L	665, 636, 604, 429, 337	2.51 : 0.78 : 0.66 : 0.37 : 1	71
$NH_2(CH_2)_7NH_2$	PhH – L	664, 636, 603, 428, 334	3.41 : 1 : 0.87 : 0.43 : 1	71
$HO(CH_2)_2NH(CH_2)_3NH_2$	PhH – L	670, 640, 608, 437, 338	1.88 : 0.67 : 0.6 : 0.45 : 1	71
Pip	PhH – L	663, 636, 605, 426.5, 334	2.01 : 0.71 : 0.65 : 0.29 : 1	71
	DMSO – L	663, 642, 602, 434	–	69
	CH_2Cl_2	659, 598, 425, 340	–	87
4-$MeC_5H_{10}N$	PhH – L	662, 635, 602, 427, 335	2.02 : 0.61 : 0.51 : 0.35 : 1	71
Mor	PhH – L	660, 633, 601, 423, 332	2.05 : 0.82 : 0.66 : 0.28 : 1	71
Et_2NH	PhH – L	662, 637, 602, 426, 333	1.61 : 0.53 : 0.45 : 0.32 : 1	71
Pr_2NH	PhH – L	663, 637, 603, 426.5, 334	1.61 : 0.52 : 0.44 : 0.28 : 1	71
Py	DMSO – L	655(5.07), 593(4.47), 413(4.32), 332(4.82)	–	79
	CH_2Cl_2	651, 591, 412, 328	–	68
3-MeC_5H_4N	$CHCl_3$	655, 630, 595, 415	–	69
4-MeC_5H_4N	$CHCl_3$	656, 630, 595, 412.5	–	69
	$CHCl_3$	656, 594, 410, 328	–	90
	CH_2Cl_2	652, 592, 413, 331	–	87
3,4-$Me_2C_5H_3N$	$CHCl_3$	656, 630, 595, 412.5	–	69
3,5-$Me_2C_5H_3N$	$CHCl_3$	656, 630, 595, 415	–	69
3-OHC_5H_4N	DMSO	656, 630, 595, 412	–	69
4-OHC_5H_4N	DMSO	662, 635, 602, 432	–	69
3-ClC_5H_4N	$CHCl_3$	653, 627, 592, 446, 407	–	69
4-ClC_5H_4N	DMSO	680, 642, 613, 555	–	69
3,5-$Cl_2C_5H_3N$	$CHCl_3$	650, 625, 591, 465, 397	–	69
3-$CHOC_5H_4N$	DMSO	655, 630, 595, 410	–	69
4-$CHOC_5H_4N$	DMSO	654, 630, 595, 520 sh, 410	–	69
3-CNC_5H_4N	$CHCl_3$	651, 625, 59,1 482, 402	–	69
4-CNC_5H_4N	$CHCl_3$	652.5, 625, 591, 527 sh, 405	–	69
Im	$CHCl_3$	663, 640, 602, 430	–	69
	CH_2Cl_2	657, 596, 423, 339	–	87
MeIm	CH_2Cl_2	658, 597, 423, 338	–	87
	PhH – L	659, 632, 597, 423.5, 340	2.89 : 0.8 : 0.69 : 0.34 : 1	76
	PhH – L	655, 594, 408, 335	1.48 : 0.38 : 0.27 : 1	76

Table 4 (continued).

L	Solvent	Positions of bands in electronic absorption spectra/nm ($\log \varepsilon$)	Relative intensity	Ref.
	PhH – L	654, 595, 412, 327	1.71 : 0.45 : 0.23 : 1	76
CN^-	CH_2Cl_2	664, 602, 426, 394, 310	–	87
CN^-/N_2H_4	$CH_2Cl_2 - N_2H_4$	663, 635, 600, 425, 357, 310	–	50
NH_3/CO	CH_2Cl_2	659, 596, 363, 317, 288	–	87
N_2H_4	$CH_2Cl_2 - N_2H_4$	660, 633, 597, 417, 327	–	50
Bu^tNC	$CHCl_3$	658, 598, 387 sh, 326	–	91
cyclo-$C_6H_{11}NC$	$CHCl_3$	658, 598, 386 sh, 325	–	91
PhNC	$CHCl_3$	658, 598, 325	–	91
$Me_2C_6H_3NC$	$CHCl_3$	658, 598, 393 sh, 325	–	91
o-MeC_6H_4NC	$CHCl_3$	663, 601, 388 sh, 319	–	91
m-MeC_6H_4NC	$CHCl_3$	662, 598, 391, 324	–	91
p-MeC_6H_4NC	$CHCl_3$	663, 599, 392, 324	–	91
$Pr^iC_6H_4NC$	$CHCl_3$	662, 598, 391, 325	–	91

Note. Pip is piperidine, Mor is morpholine and Im is imidazole.

In some cases, the position of the charge-transfer band can by used for analytical purposes, for example, for the determination of CO concentration. Thus when CO was bubbled through a solution of $PcFePy_2$, the intensity of the charge-transfer band decreased as the amount of the resulting PcFe(CO)Py complex increased.[78] Analogously, in the reaction of the $PcFePy_2$ complex with isocyanides, the intensity of the band of the initial complex (at 420 nm) first decreased [the formation of PcFePy(NCR), which gave weak bands at 420 and 394 nm] and then disappeared [the formation of $PcFe(NCR)_2$, which gave a charge-transfer band at 394 nm].

The Mössbauer spectra of polycrystalline samples or frozen solutions of the $PcFeL^1L^2$ complexes were examined (Table 5).[9, 46, 47, 69, 71, 76, 86, 93–98] The spectra of freshly prepared samples of $PcFeL^1L^2$ are manifested as doublets and their parameters are characteristic of low-spin ($S = 0$) iron(II) complexes.[99, 100] The δ values vary rather slightly, whereas the ΔE_Q value varies over a wider range depending on the nature of the ligand (see Table 5). The isomer shift reflects the *s*-electron density at the iron nucleus.[99] Consequently, an increase in the population of the 4*s* orbital of the iron atom leads to a decrease in the δ value. For the complexes under consideration, an increase in the population of the 4*s* orbital of the central atom results directly from an increase in the σ-donor character of the axial ligand and from the fact that the $3d_{z^2}$ and 4*s* orbitals of the central iron atom have the same symmetry and can be mixed.[99] The ΔE_Q value, which characterises the electric field gradient about the iron nucleus, is more sensitive to the structure of the axial ligand (see Table 5).[99]

$$\Delta E_Q = 1/2eQV_{zz}(1 + 1/3\eta^2)^{1/2}, \quad (1)$$

where $V_{zz} = eq$, $\eta = (|V_{xx} - V_{yy}|)/|V_{zz}|$.

For the $PcFeL_2$ complexes, $V_{xx} \approx V_{yy}$, and, consequently, $\eta \approx 0$;[76, 95, 101] the electric field gradient has a positive sign.[95, 101] For the low-spin iron(II) complexes, the q parameter can be represented as the sum $q = q_{lat} + q_{val} + q_{mo}$.[99, 102, 103] The first member q_{lat} corresponds to the lattice contribution to the electric field gradient. This value decreases proportionally to the cube of the distance and is negligibly small for bulky complexes. The third member q_{mo} is associated with the difference in the population of different MOs belonging to the same irreducible representation. For the low-spin iron(II) complexes, the ground electronic state has the $(d_{xy})^2(d_{xz},d_{yz})$ configuration,[4] and, consequently, this term is equal to zero. The term q_{val} reflects the symmetry of the population of the atomic orbitals of the iron atom and its σ and π interactions with the ligands. This term can be written as follows[99, 103]

$$q_{val} = 4/7(1 - R) < r^{-3} >_{3d} [n_{x^2-y^2} + n_{xy} - n_{z^2} - \\ - 1/2(n_{xz} + n_{yz})],$$

where R is the Sternheimer factor for antishielding of the iron nucleus, $< r^{-3} >_{3d}$ is the radial component of the $3d$ wave function and n is the population of the corresponding AO.

If the coordination environment about the iron atom is nearly octahedral, the q_{val} term for the low-spin t_{2g} configuration is equal to zero.[99, 103] In the case of axial distortion, the q_{val} term makes the major contribution to the electric field gradient in complexes of the Pc^RFeL_2 type. Actually, the quadrupole splitting in nearly octahedral complexes with isocyanide ligands is small,[9, 90] whereas this splitting in complexes with nitrogen-centred axial ligands is significant (see Table 5).[46, 68, 69, 71, 93, 95–97] An increase in the ΔE_Q value is observed in the following series of axial ligands: isocyanides ≈ cyanides < CO < phosphites < (CO)L ≈ phosphines < pyridines, alkylamines and other nitrogen-containing ligands. Analysis of Eqn (1) demonstrates that the quadrupole splitting should decrease as both the σ-donor and π-acceptor properties of the axial ligands are strengthened. However, the observed ΔE_Q values for some complexes with ligands exhibiting pronounced π-acceptor properties (CO or isocyanides) are higher than the expected values (see Table 5).[47, 76] To account for this anomalous behaviour, hypotheses for the *cis* and *trans* effects of the axial ligands on the phthalocyanine macrocycle were invoked.[76] However, the mechanism that causes a decrease in the quadrupole splitting is still an open question.

Attempts were also made to interpret the available results with the use of empirical and semiempirical approaches. Thus a simple empirical procedure was proposed for the estimation of the ΔE_Q value for the $PcFeL_2$ complexes using absolute partial quadrupole splittings.[104] A reasonable correlation between the ΔE_Q values and the basicity was obtained.[46, 92] A correlation between the ΔE_Q values and the steric properties of alkylamines was also found.[71] An approach based on perturbation theory was also proposed for the estimation of the ΔE_Q values for all types of axial ligands.[46, 92]

The effect of circulating currents of the extended π system on the chemical shifts is clearly manifested in the ^1H NMR spectra of the Pc^RFeL_2 complexes. In all cases, the signals of the coordinated ligands are shifted upfield compared to the signals of the initial amines (Table 6)[72, 90, 105–109] The high selectivity of axial coordination, high induced shifts of the proton signals and the possibility of the prediction of their positions on the basis of the results of quantum-chemical calculations allow one to solve successfully a number of analytical problems.[105–108]

Table 5. Parameters of Mössbauer spectra of the $PcFeL^1L^2$ complexes.

