

Synthesis and Properties of Fe^{III}–N=Mn^{IV} Heterometallic Complex with Tetra-*tert*-butylphthalocyanine Ligands[⊗]

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*Heterometallic N-bridged complex PcFeNMnPc (Pc – tetra-*tert*-butylphthalocyanine) was synthesized by interaction of PcMn^V=N with PcFe^{II}. As evidenced from UV-vis, IR and EPR data, this complex can be easily oxidized by dioxygen with formation of a stable green cation-radical with one unpaired electron. In protic solvents or in the presence of bases this compound gives blue Mn^{IV}=N-Fe^{III} complex with asymmetrical bond distribution in comparison with well known diiron PcFe^{+3.5}NFe^{+3.5}Pc derivatives.*

Keywords: Phthalocyanine, iron, manganese, synthesis, nitrido, spectral properties, heterobimetallic complex.

Introduction

Due to their exceptional optical and electronic properties as well as high chemical and thermal stability, metallophthalocyanines (MPc) have become the compounds of a great importance with a wide range of applications in industry, medicine and research. They are widely used as dyes and pigments, oxidation catalysts, molecular and photoconductors, liquid crystalline materials, sensors and agents in anticancer photodynamic therapy.^[1-3] Unique properties of these compounds mainly are attributed to the aromatic 18 π electron conjugated macrosystem, which is able to stabilize different reduced and oxidized forms.

Dimeric metallophthalocyanines containing one metal cation and two Pc ligands («sandwich» like complexes)^[4-5] or two transition metal cations (μ -*X*-dimers, where *X* = O (μ -oxo), N (μ -nitrido), C (μ -carbido) constitute two of the most interesting classes of MPc. The progress in synthesis and characterization of latter compounds was recently reviewed by Ercolani and co-workers.^[6]

The studies of iron phthalocyanines as catalysts for oxidation processes showed that FePc in μ -oxo dimeric form in several cases exhibited better catalytic properties (activity and selectivity) than mononuclear FePc when using *tert*-butylhydroperoxide^[7,8] and hypervalent iodine compounds^[9,10] as oxidants. The high catalytic activity of μ -oxo dimeric complexes was unexpected since they are generally considered as catalytically inert species. High-valent iron oxo complexes were proposed to be oxidizing species and better catalytic properties of μ -oxo dimeric iron phthalocyanines have been explained by better stabilization

of high-valent states in dimers due to delocalization of the charge on two iron atoms. However, these μ -oxo dimers are not completely stable under catalytic conditions and undergoes monomerization that results in the decrease of selectivity of oxidations.^[7,8]

In the search for the stable binuclear iron phthalocyanine complexes we turned to *N*-bridged diiron phthalocyanine complexes.^[11-16] These complexes possessing very interesting properties have never been evoked as catalysts before our work. We have discovered that *N*-bridged diiron phthalocyanines exhibit exceptional catalytic properties. For instance, PcFe^{+3.5}NFe^{+3.5}Pc complex with ^tBu substituents activates hydrogen peroxide to afford a very strong oxidizing species which catalyzed the oxidation of one of the most difficult-to-oxidized organic compounds – methane to formic acid and formaldehyde under very mild conditions: in pure water at 25–60°C.^[11] The oxidation of methane was unambiguously evidenced using labelled ¹³CH₄. This represents the first example of a bio-inspired oxidation of methane. Moreover, the same complex catalyze the oxidation of benzene to phenol *via* intermediate formation of benzene oxide accompanied by a NIH shift that is usually associated with oxidation performed by cytochrome P-450 and toluene monooxygenase involving a high-valent iron oxo species.^[12] These results strongly suggested that similar high-valent but diiron oxo complex could be involved in oxidations performed by PcFeNFePc – H₂O₂ system.^[13] Indeed, positive electrospray ionization-mass spectrometry data and isotope labelling experiments with ¹⁸O demonstrated the formation of high-valent formally Fe^{IV}=N-Fe^V=O complex which should be an extremely strong oxidant and active intermediate in these reactions.^[11] The oxidation of methane was carried out in homogeneous as well as in heterogeneous conditions using (PcFe)₂N complex supported onto silica. The heterogeneous oxidation in water is the most suitable approach from practical point of view

⊗ This contribution is dedicated to professor Vasilij Fedorovich Borodkin on the occasion of his 100th Anniversary.

⊗ Статья посвящена 100-летию юбилею профессора Василия Фёдоровича Бородинкина.

allowing the optimal use of oxidant, avoiding formation of side products owing to oxidation of organic solvent and providing environmentally friendly process. The supported catalyst was quite stable under reaction conditions and could be separated and re-used without appreciable decrease of the catalytic activity. Other important feature of this complex is the high catalytic activity in oxidations of mercaptanes and thiophenols by oxygen.^[14] In comparison with monomeric cobalt and iron derivatives (PcFe)₂N complex catalyze this reaction in acidic and neutral media. In order to increase the choice of *N*-bridged diiron complexes we have prepared μ -nitrido diiron phthalocyanines with electron-withdrawing alkylsulfonyl substituents.^[15,16] In order to estimate the reactivity of these novel complexes towards oxidation of aliphatic C-H vs. aromatic oxidation we have studied the oxidation of toluene and *p*-xylene by ^tBuOOH. Significantly, only traces of products of aromatic oxidation were detected by GC-MS. The principal products of benzylic oxidation were benzoic and *p*-toluic acids, respectively, formed with yields 73-83 % depending on experimental conditions.^[15]

Obviously, the preparation of novel *N*-bridged binuclear complexes will enlarge the choice of these complexes having different electronic and catalytic properties that allow gaining deeper insight into this new catalytic chemistry. Herein, we publish the preparation of novel mixed μ -nitrido iron manganese phthalocyanine complex with localized structure and investigation of its properties.

