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Synthesis and spectral properties of iron(III) tetra-*tert*-butylphthalocyanine complexes

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Bu

But

L = acac, Cl

Two tetra-*tert*-butylphthalocyanine complexes of iron(III) were synthesized in high yields from the phthalocyanine ligand and iron(III) salts; the oxidation state of iron was confirmed by Mössbauer and EPR spectroscopy. The existence of an acid–base equilibrium during spectro-photometric titration was revealed. The ^{But}PcFeCl complex catalyzed chlorination of benzene.

Phthalocyanines attract attention due to broad possibilities for structure modification: variation of substituents,^{1–7} expansion of the π -system,^{8–17} introduction of various metals,^{18–22} synthesis of sandwich complexes,^{23–25} and replacement of the axial ligand.²⁶ These modifications considerably affect the spectral, semiconductor and catalytic properties of phthalocyanine complexes,^{9,23,27,28} which opens broad prospects for compounds possessing required properties.

A substituted iron(III) phthalocyanine was chosen as the object of this study. The choice of iron as the central ion was caused by its ability to change the oxidation state and by the possibility of introduction of various axial ligands. Iron complexes find application as organic semiconductors, catalysts and photosensitive materials.^{29–31} It is important to note that, as compared to iron(II) complexes, phthalocyanine and porphyrin complexes of iron(III)



Scheme 1 Reagents and conditions: i, Fe(acac)₃, DBU, *o*-DCB, Δ ; ii, FeCl₃, DBU, *o*-DCB, Δ .

have been studied less thoroughly, reliable proof of their structure and properties being unavailable in the literature until recently.³⁰

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We chose bulky *tert*-butyl groups as the peripheral substituents as they essentially improve the solubility and decrease aggregation.^{3,4,32} By analogy with the preparation procedure of phthalocyanine complexes of lanthanides developed in our laboratory,³³ we synthesized the target compounds by metallation of *tert*-butyl substituted phthalocyanine ligand **1** with iron(III) salts (Scheme 1).[†] The reaction was carried out under reflux in 1,2-dichlorobenzene (*o*-DCB) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. Two iron sources

[†] Immediately before the synthesis, $Fe(acac)_3$ and $FeCl_3$ salts were kept in a drying cabinet at 90 °C under reduced pressure. Phthalocyanine **1** was synthesized as reported previously.³²

Iron(III) 2(3),9(10),16(17),23(24)-tetra-tert-butylphthalocyaninate acetylacetonate **2a**. Ligand **1** (0.24 g, 0.33 mmol), Fe(acac)₃ (0.18 g, 0.50 mmol) and DBU (35.00 mg, 0.23 mmol) were refluxed in *o*-DCB (10 ml) for 1.5 h until the starting ligand was consumed. The reaction was monitored using UV-VIS spectroscopy and TLC (Al₂O₃, toluene as the eluent). The reaction mixture was cooled to room temperature, and CHCl₃ (25 ml) was added. The insoluble admixtures were filtered off. The solvent was removed from the filtrate. The resulting dry residue was treated with 80% methanol (3×50 ml). The solid remained was dried in a drying cabinet under reduced pressure at 90 °C. The yield of complex **2a** was 172 mg (72%). MS (MALDI-TOF), *m/z*: 792 [M–acac]⁺⁺, 809 [M–acac+OH]⁺⁺. UV-VIS [toluene, λ_{max}/nm (*I*/I_{max})]: 456 (0.31), 597 (0.24), 661 (1.00).

Iron(III) 2(3),9(10),16(17),23(24)-tetra-tert-butylphthalocyaninate chloride **2b.** Ligand **1** (0.21 g, 0.28 mmol), FeCl₃ (64.90 mg, 0.40 mmol) and DBU (35.00 mg, 0.23 mmol) were refluxed in *o*-DCB (10 ml) for 1.5–2 h until the starting ligand was consumed. The reaction was monitored using UV-VIS spectroscopy and TLC (Al₂O₃, toluene as the eluent). The mixture was cooled to room temperature, and CHCl₃ (25 ml) was added. The insoluble admixtures were filtered off. The solvent was removed from the filtrate. The resulting dry residue was treated with 80% methanol (3×30 ml). The solid remainder was dried in a drying cabinet under reduced pressure at 90 °C. The yield of complex **2b** was 188 mg (81%). MS (MALDI-TOF), *m/z*: 780 [M–Cl–CH₂+H]⁺⁺, 792 [M–Cl]⁺⁺, 809 [M–Cl+OH]⁺⁺. UV-VIS [toluene, λ_{max}/nm (*I*/*I_{max})*]: 704 (1.00).