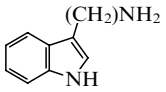
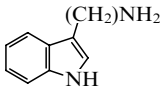
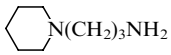
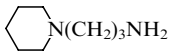
L^1	L^2	T /K	δ [a] /mm s^{-1}	ΔE_Q /mm s^{-1}	Ref.
Pr^nNH_2	Pr^nNH_2	300	0.50	1.97	97
Pr^iNH_2	Pr^iNH_2	298	0.51	2.02	71
Bu^nNH_2	Bu^nNH_2	77	0.34 [b]	1.94	93
Bu^sNH_2	Bu^sNH_2	298	0.52	1.97	71
Bu^tNH_2	Bu^tNH_2	298	0.61	2.38	71
$CF_3CH_2NH_2$	$CF_3CH_2NH_2$	298	0.62	2.49	71
		298	0.48	1.95	71
		298	0.51	1.96	71
		298	0.46	1.76	71
$NH_2(CH_2)_4NH_2$	$NH_2(CH_2)_4NH_2$	298	0.48	1.84	71
Mor	Mor	298	0.53	2.31	71
Et_2NH	Et_2NH	300	0.51	2.22	97
		298	0.52	2.20	71
Pip	Pip	77	0.364 [b]	2.19	69
		77	0.33 [b]	2.21	93
		295	0.28 [b]	2.34	95
		115	0.36 [b]	2.25	
		4.2	0.34 [b]	2.24	
		300	0.52	2.22	98
$4\text{-}MeC_5H_{10}N$	$4\text{-}MeC_5H_{10}N$	298	0.53	2.27	71
MeIm	MeIm	298	0.48	1.71	71
		298	0.51	1.79	73
		77	0.57	1.76	
		298	0.53	1.94	73
		298	0.51	1.73	73
		77	0.55	1.68	
Im	Im	77	0.313 [b]	1.74	69
		77	0.29 [b]	1.75	93
		295	0.54	1.79	96
		195	0.59	1.76	
		77	0.63	1.71	
Py	Py	77	0.322 [b]	1.94	69
		293	0.26 [b]	2.02	93
		77	0.33 [b]	1.97	
		300	0.53	2.01	98
		295	0.53	2.05	96
		195	0.58	2.00	
		77	0.62	1.89	
$3\text{-}MeC_5H_4N$	$3\text{-}MeC_5H_4N$	77	0.321 [b]	1.87	69
		295	0.55	1.95	96
		195	0.60	1.88	
		77	0.61	1.81	
$4\text{-}MeC_5H_4N$	$4\text{-}MeC_5H_4N$	77	0.347 [b]	1.97	69
		295	0.55	1.96	96
		195	0.58	1.89	
$3,4\text{-}Me_2C_5H_3N$	$3,4\text{-}Me_2C_5H_3N$	77	0.342[b]	1.98	69
$3,5\text{-}Me_2C_5H_3N$	$3,5\text{-}Me_2C_5H_3N$	77	0.338[b]	1.95	69
$3\text{-}OHC_5H_4N$	$3\text{-}OHC_5H_4N$	77	0.355[b]	1.90	69
$4\text{-}OHC_5H_4N$	$4\text{-}OHC_5H_4N$	77	0.265[b]	1.80	69
$3\text{-}ClC_5H_4N$	$3\text{-}ClC_5H_4N$	77	0.343[b]	1.91	69
$4\text{-}ClC_5H_4N$	$4\text{-}ClC_5H_4N$	77	0.389[b]	2.45	69
$3,5\text{-}Cl_2C_5H_3N$	$3,5\text{-}Cl_2C_5H_3N$	77	0.360[b]	2.05	69

Table 5 (continued).

L^1	L^2	T /K	δ [a] /mm s^{-1}	ΔE_Q /mm s^{-1}	Ref.
3-$CHOC_5H_4N$	3-$CHOC_5H_4N$	77	0.345[b]	1.97	69
4-$CHOC_5H_4N$	4-$CHOC_5H_4N$	77	0.325[b]	1.84	69
3-CNC_5H_4N	3-CNC_5H_4N	77	0.355[b]	2.17	69
4-CNC_5H_4N	4-CNC_5H_4N	77	0.340[b]	1.90	69
Pyz	Pyz	298	0.5	2.006	9
$MeC_4H_3N_2$	$MeC_4H_3N_2$	298	0.498	1.895	9
2,3-$Me_2C_4H_2N_2$	2,3-$Me_2C_4H_2N_2$	298	0.498	1.968	9
$ClC_4H_3N_2$	$ClC_4H_3N_2$	298	0.513	2.149	9
$EtC_4H_3N_2$	$EtC_4H_3N_2$	298	0.504	2.016	9
		298	0.15[b]	1.79	9
		298	0.53	2.20	47
DMSO	DMSO	298	0.50	2.08	47
PEt_3	PEt_3	291	0.16[b]	1.54	86
		78.6	0.25[b]	1.47	
PBu_3	PBu_3	291	0.15[b]	1.57	86
		78.8	0.24[b]	1.47	
		4.3	0.23[b]	1.45	
$P(OEt)_3$	$P(OEt)_3$	291	0.13[b]	1.07	86
		78.8	0.17[b]	0.99	
		4.3	0.18[b]	0.95	
$P(OBu)_3$	$P(OBu)_3$	298	0.42	1.05	86
		77	0.48	0.96	
CO	THF	298	0.36	1.82	76
CO	H_2O	298	0.37	1.75	76
CO	$OPPh_3$	298	0.36	1.69	76
CO	HMPT	298	0.36	1.60	76
CO	DMSO	298	0.36	1.56	76
CO	DMF	298	0.35	1.56	76
CO	MeOH	298	0.37	1.56	76
CO		298	0.38	1.55	76
CO	Et_2NH	298	0.35	1.45	76
CO	Pip	298	0.37	1.27	76
CO	Py	298	0.37	1.19	76
CO	Pr^nNH_2	298	0.36	1.11	76
CO	NH_3	298	0.38	1.02	76
CO	CO	298	0.36	0.82	76
CN	CN	77	0.19[b]	0.56	93
Bu^tNC	Bu^tNC	298	0.16[b]	0.79	9
cyclo-$C_6H_{11}NC$	cyclo-$C_6H_{11}NC$	298	0.13[b]	0.69	9
PhNC	PhNC	298	0.11[b]	0.67	9
$Me_2C_6H_3NC$	$Me_2C_6H_3NC$	298	0.12[b]	0.70	9
Cl_4C_6HNC	Cl_4C_6HNC	298	0.09[b]	0.67	9
$Me_2C_6H_2(NC)_2$-1,4	$Me_2C_6H_2(NC)_2$-1,4	298	0.11[b]	0.65	9
$C_6Me_4(NC)_2$-1,4	$C_6Me_4(NC)_2$-1,4	298	0.12[b]	0.66	9

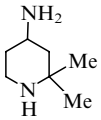
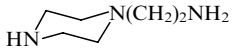
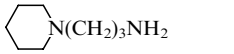
Note. Pyz is , HMPT is hexamethylphosphotriamide; [a] relative to sodium nitroprusside; [b] relative to metallic iron.

Studies of the thermal stability of a number of the Pc^RFePy_2 complexes demonstrated that both ligand molecules are eliminated in one stage. Electron-withdrawing substituents in the macrocycle increase thermal stability, whereas electron-donating substituents decrease this stability compared to that of the unsubstituted analogue.[70]

Among axially coordinated PcFe(II) complexes, polymeric compounds of the general formula $(Pc^RFeL)_n$ belong to a special group.[9, 13, 109–113] These compounds attract great interest because of their semiconducting properties.[114–119] Since several comprehensive reviews devoted to this subject are available,[9, 13, 110, 112] we restrict ourselves to consideration of the major representatives of this group.

Polymeric complexes $(Pc^RFeL)_n$ were synthesised by the reactions of Pc^RFe with different bidentate ligands, such as pyrazine, tetrazine, 4,4′-dipyridyl, 1,4-diisocyanobenzene, 4-phenylenediamine and 9,10-anthracenodiisocyanide, which serve as cross-linking agents. These complexes can be divided into two groups according to their semiconducting properties. The first group involves complexes exhibiting good semiconducting properties only upon doping with halogens or other electron acceptors. The second group consists of complexes exhibiting semiconduct-

Table 6. Parameters of ^{1}H NMR spectra of the axially coordinated ligands in the $PcFeL_2$ complexes.

L	Solvent	Positions of signals for protons of the coordinated ligand			Ref.
		NH_n	α-CH_n	β-CH_n	
$MeNH_2$	CD_2Cl_2	−7.28	−2.73		108
	$CDCl_3$	−7.28	−2.73		106
	C_6D_6	−8.75	−3.70		107
Pr^iNH_2	CD_2Cl_2	−7.46	−3.09	−1.94	108
	$CDCl_3$	−7.67	−3.15	−1.94	73
Bu^sNH_2	CD_2Cl_2	−7.36	−3.49	−2.06	108
	$CDCl_3$	−7.78	−3.49	−2.06	73
Bu^nNH_2	CD_2Cl_2	−7.28	−2.98	−1.41	108
	$CDCl_3$	−7.44	−3.01	−1.41	73
Bu^iNH_2	CD_2Cl_2	−7.29	−3.21	−1.31	108
	$CDCl_3$	−7.45	−3.26	−1.16	73
n-$C_5H_{11}NH_2$	CD_2Cl_2	−7.17	−3.01	−1.42	108
n-$C_6H_{13}NH_2$	CD_2Cl_2	−7.17	−3.00	−1.41	108
	$CDCl_3$	−7.42	−3.00	−1.42	106
$Bu^nCH(Et)CH_2NH_2$	CD_2Cl_2	−7.38	−3.01	−1.49	108
$(EtO)_3Si(CH_2)_3NH_2$	CD_2Cl_2	−7.18	−2.98	−1.26	108
	CD_2Cl_2	−7.48	−3.23	−2.23	108
Pip	CD_2Cl_2	−7.89	−3.12	−1.46	108
Et_2NH	CD_2Cl_2	−7.97	−3.12	−1.80	108
$NH_2(CH_2)_3NH_2$	CD_2Cl_2	−6.43	−2.86	−1.24	108
$NH_2(CH_2)_4NH_2$	CD_2Cl_2	−6.46	−3.01	−1.31	108
	$CDCl_3$	−6.58	−3.05	−1.4	105
$NH_2(CH_2)_5NH_2$	CD_2Cl_2	−7.06	−3.00	−1.39	108
$NH_2(CH_2)_7NH_2$	CD_2Cl_2	−7.15	−3.09	−1.43	108
	CD_2Cl_2	−6.65	−2.86	−0.70	108
	$CDCl_3$	−6.81	−2.80	−0.3	108
	C_6D_6	−7.10	−3.22	−1.18	108
	$CDCl_3$	−6.18	−2.9	−0.98	108
$HO(CH_2)_2NH_2$	CD_2Cl_2	−6.85	−2.95	−2.14	108
$HO(CH_2)_2NH(CH_2)_2NH_2$	CD_2Cl_2	−6.06	−2.74	−1.18	108
4-MeC_5H_4N	$CDCl_3$		1.95	4.78	90
Pyz	$CDCl_3$		1.92	6.01	90

ing properties without doping (Table 7). Polymeric compounds of the first type are stable up to 100–130 °C and lose their semiconducting properties in the absence of the doping agent. All complexes except for compounds containing tetrazine as the axial ligand belong to this type. Tetrazine-containing polymers belong to the second type. The latter are thermally more stable and have no need of doping.[9, 13, 110, 112]

Of the axially coordinated TAP^RFeL_2 complexes reported in the literature, only complexes of iron octaphenylporphyrazine, where L is a pyridine-type ligand, alkylamine or the cyanide ion, were systematically studied by electronic and Mössbauer spectroscopy (Table 8).[58, 120–122] All complexes of this type belong to low-spin iron(II) compounds. The δ and ΔE_Q values (relative to sodium nitroprusside) were determined for some octaphenyl-substituted complexes:

Complex	δ/mm s^{-1}	ΔE_Q/mm s−1	Ref.
$TAP^{Ph}FePy_2$	0.47	2.26	58
$TAP^{Ph}Fe(4\text{-}MeC_5H_4N)_2$	0.45	2.30	58
$TAP^{Ph}FeIm_2$	0.18	2.12	58
	0.50	2.10	120, 121

The electronic absorption spectra of the octaphenyl-substituted $TAP^{Ph}FeL_2$ complexes with pyridine-type ligands are analogous in general appearance to those of the $PcFeL_2$ complexes (Fig. 2).[6, 57, 58] The band at 550 nm was attributed to the

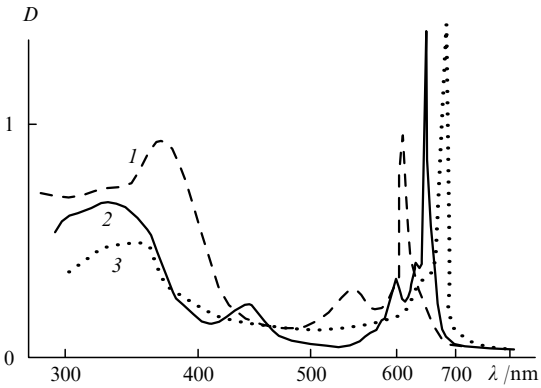


Figure 2. Electronic absorption spectra of the complexes $TAP^{Ph}FePy_2$ (*1*), $PcFePy_2$ (*2*) and 2,3-$NcFePy_2$ (*3*) in benzene.

Table 7. Selected characteristics of the polymeric complexes of iron phthalocyanines $(Pc^RFeL)_n$ and iron naphthalocyanines $(Nc^RFeL)_n$.[9, 13, 110–114]

R^1	R^2	R^3	R^4	L	σ /S cm^{-1}	T /K	δ [a] /mm s^{-1}	ΔE_Q /mm s^{-1}	Other characteristics [b]
Phthalocyanines									
H	H	H	H	$C_6H_4(NC)_2$-1,4	2×10^{-5}	293	0.12	0.68	ν_{NC} 2100
n-C_7H_{15}	H	H	H	$C_6H_4(NC)_2$-1,4	2×10^{-10}	82	0.18	0.57	λ_{max} 671, 607, 394, 321; ν_{NC} 2095
H	n-C_5H_{11}	H	H	$C_6H_4(NC)_2$-1,4	2×10^{-6}	82	0.18	0.48	λ_{max} 679, 610, 466, 395, 342, 303; ν_{NC} 2098
H	n-C_7H_{15}	n-C_7H_{15}	H	$C_6H_4(NC)_2$-1,4	4×10^{-9}	82	0.18	0.45	λ_{max} 680, 612 sh, 459, 331, 302; ν_{NC} 2100
H	n-C_5H_{11}	n-C_5H_{11}	H	$C_6Me_4(NC)_2$-1,4	$<10^{-12}$				
H	n-$C_6H_{13}O$	H	H	$C_6Me_4(NC)_2$-1,4	$<10^{-12}$				
H	H	H	H	$C_6Me_4(NC)_2$-1,4	1×10^{-7}				
H	H	H	H	Pyz	2×10^{-5}	298	0.5 [c]	2.009	
H	H	H	H	Tz	2×10^{-2}	298	0.13	2.23	
H	Me	Me	H	Pyz	9×10^{-6}				
H	Me	Me	H	Tz	1×10^{-3}				
H	H	H	H	Me_2Tz	4×10^{-3}				
H	CN	CN	H	Pyz	5×10^{-9}				
H	CN	CN	H	Tz	1×10^{-6}				
H	Bu^t	H	H	Pyz	5×10^{-11}				
H	Bu^t	H	H	Tz	9×10^{-9}				
H	Et	H	H	Pyz	8×10^{-9}				
H	Et	H	H	Tz	2×10^{-4}				
H	H	H	H	dabco	1×10^{-9}				
H	H	H	H	bipy	2×10^{-8}	298	0.24	2.00	
Doped phthalocyanines									
H	H	H	H	Pyz	4×10^{-2}				doped with $(BF_4)_{0.45n}$
H	H	H	H	Pyz	3×10^{-2}				$(PF_6)_{0.5n}$
H	H	H	H	Pyz	1×10^{-5}				$(HSO_4)_{0.4n}$
H	H	H	H	Pyz	1×10^{-6}				$(SCN)_{0.3n}$
H	H	H	H	Pyz	3×10^{-3}				$(ClO_4)_{0.3n}$
H	H	H	H	Pyz	2×10^{-1}				$I_{2.5n}$
H	H	H	H	$C_6H_4(NC)_2$-1,4	7×10^{-3}				$I_{1.4n}$
H	H	H	H	$C_6H_4(NC)_2$-1,4	3×10^{-2}				$I_{3.0n}$
H	H	H	H	$C_6Me_4(NC)_2$-1,4	1×10^{-3}				$I_{1.5n}$
H	H	H	H	$C_6Me_4(NC)_2$-1,4	2×10^{-2}				$I_{3.0n}$
H	n-C_5H_{11}	n-C_5H_{11}	H	$C_6Me_4(NC)_2$-1,4	9×10^{-7}				$I_{1.8n}$
H	n-$C_6H_{13}O$	H	H	$C_6Me_4(NC)_2$-1,4	2×10^{-10}				$I_{2.5n}$
1,2-Naphthalocyanine									
H	H	H	H	$C_6H_4(NC)_2$-1,4	6×10^{-10}				λ_{max} 712, 387; ν_{NC} 2090
2,3-Naphthalocyanines ($R^5 = R^6 = H$)									
H	H	H	H	$C_6H_4(NC)_2$-1,4	2×10^{-3}	293	0.13	0.58	ν_{NC} 2124
n-$C_6H_{13}O$	H	H	H	$C_6H_4(NC)_2$-1,4	4×10^{-6}	82	0.17	0.51	λ_{max} 771, 690 sh, 346; ν_{NC} 2102
H	n-$C_6H_{13}O$	H	H	$C_6H_4(NC)_2$-1,4	1×10^{-5}	82	0.18	0.47	λ_{max} 778, 692 sh, 365; ν_{NC} 2093
H	n-$C_6H_{13}O$	n-$C_6H_{13}O$	H	$C_6H_4(NC)_2$-1,4	2×10^{-6}				λ_{max} 765, 686, 359; ν_{NC} 2095
H	H	H	H	Pyz	5×10^{-5}	298	0.26	1.90	
H	H	H	H	Tz	0.3	298	0.19	1.97	

Note. Tz is tetrazine, Me_2Tz is dimethyltetrazine, dabco is 1,4-diazabicyclo[1.2.2]octane, bipy is 2,2′-bipyridyl; [a] relative to metallic iron; [b] ν_{NC} in cm^{-1}, λ_{max} (electronic absorption spectrum) in nm; [c] relative to sodium nitroprusside.

Fe → TAP $[e_g(d\pi) \rightarrow e_g(\pi^*)]$ charge transfer.[58] However, this assignment has recently come under strong criticism and this band was attributed[120, 121] to the Fe → TAP $[e_g(d_\pi) \rightarrow b_{1u}(\pi^*)]$ charge transfer. In the electronic absorption spectra of the TAP^RFeL_2 complexes containing alkylamines or the cyanide ion as the axial ligands, the intensity of the charge-transfer band at 500 nm is virtually equal to that of the Q band. However, taking into account that the above-mentioned complexes were not characterised by other spectroscopic methods, these data must be considered with caution.[120–122]

Among complexes of iron naphthalocyanines, compounds containing isocyanide axial ligands have been studied in most detail (Table 9).[48, 94, 123–126]

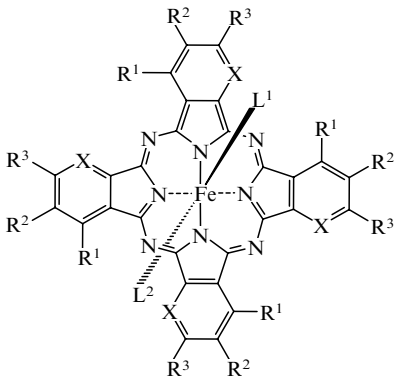


Table 8. Characteristics of the TAP^{R}FeL$_2$ complexes ($R^1 = R^2$ = Et or Ph).

R	L	Positions of bands in electronic absorption spectra/nm (log ε)	Relative intensity	Ref.
Ph	CN	643(4.39), 572(4.38), 451 sh, 383(4.46) (see [a])		122
		643(4.27), 574(4.59), 457 sh, 374(4.62) (see [b])		
Ph	Py	610, 595 sh, 571, 513, 483 sh, 434 sh, 364	0.97 : 0.3 : 0.33 : 1	58
Ph	4-MeC$_5$H$_4$N	621, 599 sh, 571, 519, 485 sh, 422 sh, 363	0.84 : 0.33 : 0.33 : 1	58, 120, 121
Ph	4-EtC$_5$H$_4$N	621, 599 sh, 571, 517, 483 sh, 424 sh, 361	0.8 : 0.4 : 0.29 : 1	58
Ph	3,4-Me$_2$C$_5$H$_3$N	621, 595 sh, 575 sh, 520, 424 sh, 365	0.77 : 0.34 : 1	58
Ph	4-CH$_2$=CHC$_5$H$_4$N	621, 595 sh, 570, 510, 481, 425 sh, 362	0.75 : 0.33 : 0.33 : 0.35 : 1	58
Ph	3-ClC$_5$H$_4$N	616, 592 sh, 567, 488, 454, 423, 362	0.89 : 0.36 : 0.31 : 0.37 : 0.42 : 1	58
Ph	4-ClC$_5$H$_4$N	615, 592 sh, 568, 424 sh, 356	0.69 : 0.25 : 1	58
Ph	Im	627, 599 sh, 575 sh, 539, 445 sh, 366	0.69 : 0.48 : 1	58, 120, 121
Ph	MeIm	629, 581 sh, 539, 450 sh, 365	0.77 : 0.43 : 1	58
Ph	PhNH$_2$	627, 602 sh, 581 sh, 530, 450 sh, 370	0.53 : 0.34 : 1	58
Ph	NH$_3$	631, 602 sh, 585 sh, 537, 424 sh, 365	0.68 : 0.37 : 1	58
Ph	Pip	629, 602 sh, 581 sh, 537, 420 sh, 366	0.68 : 0.45 : 1	58
		623, 535, 367	0.52 : 0.44 : 1 (see [c])	
Ph	cyclo-C$_6$H$_{11}$NH$_2$	631, 606 sh, 585 sh, 536, 420 sh, 363	0.53 : 0.35 : 1	58
Ph	Pr^{i}NH$_2$	627, 545, 371	0.82 : 0.70 : 1 (see [c])	120, 121
Ph	Pr$^n_2$NH	622, 538, 364	0.82 : 0.49 : 1 (see [c])	120, 121
Ph	Et$_2$NH	622, 536, 364	0.81 : 0.56 : 1 (see [c])	120, 121
Ph	Mor	623, 533, 365	0.81 : 0.59 : 1 (see [c])	120, 121
Ph	n-C$_5$H$_{11}$NH$_2$	628, 541, 366	0.83 : 0.71 : 1	120, 121
Et	Py	586, 564 sh, 541, 458, 332 (see [d])		57
Et	MeIm	590, 574 sh, 550 sh, 491, 333, 315 sh (see [e])		57

[a] In CH_2Cl_2; [b] in acetone; [c] in acetonitrile; [d] in PhH – Py; [e] in PhH.