Figure 1 Mass spectrum of ^{Bul}PcFe(acac). The insets show (*a*) the peak of [M-acac] and (*b*) the theoretically calculated isotope distribution for this peak.

were tested to study the effect of the counter-ion nature on the yield of the target compounds, namely, iron(III) acetylacetonate and iron(III) chloride. In the case of iron chloride, the yield of compound **2b** was higher probably due to smaller steric hindrance in comparison with acetylacetonate.

Complexes **2a**,**b** were characterized[‡] by MALDI-TOF mass spectrometry. Figure 1 demonstrates the mass spectrum of the ^{But}PcFe(acac) complex **2a** as an example. The mass spectrum contains a fragmentation peak with abstraction of the axial ligand. Its isotopic pattern agrees with the theoretically calculated one. Furthermore, a peak corresponding to the elimination of the axial ligand and addition of a hydroxy group is also observed. This is the evidence of a high mobility of the axial ligand in the complexes **2a**,**b**.

The absorption spectra of complexes 2a,b were recorded in toluene. Figure 2 demonstrates the spectrum of ^{Bu'}PcFe(acac) 2a as an example. Interestingly, a number of charge transfer bands are observed for complex 2a, the most prominent line being at 456 nm. This phenomenon is typical of iron(III) complexes.³⁰

The possibility of protonation of phthalocyanine complexes allowed us to perform the acid–base spectrophotometric titration of ^{Bu'}PcFe(acac) **2a** (Figure 3). The spectrum changes upon gradual addition of acetic acid: the Q-band shifts from 668 to 680 nm, the broadened bands appear at 550 and 800 nm, while the shoulder at 700 nm disappears. The original spectrum shape is recovered completely upon addition of a few drops of a base



Figure 2 UV-VIS spectrum of ^{But}PcFe(acac) in toluene.

[†] UV-VIS spectra were recorded in quartz cells (1×1 cm) using a Helios- α spectrophotometer. TLC was performed on Merck Aluminium Oxide F₂₅₄ neutral plates. MALDI-TOF mass spectra were recorded on a VISION-2000 instrument.

Mössbauer absorption spectra were obtained on an MC1104EM express Mössbauer spectrometer manufactured by 'Kordon' (Rostov-on-Don). ⁵⁷Co in a metallic rhodium matrix with 1 mC activity from 'RITVERTs' (St. Petersburg) was used as the γ -radiation source. To record the spectra, ground powdered samples in a plastic cell were placed into a vacuum cryostat. Spectra were recorded both at room temperature and at liquid nitrogen temperature. The temperature of the samples was controlled to within ±2°. Mathematical processing of experimental Mössbauer spectra was performed for high resolution spectra using the Univem MS 9.08 program. The spectra were described by a combination of symmetric doublets. Chemical shifts are reported relative to α -Fe.

EPR spectra were recorded in the X range using a Bruker EMX plus spectrometer.



Figure 3 Spectrophotometric titration of a ^{But}PcFe(acac) solution in DMF with acetic acid (the solid lines indicate the starting and final forms; dotted lines indicate intermediate forms).

(DBU). This phenomenon and the existence of isobestic points indicate an equilibrium process.

The Mössbauer spectrum of ^{But}PcFe(acac) **2a** at room temperature [Figure 4(*a*)] is a slightly asymmetric doublet that is satisfactorily approximated by a model involving two symmetric doublets. The isomeric shifts of both doublets (Table 1) do not allow the oxidation state of iron to be determined unambiguously due to a high degree of covalency of bonds between iron and nitrogen atoms of the phthalocyanine ligand. The values obtained can correspond both to high-spin iron(III) (S = 5/2) in Fe³⁺N₄ moieties³⁴ and to low-spin iron(II) (S = 0) in Fe²⁺N₄ moieties.³⁵ On the other hand, doublets with a similar isomeric shift were assigned to iron(III) compounds elsewhere.³⁶ Furthermore, low quadrupole splitting (0.6–0.8 mm s⁻¹) is also typical of high-spin iron(III) compounds.³⁷

The Mössbauer spectra for the same sample cooled to liquid nitrogen temperature (78 K) [Figure 4(b)] considerably differ

Table 1 Parameters of Mössbauer spectra of ^{But}PcFe(acac) 2a.^a

<i>T</i> /K	Sub- spectrum	$\frac{\delta~(\pm 0.01)}{\rm mm~s^{-1}}$	Δ (±0.01)/ mm s ⁻¹	$\Gamma_{\rm exp}$ (±0.03)/ mm s ⁻¹	I (±0.5) (%)	S (±5) (%)
295	1	0.30	0.72	0.60	6.3	78
	2	0.47	0.76	0.32	3.3	22
78	1	0.04	0.95	0.29	6.3	17
	2	0.23	2.65	0.78	0.8	6
	3	0.42	0.44	0.19	3.2	6
	4	0.51	0.80	0.48	15.6	71

^{*a*} δ is isomeric shift, Δ is quadrupole splitting, Γ_{exp} and *I* are the resonance line width and intensity, *S* is relative area of the subspectrum.