Four structural isomers are possible for derivatives of 1,2-Nc^{R}FeL$_2$. An individual isomer, which contains the *tert*-butylisocyanide and cyclohexylisocyanide ligands and is characterised by C_{4h} symmetry, was isolated and its structure was established.[48, 49] Due to the strong π-acceptor properties of the axial ligands, the Fe – C_{ax} bond length is smaller than the Fe – N(Pc) distance (see Table 1). On the whole, the spectral characteristics and properties of the 1,2-Nc^{R}FeL$_2$ complexes are very similar to those of Pc^{R}FeL$_2$ (see Tables 4 – 7). In the 2,3-Nc^{R}FeL$_2$ complexes, linear annelation of an additional benzene ring (contrary to angular annelation resulting in 1,2-NcFe) leads to a sharp change in the properties of these compounds, which is manifested, for example, in a strong bathochromic shift of the Q band in the electronic absorption spectra and in enhancement of the semiconducting properties (see Tables 7 and 9, Fig. 2).[9, 13, 110, 112] An extension of the π-system of the macrocycle leads to a decrease in the stability of the complexes containing the 2,3-Nc^{R}Fe fragment.[123 – 126]

Table 9. Properties of axially coordinated complexes of iron naphthalocyanines and pyridinoporphyrazines.

R^1	R^2	R^3	X	L	Positions of bands in electronic absorption spectra /nm	ν_{NC} /cm^{-1}	Ref.
1,2-Naphthalocyanines							
CH=CHCH=CH		H	CH	Bu^{t}NC	653, 594, 353	2140	48
				cyclo-C$_6$H$_{11}$NC	654, 594, 354	2155	
				Bu^{n}NC	654, 595, 354	2153	
CH=CBu^{t}CH=CH		H	CH	Py	666, 604, 353		49
				Bu^{t}NC	662, 602, 354		
CH=CMeCH=CH		H	CH	Py	668, 606, 354		49
CH=CPhCH=CH		H	CH	Py	670, 607, 364		49
2,3-Naphthalocyanine							
H	CH=CHCH=CH		CH	C$_6$H$_4$(NC)$_2$-1,4		2145	94
Tetrakis(2,3-pyridino)porphyrazines							
H	H	H	N	Bu^{t}NC	627, 573, 339	2157	91
				cyclo-C$_6$H$_{11}$NC	628, 574 sh, 398 sh, 339	2171	
				PhNC	633, 577 sh, 332	2141	
				Me$_2$C$_6$H$_3$NC	632, 577 sh, 393 sh, 331	2140	
				o-MeC$_6$H$_4$NC	634, 579 sh, 393 sh, 331	2136	
				m-MeC$_6$H$_4$NC	634, 580 sh, 330	2134	
				p-MeC$_6$H$_4$NC	633, 579 sh, 391 sh, 332	2144	
				p-Pr^{i}C$_6$H$_4$NC	634, 579 sh, 394 sh, 332	2144	

Complexes of iron tetrakis(2,3-phenanthro)porphyrazine were prepared by photochemical oxidation of *trans*-1,2-dicyano-1,2-diphenylethylene in the presence of iodine followed by template condensation with iron compounds and axial coordination with different isocyanides.[127] These complexes were characterised by electronic and Mössbauer spectroscopy. In addition, complexes of iron tetrakis(2,3-pyridino)porphyrazine with isocyanides as axial ligands were prepared and characterised (see Table 9).[91]

2. Iron(III) complexes

In spite of the fact that azaporphin iron(III) complexes have been considered in the literature over several decades, convincing evidence for the existence of Pc complexes of iron(III) has been reported, and furthermore their properties, have been described only recently. Oxidation of a solution of $Na_2[PcFe^{II}(CN)_2]$ in dichloromethane with bromine afforded the six-coordinate $Na[PcFe^{III}(CN)_2]$ complex.[55] In the electronic absorption spectra, this process is characterised by distinct isosbestic points (Fig. 3). The $Na[PcFe^{III}(CN)_2]$ complex can also be prepared by oxidation of $Na_2[PcFe^{II}(CN)_2]$ with cumene hydroperoxide[128] or by the reactions of $Na[PcFe^{III}(OH)_2]$ with cyanides.[50] The $[PcFe^{III}(CN)_2]^-$ complex was characterised in detail by electronic absorption, Mössbauer, IR, Raman, ESR and circular dichroism spectra, magnetic susceptibility data and X-ray diffraction analysis (Table 10).[50, 55, 129] The magnetic susceptibilities, the parameters of the Mössbauer spectra and the character of the electronic absorption spectra demonstrate that this compound can be described as a low-spin ($S = 1/2$) iron(III) complex with the $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic configuration. The presence of a hole in the d_π orbital of the central atom results in the appearance of a series of L(Pc)–Fe charge-transfer bands in the electronic absorption spectra. The most detailed assignment of the bands in the electronic absorption spectrum of the $Na[PcFe^{III}(CN)_2]$ complex was made by Ough and Stillman.[55] Based on the analysis of the magnetic circular dichroism and electronic absorption spectra, two Fe → L(Pc) and four Fe → Pc charge-transfer bands were identified.[55] According to the data from X-ray diffraction analysis[50] (see Table 1), the Fe–C_{ax} bond length in $PNP[PcFe^{III}(CN)_2]$ is larger than the Fe–N(Pc) bond length. This complex is more similar in structure to compounds of the $PcFe^{II}L_2$ type with nitrogen-containing axial ligands[43–46] and differs from analogous complexes with axial ligands exhibiting strong π-acceptor properties.[48, 49] The reactions of $[PcFe^{III}(CN)_2]^-$ with pyridine and imidazole afforded compounds with composition $PcFe^{III}(CN)L$, whereas the reaction with hydrazine was accompanied by reduction of the iron ion to form $[PcFe^{II}(CN)(N_2H_4)]^-$.[50] Complexes of the $PcFe^{III}(CN)L$ type can also be prepared by the reactions of the ligand L with the cyanide complex $[PcFe^{III}(CN)]_n$.[130] The reactions of $Na[PcFe^{III}(CN)_2]$ with acids yielded complexes of the $Pc^{+\cdot}Fe^{III}(CN)X$ type containing the phthalocyanine radical cation. Finally, $Na[PcFe^{III}(CN)_2]$ can be reduced to the cyanide iron(II) complex under the action of different reducing agents.[50]

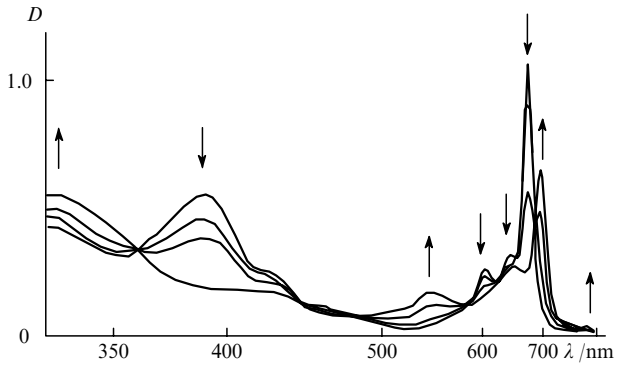


Figure 3. Dynamics of oxidation of the $[Pc^tFe^{II}(CN)_2]^{2-}$ complex with cumene hydroperoxide to form $[Pc^tFe^{III}(CN)_2]^-$.

Complexes of the general formula $PNP(PcFe^{III}XY)$ (X = Y) were synthesised[89, 129] and characterised by electronic absorption, Mössbauer and ESR spectra as well as by magnetic susceptibility data (see Table 10). These compounds exhibit the following characteristic features: (1) the electronic absorption spectra of all complexes have additional Pc → Fe and Fe → Pc charge-transfer bands in the region of 400–800 nm, and the Q band is bathochromically shifted compared to that for the $PcFeL_2$ complexes; (2) in most cases, the electronic absorption spectra are typical of axially coordinated low-spin ($S = 1/2$) iron(III) complexes;[131, 132] (3) in all the studied complexes, except for the cyanide complex, the quadrupole doublets in the Mössbauer spectra are characterised by substantial asymmetry; a low-intensity broad component of the doublet for the complexes with the Fe–O_{ax} bond is observed at low rates, whereas this component for the complexes with the Fe–N_{ax} bonds is observed at higher rates,[129] as in the case of the well-studied iron(III) complexes with porphyrin ligands[100, 133] {for the azide complex anion $[PcFe^{III}(N_3)]^-$, the sign of the electric field gradient was found to be negative[134]}; (4) magnetic moments for all the complexes studied are in the range of 2.0–2.5 μ_B at room temperature. Based on the data from mag-

Table 10. Physicochemical properties of the $[PcFe^{III}XY]^n$ complexes ($S = 1/2$).[89, 128, 130]

n	X	Y	T/K	δ [a] /mm s^{-1}	ΔE_Q /mm s^{-1}	μ/μ_B (T/K)	Factor g in ESR spectra	Positions of bands in electronic absorption spectra /nm
−1	OH	OH	4.2	0.18	2.22	2.31 (300) 2.06 (4.2)	2.31, 2.11, 1.96	800, 690, 630, 575, 450, 360
−1	OPh	OPh	4.2	0.22	2.64	2.3 (300)	2.31, 2.12, 1.93	
−1	NCO	NCO	4.2	0.29	2.25	2.44 (300) 1.96 (4.2)	broad lines	775, 685, 673, 655, 645, 610, 555, 435, 375, 330, 280
−1	NCS	NCS	4.2	0.26	2.65	2.4 (300)	the same	790, 690, 673, 645, 610, 565, 525, 485, 385, 330
−1	N_3	N_3	4.2	0.21	2.49	2.05 (300) 1.76 (4.2)	2.41, 2.07, 1.79	
−1	CN	CN	4.2	0.11	0.99	2.49 (300) 1.89 (4.2)	2.41, 2.07, 1.79 2.00 (broad peak)	775, 685, 650, 620, 600, 540, 500, 425, 400, 322 781, 755, 688, 663, 646, 623, 603, 545, 421, 399, 325, 285
0	Py	CN	293	0.04	1.57			783, 690, 651, 595, 555, 510, 412, 317 (see [b])
0	Bu^{t}Py	CN	293	0.04	1.57			see [c]
0	Pyz	CN	293	0.05	1.60			

[a] Relative to sodium nitroprusside; [b] ν_{CN} 2131 cm^{-1}, $\sigma_{RT} = 1 \times 10^{-10}$ S cm^{-1}; [c] ν_{CN} 2132 cm^{-1}, $\sigma_{RT} = 6 \times 10^{-5}$ S cm^{-1}.

netic circular dichroism and electronic absorption spectroscopy, it was concluded [55] that the phthalocyanine ligand in the $[PcFe^{II}(CN)_2]^{2-}$ complex behaves as a σ-donor and a π-acceptor and the result of oxidation of the iron ion yielding $[PcFe^{III}(CN)_2]^-$ is that the phthalocyanine ligand behaves as a σ- and π-donor. Of special note is the $PcFe^{III}(NO)Py$ complex, which was prepared by a ligand exchange reaction. Based on the data from magnetic susceptibility and Mössbauer spectroscopy, this complex should be assigned to low-spin ($S = 1/2$) iron(III) compounds. For this complex, two isomeric forms that differ in the site of localisation of the electron hole are possible:

$$PcFe^{II}(NO^*)Py \leftrightarrow PcFe^{III}(NO)Py.^{97}$$

Polymeric iron(III) complexes linked through bridging ligands, *viz*., $[PcFe^{III}(CN)]_n$, $[2,3\text{-}NcFe^{III}(CN)]_n$ and $[PcFe^{III}(SCN)]_n$, were synthesised [110, 112] analogously to polymeric iron(II) complexes. The resulting polymers are characterised by high thermal stabilities (up to 250 °C) and rather high conductivities at room temperature (10^{-5}–10^{-3} S cm^{-1}).

The octaphenyl complex $(Bu_4N)[TAP^{Ph}Fe^{III}(CN)_2]$ [122] is the only tetraazaporphin complex of this type characterised by IR and electronic absorption spectroscopy and elemental analysis. Oxidation of the Fe^{2+} ion in this complex to the Fe^{3+} ion, unlike oxidation of the corresponding phthalocyanine complexes, results in a hypsochromic rather than bathochromic shift of the Q band.

3. 'Acidic' complexes of iron phthalocyanine and its analogues

Barrett and coworkers [17] were the first to prepare the so-called 'chlorine-containing' PcFe complex by heating PcFe with concentrated hydrochloric acid. This compound was also synthesised by the reaction of the PcFe μ-oxo dimer,[6, 56, 135] $PcFe(en)_2$ complexes,[50] where en is ethylenediamine, or the $PNP[PcFe^{III}(OH)_2]$ complex [89, 129] with hydrochloric acid as well as in a direct reaction, for example, upon boiling of a mixture of anhydrous $FeCl_3$ with phthalonitrile in 1-chloronaphthalene.[89]

Originally, a structure with the chlorine atom at the Fe^{III} atom, *viz*., $PcFe^{III}Cl$ (**1**), was assigned to the resulting compound.[17] However, Lever [53] gave preference to the hydrochloride structure $PcFe^{II}\cdot HCl$ (**2**), because an attempt to sublime the resulting complex *in vacuo* resulted in the formation of PcFe and elimination of hydrogen chloride. Later, Lever, on the basis of magnetic susceptibility data, returned to the initial hypothesis that the complex has the structure of 'chlorine-containing' iron(III) phthalocyanine.[52] Since then, the above-considered notions of the structures of these compound and analogous five-coordinate complexes with axial acido ligands X co-exist. Thus on the basis of spectral data alone (Table 11), 'acidic' complexes of iron phthalocyanine were assigned to iron(III) derivatives with the mixed-spin ($S = 5/2$–$3/2$) electronic state (structure **1**).[89, 129] Based on the chemical properties and spectral data, these complexes were alternatively considered as iron(II) derivatives with intermediate ($S = 1$) spin (structure **2**),[6, 7, 56, 136–138] and it was believed that the proton is most likely localised on the pyrrolenine nitrogen atom.[6, 138]

The electronic absorption spectra of the HPcFeX complexes are characterised by the presence of a charge-transfer band (at ~ 820–860 nm) in the near IR region along with an intense Q band in the long-wavelength region (at ~ 660 nm). The position of this charge-transfer band depends on the nature of the ligand X (see Fig. 1, Table 11).[56, 89] The presence of the low-energy charge-transfer band in the near IR region is easily explained in the framework of both structures described above. The position of the Q band in the spectra of HPcFeX virtually coincides with those in the electronic absorption spectra of the $PcFe^{II}L_2$ (see Refs 47 and 68–77) and $PcFe^{II}L(DMSO)$ [79–84] complexes and differs substantially from the position of the Q band in the electronic absorption spectra of the bisaxially coordinated iron(III) complexes $[PcFe^{III}X_2]^-$ (see Table 10).[89, 129] In the Mössbauer spectra (see Table 11) of the 'acidic' complexes, the ΔE_Q values are very large, which is untypical of both high- and low-spin iron(III) complexes with macrocyclic ligands.[86, 99, 100, 103, 139] However, these values correlate well with the hypothesis that the iron ions in these complexes exist in an intermediate spin state ($S = 3/2$).[99, 100, 103] The only principal fact, which is inconsistent with this suggestion, is that the asymmetry of the doublet, which is characteristic of iron(III) complexes, is absent in the Mössbauer spectra.[100, 133] At the same time, the parameters of the Mössbauer spectra of the 'acidic' complexes are similar to those of the iron(II) complexes containing macrocyclic ligands and the iron ion in the intermediate spin state ($S = 1$).[99, 100, 103] The electronic absorption spectra and magnetic susceptibility data of the 'acidic' complexes are avaialble only for unsubstituted phthalocyanines (see Table 11).[89, 129] Unlike the low-spin $[PcFe^{III}X_2]^-$ complexes whose electronic absorption spectra are typical of the d^5 electronic configuration (see Table 10),[129] most of the 'acidic' complexes either give broad lines or do not give signals at all. The spectra of solid samples differ from each other (see Table 11). Moreover, even the complexes with the same ligand X gave different spectra.[129] At the same time, the electronic absorption spectra of the analogous high-spin porphyrin complexes [100] and the corresponding porphyrazine complexes containing iron in the intermediate spin state (which are considered below) both in frozen matrices and in the solid state are identical and typical of axial iron(III) complexes. However, if the structure **2** is correct, the electronic absorption spectra should not be observed due to the rapid spin-lattice relaxation typical of paramagnetic iron(II) complexes.[132] Based on the data from magnetic susceptibility (see Table 11), the 'acidic complexes' were assigned to compounds in which the central iron ions are in the mixed-spin ($S = 3/2$–$5/2$) electronic state [89, 129] because the magnetic susceptibilities differ from the spin-only values ($S = 3/2$ $\mu_B = 3.87$; $S = 5/2$ $\mu_B = 5.92$). However, the experimental values are close to those for iron(II) complexes with intermediate spin in the case of strong coupling between ground state spin and orbital angular momenta.[51–53] For example, the magnetic susceptibilities of the

Table 11. Spectral characteristics of 'acidic' complexes of iron phthalocyanine of the HPcFeX type.[56, 129]

X	Positions of bands in electronic absorption spectra /nm	δ (4.2 K) /mm s^{-1}	ΔE_Q (4.2 K) /mm s^{-1}	μ_{eff}/μ_B		Factor g in ESR spectra
				300 K	4.2 K	
F	832, 758, 710, 655, 615, 600, 465, 368					
Cl	832, 758, 655, 595, 485, 450	0.28	2.94	4.53	3.25	4.67, 2.0
Br	840, 710, 658, 590, 450	0.28	3.12	4.09	3.2	broad lines
I	848, 710, 690, 595, 465	0.28	3.23	3.62	2.32	–
CF_3CO_2		0.28	3.08	4.08	3.39	signal was not observed
CCl_3CO_2		0.29	3.07	3.90	3.06	2.0
HCO_2				4.09		~6.3, ~4.3
CF_3SO_3				4.14		signal was not observed
Ts				4.17		the same

Table 12. Spectral characteristics of the TAP^RFeX complexes ($R^1 = R^2$ = Et, EtS or Ph).[140, 142–144]

R	X	Positions of bands in electronic absorption spectra /nm	T[a] /K	δ /mm s^{-1}	ΔE_Q /mm s^{-1}	Factor g in ESR spectra	μ_{eff} /μ_B	Data of X-ray diffraction analysis (bond lengths /Å)		
								Fe–X	$Fe–N_4$	Fe–N
Et	Cl	318, 364, 436, 555, 672	298	0.28	2.98	3.98, 1.99	3.89	2.278	0.352	1.929
			80	0.37	3.0					
Et	ClO_4	312, 375, 497, 582, 711	300	0.35	4.38	3.98, 1.99	3.87	2.091	0.263	1.913
Et	PF_6	312, 372, 505, 558, 687	300	0.3	4.02	4.05, 2.04	3.44–3.94			
Et	SbF_6	322, 372, 509, 588, 722				4.07, 2.01	3.55–3.79			
Et	CF_3CO_2	310, 371, 445, 566, 684	300	0.23	3.36	3.55, 2.01	3.80–4.06			
Ph	F	665, 533, 435, 318	300	0.2	3.0					
			140	0.28	2.99					
			82	0.29	2.97					
Ph	Cl	709, 544, 431, 335	300	0.23	2.15		3.44			
			82	0.26	2.85					
Ph	Br	716, 548, 432, 329	300	0.19	2.75		2.98; 4.66[b]			
			82	0.25	3.04					
Ph	I	723, 561, 444, 328	300	0.19	3.21					
			82	0.24	3.39					
Ph	HSO_4	721, 563, 440, 329	300	0.16	3.25					
			82	0.28	3.58					
EtS	Cl					4.3, 2.36;[b] 2.17, 1.96;[b] 3.92, 1.96[b]		2.308	0.286	1.936
Et	NO	590, 350, 316	100	0.21	1.95	1.99		1.931	0.308	1.721

[a] Temperature at which the Mössbauer spectra were recorded; [b] data from different studies.