Figure 4 Mössbauer spectra of complex ^{But}PcFe(acac) **2a** at (*a*) 295 and (*b*) 78 K and models for their description (the numbers indicate the numbering of the subspectra in Table 1).

from the spectra obtained at room temperature. First, we should note the twofold increase in the overall resonance absorption effect which is characteristic of iron complexes with large organic ligands.^{38,39} The spectrum itself can be satisfactorily described by a model involving four symmetric doublets with strongly differing parameters. In this model, minor components are described by doublets with maximum values of quadrupole splitting and line widths (subspectrum 2) and with minimum values of similar parameters (subspectrum 3). On the one hand, these subspectra can be components of a sextet that is indicative of weak intermolecular interactions of iron atoms and is not resolved due to relaxation phenomena. On the other hand, these subspectra may correspond to independent iron atoms in strongly differing environments. In such a case, the doublet with a large line width (line 2) is attributed to iron atoms in an unordered environment (amorphous phase), whereas, conversely, the doublet with a very small width (line 3) corresponds to atoms in a highly ordered environment (crystalline phase).

The doublet with the smallest isomer shift (subspectrum *I*) can be ascribed to iron(II) or iron(III) atoms in the low-spin state (S = 0 or 1/2, respectively). The presence of considerable quadrupole splitting indicates that this doublet belongs to iron(III) atoms. The appearance of this doublet at low temperatures indicates that there is a thermal crossover transition for a fraction of the complexes corresponding to this substance.

However, assuming that the transition was complete, one may suppose that the doublet in question matches the doublet in subspectrum 2 at room temperature. In such a case, the doublet in subspectrum 4 at low temperature corresponds to the doublet in subspectrum 1 at room temperature. The absence of a strong temperature dependence of quadrupole splitting for this doublet also indirectly supports that it belongs to an iron(III) complex.

The EPR spectrum of a ^{But}PcFe(acac) **2a** solution in toluene recorded at room temperature (Figure 5) contains a broad structureless anisotropic signal with a *g*-factor that is typical of phthalocyanine compounds of low-spin iron(III).³⁵ Note that, according to literature data, two signals are observed for nonsubstituted iron(III) phthalocyanine⁴⁰ and iron(III) azaporphyrin analogues in EPR spectra recorded at low temperatures: with $g \approx 2$ and $g \approx 5$.⁴¹ In this case, high *g*-factor values probably correspond to high-spin iron(III).⁴²

The observed distinctions from Mössbauer spectroscopy data concerning the spin state of iron(III) may be both due to the large difference of the characteristic time of EPR spectroscopy in comparison with Mössbauer spectroscopy and to differences/ changes in the structure and composition of complexes in the solid phase and in solutions.^{38,40}

We tested ^{But}PcFeCl **2b** as the catalyst of chlorination of benzene (Scheme 2). If the reaction was carried out for 48 h in the light, the products contained 1,2,3,4,5,6-hexachlorocyclohexane resulting from radical chlorination. Its mass spectrum contains characteristic peaks: 113 ($C_6H_5Cl^+$), 147 ($C_6H_5Cl^+_2$), 183 ($C_6H_5Cl^+_3$), 219 ($C_6H_5Cl^+_4$), 254 ($C_6H_5Cl^+_5$), 290 ($C_6H_5Cl_6$).



Figure 5 EPR spectrum of ^{But}PcFe(acac) in toluene.



Scheme 2 Reagents and conditions: i, Cl_2 , ^{Bu'}PcFeCl 2b, hv; ii, Cl_2 , ^{Bu'}PcFeCl 2b, in the dark.

The second product was chlorobenzene, whose mass spectrum contained peaks: 77 (Ph⁺), 112 (PhCl).

If the reaction was carried out for 30 min in the dark, it proceeded selectively to give chlorobenzene (see Scheme 2). The catalyst (^{Bu'}PcFeCl) underwent partial oxidation without destruction of phthalocyanine macrocycle.

A more detailed study of chlorination processes will be performed separately.

In conclusion, we obtained hitherto unreported tetra-*tert*-butylphthalocyanine complexes of iron(III) in high yields. The structure and oxidation state of iron were confirmed by UV-VIS spectroscopy, mass spectrometry, Mössbauer and EPR spectroscopy. The target complex was successfully used as the catalyst in benzene chlorination, both radical and electrophilic.

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