PcFe complexes, iron octaethylporphyrazine and iron tetraphenylporphin at room temperature (3.85,[51–53] 3.82[57] and 4.4 μ_B,[139] respectively) are close to the μ_{eff} values for the 'acidic' complexes (see Table 11). The chemical behaviour of the 'acidic' complexes, *viz*., the elimination of HCl and the formation of PcFe upon sublimation of the 'chlorine-containing' PcFe complex,[53] the absence of products of radical nature and hydrogen in the reaction of PcFe with HCl,[6, 56] the formation of 'acidic' complexes from the μ-oxo iron(II) dimer (the form 690)[56, 135] and the absence of redox-conversion products, indicate that the iron ions in these complexes exist, most likely, in the divalent rather than trivalent state. Moreover, the reactions of the μ-oxo PcFe(III) dimer (the form 630) with acids afforded unstable products whose electronic absorption spectra are quite different from those of the 'acidic' complexes.[7]

Therefore, taking into account all the above-considered facts, the structure **2** seems to be preferable. However, the unambigous elucidation of the structures of 'acidic' complexes of readily soluble PcFe derivatives calls for further investigations of these compounds both by physical (primarily, electronic absorption spectroscopy and magnetic susceptibility studies) and chemical methods.

In the series of 'acidic' porphyrazine iron complexes, octaethyl-,[57, 140] octaphenyl-[141, 142] and octa(ethylthio)porphyrazine[143] derivatives were studied. These complexes were prepared either by the reactions of the corresponding μ-oxo dimers[57, 141–143] or anionic dihydro complexes[143] with acids or by ligand exchange reactions.[140] Based on the data from magnetic susceptibilities and on the parameters of the Mössbauer and electronic absorption spectra in frozen matrices (Table 12), the octaethyl- and octaphenylporphyrazine complexes were assigned to iron(III) derivatives with intermediate ($S = 3/2$) spin. This assignment is consistent with the data from X-ray diffraction analysis (see Table 12).[57, 140] However, the chemical properties and the electronic absorption spectra of 'acidic' complexes of *tert*-butyl-substituted analogues[6] can be better explained on the basis of the structure **2**. Therefore, we believe that final conclusions cannot be made.

An unusual coordination about the central atom was observed in the 'acidic' complex of octa(ethylthio)porphyrazine.[143] According to the data from X-ray diffraction analysis, the coordination sphere about the central atom is formed by four nitrogen atoms of the macrocyclic ligand, the chloride ion and the sulfur atom of the peripheral substituent of the adjacent molecule. The different behaviour of this complex in the polycrystalline state and in solution was attributed to the differences in the electronic structure of these two states.[143] Thus it was suggested that the solid complex exists in the mixed-spin ($S = 5/2 – 1/2$) state, whereas this complex in solution was described as in an intermediate-spin state ($S = 3/2$).[143]

Recently, the spectroscopic parameters of the $TAP^{Et}Fe(NO)$ complex, which has been synthesised by reductive nitrosation of the 'acidic' $TAP^{Et}Fe$ complex in the presence of 2,6-dimethylpyridine, were reported (see Table 12).[144] These data made it possible to assign the complex under consideration to five-coordinate iron(II) derivatives with an angular structure of the nitrosyl ligand.

IV. μ-Oxo(-nitrido, -carbido) binuclear complexes of iron phthalocyanine and its analogues

In 1965, the reversible addition of oxygen to iron(II) tetrasulfophthalocyanine ($TSPcFe^{II}$) in aqueous solution yielding a μ-peroxo dimeric complex was reported.[145]

$$2TSPcFe^{II} + O_2 \longrightarrow TSPcFe^{II}OOTSPcFe^{II}.$$

However, the structure $TSPcFe^{III}X$ was assigned to the product of the reaction of $TSPcFe^{II}$ (λ_{max} = 670 nm) with oxygen (λ_{max} = 630 nm), although attempts to isolate and characterise this product have failed.[146, 147] In 1971, specimens of PcFe synthesised by different procedures were studied by Mössbauer spectroscopy and it was found that the spectra of the products obtained upon treatment of PcFe with 2-picoline in air and upon heating of PcFe in air (δ = 0.29 and 0.348 mm s^{-1}, ΔE_Q = 0.36 and 1.13 mm s^{-1}, respectively) differ substantially from the spectra of the initially freshly prepared PcFe (δ = 0.385 mm s^{-1}, ΔE_Q = 2.58 mm s^{-1}).[98] In the following, we will demonstrate

that the first two complexes described as 'other forms of PcFe'[98] are actually μ-oxo dimeric iron complexes.

More recently, in attempting to isolate Pc^{t}Fe by chromatography, Bundina *et al.*[56] obtained an oxygen-containing compound as the major product. Its molecular weight was approximately twice as large as that of Pc^{t}Fe and its spectral characteristics differed significantly from those reported for PcFe and its substituted analogues. Based on the spectral data and the chemical properties of chromatographically pure specimens, it was suggested that the compound under consideration had the structure of the μ-oxo dimer with an Fe—O—Fe bridge analogous to the structures of the well-studied μ-oxo dimeric porphyrin iron complexes.[148–151] In the first study,[56] the authors considered two alternative structures for the μ-oxo dimeric PcFe complexes, *viz.*, PcFe^{III}OFe^{III}Pc (**3**) and HPcFe^{II}OFe^{II}PcH (**4**), which differ in the oxidation state of the iron atom. Based on the data from elemental analysis and IR, X-ray photoelectron and electronic absorption spectroscopy as well as on the chemical behaviour of this complex, preference was given to the structure **4**. It was suggested that the hydrogen atoms were located at the pyrrolenine nitrogen atoms of the phthalocyanine ligands.[56, 152]

In 1979, a stable dimeric complex was prepared by the reaction of PcFe with oxygen in DMSO or DMF, and the structure of the μ-peroxo dimer PcFe^{III}OOFe^{III}Pc was assigned to the resulting compound.[153] However, thereafter this suggestion was rejected[154, 155] based on spectroscopic data, in particular, on the IR spectra of the complex containing the ^{18}O isotope in the μ-bridge, and the μ-oxo dimeric structure was proposed. Taking into account the results of volumetric analysis of oxygen absorption by the PcFe complex, the structure **3** with the central iron(III) ions was assigned to the μ-oxo dimer. This point of view has received support from many researchers.[135, 156–162] At present, this view predominates in spite of the fact that it has recently come under strong criticism.[7, 128, 163] Although μ-oxo dimeric complexes belong to one of the most stable coordination forms of PcFe, their electronic structures are still questionable. In this connection, let us consider the properties of these complexes in more detail.

The μ-oxo dimeric PcFe complex can be prepared according to the following procedures: (1) by bubbling air or oxygen through a solution of PcFe in sulfuric acid, as well as in DMSO, DMF or other organic solvents;[56, 154, 155] (2) by short-term boiling of a suspension of PcFe with sterically hindered aliphatic amines[157] or α-pyridines[98] in the medium of the amine or in organic solvents; (3) the solid-phase reaction of PcFe with oxygen with heating;[98] or (4) dimerisation of monomeric bisaxially coordinated PcFe complexes.[89, 156] The IR spectra of the μ-oxo dimeric PcFe complex have bands at 851 and 822 cm^{-1}, which were assigned to vibrations of the Fe—O—Fe fragment.[56, 135, 155–157] μ-Oxo dimeric Pc^{R}Fe complexes were prepared by chromatography of the Pc^{R}Fe complexes (using eluents which did not contain potential ligands, such as organic bases or acids)[56, 135, 152, 163] or according to one of the above-mentioned procedures for the synthesis of the μ-oxo dimer of PcFe.

In the electronic absorption spectra of μ-oxo dimeric PcFe complexes in noncoordinating solvents, the Q and B bands are bathochromically shifted compared to their positions in the spectra of other forms of PcFe (Table 13). This behaviour is untypical of μ-oxo dimeric phthalocyanine complexes of other metals.[62] The Q band is observed at 700 nm. In all cases, this band is broadened and has a short-wave shoulder.[6, 7, 56, 135, 152] To explain the bathochromic shift on the basis of the theory of exciton splitting, it was assumed that the phthalocyanine ligands in these complexes are nonparallel or are shifted relative to each other (slipped-stack),[128] which is untypical of the μ-oxo dimeric iron(III) complexes.[148, 149]

The unusual geometry of the μ-oxo dimeric PcFe complexes was confirmed by ^1H and ^{13}C NMR spectroscopy. As was noted in a number of studies,[6, 7, 56, 128] the spectra of these compounds are more complicated than those of other PcFe forms containing the μ-oxo fragment (see below) and are similar to those of μ-oxo dimeric silicon phthalocyanines.[164] The spectral patterns indicate that the protons of the peripheral substituents are substantially nonequivalent. This nonequivalence can be explained only on the assumption that the geometry of the μ-oxo dimeric PcFe complexes differs substantially from that typical of other μ-oxo dimeric iron complexes with macrocyclic ligands (the Fe—O—Fe angle is close to 180° and the macrocycles are parallel to each other[148, 149]).

μ-Oxo dimeric PcFe complexes in the solid state, unlike those in solution, exist as two isomeric forms possessing different

Table 13. Mössbauer and electronic absorption spectra of μ-oxo dimeric PcFe complexes (form 690).

R^1	R^2	R^3	R^4	T^a /K	δ /mm s^{-1}	ΔE_Q /mm s^{-1}	Positions of bands in electronic absorption spectra[b] /nm	Ref.
H	H	H	H	77	0.36	0.44		156, 157
					0.25	1.26		
H	Bu^t	H	H	82	0.22	1.39	363, 590, 687, 704	56, 128, 135
					0.33	0.39		
H	Et	H	H	82	0.22	1.35	363, 588, 687, 703	135
					0.35	0.45		
H	$EtOCH_2$	H	H	100	0.22	1.34	290, 358, 600, 692, 704	135
					0.35	0.43		
H	CO_2Et	H	H	82	0.22	1.35	345, 586, 690, 710	135
					0.33	0.41		
H	$CO_2C_6H_{13}$-n	H	H	82	0.22	1.35	285, 350, 586, 697, 710	135
					0.33	0.53		
H	$OCH_2CH(Et)Bu^n$	H	H	82	0.22	1.33	300, 370, 410, 610, 715	135
					0.36	0.45		
H	OCH_2Bu^t	H	H	82	0.35	0.41	295, 368, 400, 610, 711	135
H	$OCH_2C(Me)_2Bn$	H	H	82	0.22	1.34	289, 367, 593, 697, 709	135
					0.36	0.41		
H	OC_8H_{17}-n	OC_8H_{17}-n	H	82	0.22	1.34	300, 360, 425, 600, 670, 714	135
					0.34	0.52		
H	$OCH_2CH(Et)Bu^n$	$OCH_2CH(Et)Bu^n$	H	82	0.36	0.52	300, 360, 425, 600, 670, 714	135

[a] Temperature at which the Mössbauer spectra were recorded; [b] toluene as the solvent.

properties.[135, 156, 157] Dimerisation of the monomer PNP[PcFe^{III}(OH)$_2$] afforded predominantly the so-called oxo(1) isomer of the μ-oxo dimeric PcFe complex, while bubbling of air through an oxo(1) solution in sulfuric acid or short-term heating of PcFe with sterically hindered aliphatic amines or α-substituted pyridines yielded predominantly the oxo(2) isomer.[89, 129, 156, 157] According to the data from Mössbauer spectroscopy (see Table 13), chromatographically pure specimens of readily soluble μ-oxo dimeric Pc^{R}Fe complexes occur as mixtures of the oxo(1) and oxo(2) isomers, which have not been isolated in the individual state.[56, 128, 135, 152] The parameters of the Mössbauer spectra of the μ-oxo dimeric Pc^{R}Fe complexes depend only slightly on the nature of the peripheral substituents; however, the electric field gradients have negative and positive signs for the oxo(1) and oxo(2) isomers, respectively. This fact provides additional evidence for the assumption as to the difference in the geometry of the isomers.[165] In addition, the Mössbauer spectra of the μ-oxo dimeric Pc^{t}Fe complex in frozen matrices (for example, in toluene) at 77 K have only one signal belonging to the oxo(1) isomer.[6] The proponents of the hypothesis for the trivalent state of the central iron atoms believe that the oxo(1) isomer has an angular geometry, whereas the Fe–O–Fe fragment in the oxo(2) isomer is quasi-linear and both isomers are high-spin iron(III) complexes [in the oxo(1) and oxo(2) isomers, $S = 5/2$ for both Fe atoms].[157] The supporters of the concept of the divalent state suggest that the phthalocyanine ligands in the oxo(1) isomer are, most probably, in the slipped-stack orientation, whereas an angular geometry of the ligands is typical of the oxo(2) isomer. Both iron(II) ions of the latter possess intermediate spin ($S = 1$).[128, 163] In our opinion, the results obtained in magnetic susceptibility studies and the ESR spectra of the μ-oxo dimeric PcFe oxo(1) and oxo(2) complexes are less reliable.[135, 155–157] The magnetic susceptibilities of different specimens of the oxo(1) and oxo(2) isomers at room temperature vary from 2.19 to 2.23 μ_B and from 1.38 to 1.42 μ_B, respectively. The antiferromagnetic interaction constants J calculated from the magnetic susceptibilities are -120 and -195 cm^{-1}, respectively.[156, 157] On the contrary, the results of measurements of the magnetic susceptibilities for ten chromatographically pure readily soluble specimens of the μ-oxo dimeric Pc^{t}Fe complex, which have been synthesised independently,[6, 56, 152] suggest the diamagnetism of this compound. The magnetic moments are no higher than 0.48 μ_B. Therefore, it should be admitted that specimens of the μ-oxo dimeric PcFe complexes studied in Refs 135 and 155–157 are very likely to contain substantial amounts of monomeric high-spin impurities, which introduce errors into the true values of magnetic susceptibility. This conclusion agrees well with the data from ESR and Mössbauer spectroscopy.[156, 157, 163] The ESR spectra of powders of μ-oxo dimeric PcFe complexes at the boiling temperatures of nitrogen or helium have signals with a g factor of ~ 6, which is characteristic of monomeric high-spin iron(III) complexes. Some specimens give additional signals with a g factor of ~ 4.3, characteristic of monomeric complexes of iron(III) in the intermediate ($S = 3/2$) spin state.[7, 132] The ESR spectrum of a powder of the μ-oxo dimeric Pc^{t}Fe complex at 77 K has a set of lines with a g factor approximately equal to 2.[135] Under analogous conditions, very weak signals with a g factor approximating 6 were additionally observed for this compound.[163] It should be noted that all ESR data were obtained only for powdered samples. However, as has been mentioned many times,[128, 166] the ESR spectra of the phthalocyanine complexes in the solid state should be considered with caution. Thus signals with g factors close to 2 were observed for many diamagnetic phthalocyanines in the solid phase.[166] Moreover, the lack of reliable data of ESR spectroscopy, in particular, for compounds containing the Fe–O–Fe fragment, was emphasised in a recent review[149] devoted to the synthesis and properties of binuclear iron complexes. Actually, some researchers believed[163, 167] that solutions of the μ-oxo dimeric Pc^{t}Fe complex are inactive for ESR spectroscopy both at room temperature and at 77 K.

The reaction of μ-oxo dimers of PcFe with nitrogen-containing compounds afforded μ-oxo dimeric complexes in the first stage. According to the hypotheses for the structures of the initial μ-oxo dimers, the structures LPcFe^{III}OFe^{III}PcL (**5**),[168, 169] H$_2$(LPcFe^{II}OFe^{II}PcL) or (LH)$_2$[PcFe^{II}OFe^{II}Pc] (**6**)[6, 7, 56, 128, 152] were assigned to the above-mentioned complexes. Complete X-ray diffraction analysis of one of the complexes of this type (L = MeIm) demonstrated that the phthalocyanine ligands in this compound are located parallel to each other.[45] The Fe–N(MeIm) distance (2.039 Å) virtually coincides with that in the PcFe(4-MeC$_5$H$_4$N)$_2$ complex (2.04 Å).[44] The Fe–O–Fe angle is 178.9°.[45] The structure of the axially coordinated μ-oxo dimeric PcFe complex exhibits two major distinctions from the structures of the well-characterised μ-oxo dimeric complexes of iron porphyrins without axial ligands:[148–151] (1) central iron atoms lie virtually in the plane of the phthalocyanine ligand, which is in marked contrast to the structures of the porphyrin analogues in which the high-spin iron(III) ions deviate from the plane of the ligand by 0.3–0.5 Å;[100, 148, 149] (2) coordination polyhedra about the central atoms are tetragonal bipyramids, whereas the coordination polyhedra in all μ-oxo dimeric iron complexes with macrocyclic ligands are tetragonal pyramids.[148, 149] In studies[45, 168] in which the structure **5** was assigned to the axially coordinated μ-dimeric PcFe complex, the first anomaly was attributed to the fact that this complex contains low-spin ($S = 1/2$; $S = 1/2$) rather than high-spin iron(III) ions.[168] The unusual coordination polyhedron was assigned to the 'unique' properties of this class of compounds.[45] However, it was noted[128] that the above-mentioned anomalies can be readily explained assuming that the central iron atoms in the μ-oxo dimeric PcFe complexes exist in oxidation state +2 (the structure **6**). Their electronic absorption spectra are typical of μ-oxo dimeric PcFe complexes with the parallel arrangement of the phthalocyanine ligands.[62] Thus the Q band ($\lambda_{max} \approx 627$ nm) is shifted hypsochromically compared to the Q band of monomeric PcFe complexes and its position depends only slightly on the nature of the axial ligand. The data on magnetic susceptibility and the parameters of the Mössbauer spectra of these compounds are given in Table 14. Note once again that all specimens occur (according to the data from Mössbauer spectroscopy) as mixtures of different coordination forms of PcFe,[45, 168, 169] and, consequently, magnetic susceptibility data must be considered with caution. However, the parameters of the Mössbauer spectra most probably correspond to low-spin iron(II) complexes (see Tables 2 and 5) rather than to low-spin iron(III) complexes (see Table 10). The electric field gradient of the μ-oxo dimeric PcFe complex, which is axially coordinated by 4-MeC$_5$H$_4$N, has a positive sign.[134] Comparison of the Mössbauer spectra of the form 627 with the spectra of the oxo(1) and oxo(2) isomers suggests that the oxo(2) isomer and the axially coordinated μ-oxo dimeric complex are identical in geometry.

The chemical behaviour of the μ-oxo dimeric PcFe complexes was studied in detail with the aim of determining the valence state of the central iron atoms.[6, 7, 56, 128, 152] The reactions of the initial μ-oxo dimeric form of both unsubstituted and substituted PcFe (the form 690) with nitrogen-containing heterocyclic com-

Table 14. Mössbauer spectra of the form 627 of the iron phthalocyanine complexes.[168]

L	T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	μ_{eff}/μ_B
4-MeC$_5$H$_4$N	295	0.12	1.81	1.99
	77	0.19	1.75	–
	4.2	0.20	1.76	–
Pip	4.2	0.19	1.61	2.11
MeIm	4.2	0.17	1.58	2.16
Py	4.2	0.18	1.73	1.86

pounds[6, 7, 128, 152, 168, 169] or isocyanides[135] afforded complexes with composition $PcFe^{II}L_2$ as the final products. On the assumption that the form 690 has the structure **3**, this reaction should be a redox process; however, oxidation products have never been detected. Therefore, the structure **4** is more probable for the form 690. The reactions of the form 690 of the Pc^tFe complex or its axially coordinated analogue (the form 627) with cyanide anions in organic solvents afforded the well-known $Na_2[Pc^tFe(CN)_2]$ complex.[128, 167] The electronic absorption spectra for these reactions have distinct isosbestic points.

Data on the oxidation of triphenylphosphine with the μ-oxo dimer of PcFe (the form 690) under an inert atmosphere have been published:[170]

$$(PcFe^{III})_2O + PPh_3 + 4\,Py = 2\,PcFe^{II}Py_2 + Ph_3PO.$$

The formation of Ph_3PO suggests the trivalent state of the central iron atoms in the initial compound. These results are in contradiction with those obtained in the study of the reaction of the form 690 with diphenylpicrylhydrazine under oxygen-free conditions.[6] Thus it was found that the oxidation of diphenylpicrylhydrazine under strictly oxygen-free conditions did not occur at all. However, when a controlled amount of oxygen was introduced into a reactor, oxidation catalysed by the metal complex occurred. Moreover, it was demonstrated that the reaction of the form 690 with quinoline (which apparently contained an impurity of isoquinoline) yielded water (in an equimolar amount with respect to the initial form 690).[6, 152]

$$H_2(PcFe)_2O + 4\,L = 2\,PcFeL_2 + H_2O$$

This behaviour is consistent with the structure **4** for the form 690. However, it was mentioned[154, 162] that when μ-oxo dimeric PcFe complexes were prepared by the reactions with O_2, the oxygen was consumed in a ratio $O_2 : PcFe = 1 : 4$, and the only reaction product, *viz*., the μ-oxo dimer, was formed in quantitative yield. This fact contradicts the structure $[HPc^RFe]_2O$ (**4**), which can be formed from Pc^RFe and O_2 if a source of hydrogen atoms exists.

With the aim of refining the structure of the form 690, the reaction of Pc^tFe with oxygen in noncoordinating solvents (benzene and cyclohexane) was studied. It was found that: (1) the amount of oxygen consumed per mole of Pc^tFe introduced into the reaction depends on the concentration of the latter, and the $O_2 : Pc^tFe$ ratio changes from 1 : 5.0 to 1 : 2.7 in the concentration range of $6.3 \times 10^{-3} - 1.1 \times 10^{-1}$ mol litre^{-1}; (2) the μ-oxo dimer is the major but not the only reaction product; the yield of this dimer varies from 78% to 95%. It was found that the reagents were consumed in side reactions, including oxidative destruction of the macrocycle by oxygen, which is strongly activated due to coordination in the complex with Pc^tFe. Therefore, side oxidation reactions of the phthalocyanine macrocycle, substituents in this ring or other substrates can serve as a source of protons for the formation of the form 690.

The formation of the form 690 from the iron(III) derivative, *viz*., $[PcFe(OH)_2]^-$,[128, 156] also calls for explanation. In our opinion, this process is accompanied by reduction of the iron atom with the hydroxide anion, which is one of the strongest reducing agents for PcFe complexes.[171]

Oxidation of the form 690 was examined for the first time in the study.[7] The μ-oxo dimeric Pc^tFe complex (hereinafter, the form 630), which was prepared by the reactions of the form 690 with iodosobenzene or peracetic acid, was characterised by electronic absorption spectroscopy (λ_{max} = 630 nm) and Mössbauer spectroscopy (δ = 0.58 mm s^{-1}, ΔE_Q = 0.34 mm s^{-1} at 80 K). Later on, a procedure for the preparation of this compound was improved.[128] Thus this complex was prepared in virtually quantitative yield by the reaction of the form 690 with cumene hydroperoxide generated *in situ*. These authors were also the first to analyse the NMR spectra of the form 630. The reaction of the form 630 with cyanide anions afforded the known low-spin iron(III) complex, *viz*., $Na[Pc^tFe(CN)_2]$,[128] which can be also prepared by oxidation of the cyanide complex $Na_2[Pc^tFe(CN)_2]$ with bromine[55] or cumene hydroperoxide.[128] The reaction of the form 630 with hydrogen chloride yielded derivatives of iron(II) and (formally) iron(IV), *viz*., hydrochloride $Pc^tFe \cdot HCl$ and the radical cation $Pc^+ \cdot FeCl_2$, respectively.[7] All the aforesaid provides evidence for the trivalent state of the central iron atoms in the form 630. Therefore, on the basis of the spectral data and the chemical properties of the μ-oxo dimeric PcFe complexes, the forms 690 and 627 were characterised as PcFe(II) derivatives and the form 630 was characterised as the μ-oxo dimer of iron(III) phthalocyanine.[6, 7, 56, 128, 152, 163]

The reactions of PcFe with azides afforded μ-nitride PcFe complexes of the general formula $PcFe^{+3.5}NFe^{+3.5}Pc$ (Table 15).[172–174] These compounds can be oxidised electrochemically or chemically to form complexes with composition $(PcFe^{+4}NFe^{+4}Pc)^+X^-$ (see Table 15).[172] The structure of one of the resulting compounds, *viz*., $[(PcFe)_2N]Br$, was established by X-ray diffraction analysis.[175]

Table 15. Parameters of Mössbauer spectra of the μ-nitrido and μ-carbido dimeric Pc^RFe complexes.[172, 173]

Complex	δ /mm s^{-1}	ΔE_Q /mm s^{-1}
$(PcFe)_2N$	0.06	1.76
$(PcFe)_2NPF_6$	0.10	2.06
$(PcFe)_2C$	−0.16	2.69
$[(4\text{-}MeC_5H_4N)PcFe]_2C$	0.03	1.19
	0.12	0.25
$(PyPcFe)_2C$	0.01	1.16
$(PipPcFe)_2C$	0.01	1.11
$[(MeIm)PcFe]_2C$	0.01	0.94
$[(4\text{-}MeC_6H_4N)PcFe]_2NPF_6$	−0.10	1.76
$(PyPcFe)_2NPF_6$	−0.09	1.76
$(PipPcFe)_2NPF_6$	−0.09	1.73
$[(MeIm)PcFe)_2NPF_6$	−0.09	1.52

Note. The spectra were recorded at 77 K relative to metallic iron.

The reaction of PcFe with tetraiodomethane in the presence of reducing agents, such as sodium dithionite or sodium borohydride, afforded μ-carbide PcFe complexes of the general formula $PcFe^{IV}CFe^{IV}Pc$ (see Table 15).[176–179] This synthetic procedure has been improved quite recently, *viz*., the reaction of $[PcFe^{III}(OH)_2]^-$ with dichlorocarbene generated *in situ* was used.[171, 180] Unfortunately, the poor quality of crystals of the $[(MeIm)PcFe]_2C$ complex did not allow the researchers to perform a complete structure analysis of this complex.[178] However, the values of selected bond lengths and bond angles were determined. In particular, it was demonstrated that two phthalocyanine ligands in the complex are virtually parallel to each other (the Fe−C−Fe angle is 178 °).

Heterobimetallic oxo dimeric complexes of the PCrOFePc type, where P is the dianion of α-substituted porphyrin, were synthesised and their properties were studied.[181] These compounds were prepared by the reactions of $PCr^{IV}=O$ with PcFe. The synthesis, structures and properties of the μ-nitride heterodimer $(TPP)Fe^{+3.5}NFe^{+3.5}Pc$, where TPP is tetraphenylporphin, as well as of its oxidised forms were described.[182]

Among μ-oxo dimeric complexes of iron porphyrazines, derivatives of tetra-*tert*-butyl-,[6] octaphenyl-,[141] octaethyl-[57] and octa(ethylthio)-substituted[143] porphyrazines are presently available. All these compounds were characterised by electronic, IR and NMR spectra. The reaction of the pyridine adduct of iron octaphenylporphyrazine with perchloric acid followed by the addition of HN_3 afforded the corresponding μ-nitride dimeric complex, which was characterised by electronic absorption, IR, Mössbauer and ESR spectra.[183] The pyridine monoadduct of this

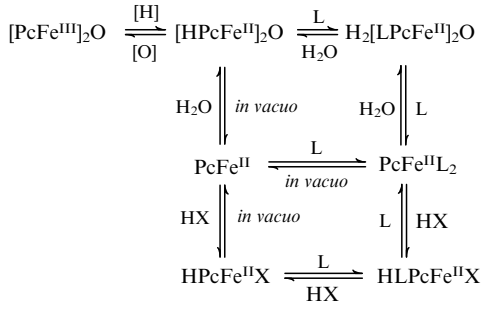
complex formed in frozen matrices adds reversibly one oxygen molecule per molecule of the initial complex.

Recently, the synthesis and selected properties of the heterobinuclear complex $TAP^{Ph}Mn=NFeTAP^{Ph}$ were reported.[184] However, the data from electronic absorption spectroscopy and mass spectrometry (primarily, the absence of the molecular ion and the $TAP^{Ph}FeN$ fragment) and the lack of Mössbauer spectra require that the suggested structure be considered with particular caution.

V. Some features of coordination chemistry of substituted iron phthalocyanines and their analogues

The interconversions of the coordination forms of iron phthalocyanines are shown in Scheme 2. As expected, the peripheral substituents in the macrocycle often break down these general regularities. Thus when bulky substituents (for example, the 2,4,6-trimethylphenyl substituents) were introduced at the α positions of the macrocycle, the μ-oxo dimeric Fe(II) and Fe(III) complexes were not formed at all due to steric hindrances caused by the substituents.[7,8] In this case (under conditions of formation of μ-oxo dimeric complexes), the corresponding monomeric hydroxo complexes $HPc^{R}Fe(OH)$ can be isolated. In an alkaline medium, the latter are converted into the corresponding oxoferryl derivatives, which undergo polymerisation upon prolonged storage.[7,8]

Scheme 2



The effect of the electronic properties of substituents on the behaviour of iron phthalocyanines is generally manifested only in the relative stabilities of particular forms and in the positions of the bands in the electronic absorption spectra. The qualitative characteristic features of this effect can be observed only in special cases. For example, due to the presence of eight electron-withdrawing substituents, iron (3,5)-octakisnitrophthalocyanine[7,8] reacts with nitrogen bases to give initially the $PcFe^{II}L_2$ complex, which is converted into the isoelectronic form $Pc^{3-\cdot}Fe^{III}L_2$ containing the stable phthalocyanine radical anion. Due to the presence of four SPh substituents in iron tetrakis-(phenylthio)phthalocyanine, the iron ion has the $^3A_{2g}[(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^2]$ electronic configuration[27] rather than the $^3E_g[(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1]$ configuration typical of $Pc^{R}Fe$. When eight electron-donating alkoxy groups are introduced into PcFe at positions adjacent to the macrocycle (at positions 1 and 4), the central iron atom is initially subjected to electrochemical oxidation, whereas the phthalocyanine ligands are oxidised in the complexes containing other substituents in the macrocycle.[109]

VI. Major fields of application of iron phthalocyanines and their analogues

High catalytic activity of PcFe in decomposition of peroxides and in oxidation of some classes of organic compounds had been discovered by Cook[185–187] back in the late 1930s. The use of iron phthalocyanines in catalysis has been expanded substantially since these years.[3,188] Thus these compounds were used as homogeneous and heterogeneous catalysts of epoxidation of alkenes,[188,189] oxidation of hydrocarbons to alcohols, aldehydes, quinones and ketones[190–194] and oxidation of arylamines,[195] phosphines,[162,196] thiols[197–199] and conjugated aromatic systems.[200] Electrodes modified with iron phthalocyanines and their analogues were used for electrooxidation of thiols,[197] electroreduction of molecular nitrogen to ammonia[201,202] and electroreduction of carbon dioxide,[203] sulfur dioxide,[204] nitrogen oxides[205] and molecular oxygen.[206–208]

The chemo- and electrochromic properties of iron phthalocyanines and their analogues as well as variations in the conducting properties of these complexes depending on the medium made it possible to use these compounds in sensors for halogens,[209] nitrogen oxides,[210] oxygen[211] and aldehydes.[212] Photochemical reactions of PcFe are well studied, which allows the use of this compound for the preparation of photosensitive materials (including those operating in the near IR region[213]), photoconducting devices,[214] photosensitive inks[215] and materials for optical data recording and storage[216,217] as well as for the production of high-contrast photographic materials.[218]

Since axially coordinated complexes of iron phthalocyanines are readily available compounds, highly sensitive and selective membranes for gas separation[219] and food storage[220] were constructed on the basis of these complexes. The use of cathodes modified with PcFe and its analogues in lithium cells with aggressive electrolytes, such as thionyl chloride and sulfur dioxide, made it possible to improve substantially their discharge characteristics.[221–225] Intercalation of iron phthalocyanine into the structures of inorganic oxides leads to the appearance of magnetic properties in the resulting materials.[226]

In the reactions with reducing agents, such as ascorbic acid, catalysed by iron phthalocyanines, different so-called active oxygen forms (primarily, oxygen-centred radicals) are generated. This made it possible to initiate studies of complexes of iron phthalocyanines and their conjugates with proteins, DNA and RNA as potential drugs in catalytic (dark) therapy of cancer.[21,227,228] In addition, high antihistamine and antiserotonin activities of PcFe derivatives were observed in a number of studies.[5,229] The use of these compounds as deodorising agents is based on their high oxidase activity.[230] Semiconducting properties of iron phthalocyanines and their analogues have received little use.[9,13] Selective axial coordination of iron phthalocyanine to nitrogen-containing compounds allows one to solve a number of analytical problems by NMR spectroscopy.[105–108]

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