Experimental

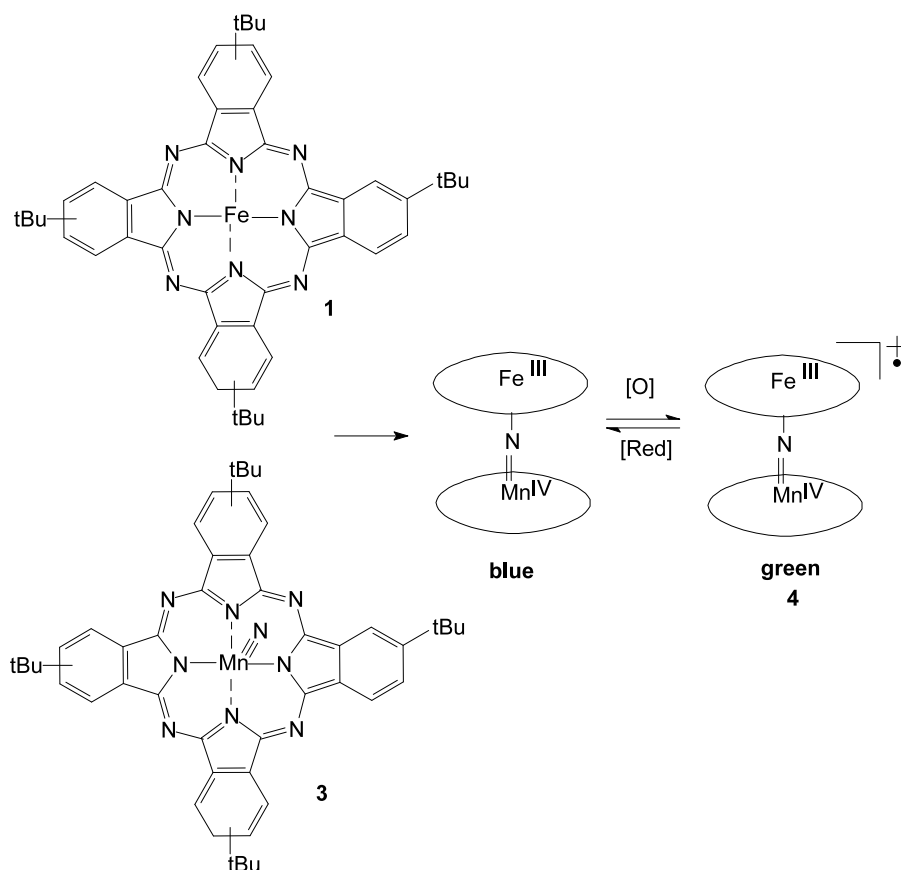
The solvents and reagents were purchased from Aldrich and used as received. The tetra-4-*tert*-butylphthalocyanine and

tetra-4-*tert*-butyl(phthalocyaninato)iron (**1**) were prepared using literature procedures.^[17,18] UV-visible spectra were recorded with a Agilent 8453 spectrophotometer. IR spectra were obtained with a Bruker Vector-20 spectrometer and EPR spectra using Bruker ESP 300E instrument with standard rectangular cavity Bruker ER 4102ST at 77K. Mass spectra were recorded on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive ions in the ESI mode. Samples in dichloromethane:acetonitrile (1:1) containing 0.1 % of formic acid were infused directly into the source using a syringe pump. The following source parameters were applied: spray voltage 3.0 kV, nitrogen sheath gas flow 10 arbitrary units.

Tetra-4-tert-butyl(phthalocyaninato)manganese(III) acetate, **2**. 0.1 g of tetra-4-*tert*-butylphthalocyanine (135 μ mol) was dissolved in 10 ml of pyridine and 0.2 g (1600 μ mol) of MnCl₂ was added to the solution. The resulting solution was stirred at 100°C during 6 hours. After cooling, the reaction mixture was poured in 100 ml of 50 % acetic acid. Green precipitate was filtered and washed with water. The complex **2** was further purified by column chromatography (SiO₂) using CH₂Cl₂:MeOH (10:1) mixture. Yield of **2**: 0.068 g (59 %). UV-vis (CH₂Cl₂) $\lambda_{\max}$ nm (rel. intensity): 370 (0.451), 531 (0.155), 659 (0.169), 730 (1.00).

Nitrido(tetra-4-tert-butyl(phthalocyaninato)manganese(V), 3. Compound **2** (0.04 g, 47 μ mol) and NaN₃ (0.1 g, 1500 μ mol) were heated in 10 ml of xylene at 140°C with stirring under argon during 8 hours. After cooling, the excess of sodium azide was separated by filtration. Complex **3** was purified by column chromatography (SiO₂) using benzene as the eluent. After evaporation of solvent **3** was obtained as blue powder (0.032 g, 84 %). *m/z* (ESI) (%) 806.3 (100) [(M)⁺]. IR (KBr) $\nu_{\max}$ cm⁻¹: 1078 ($\nu_{\text{Mn=N}}$). UV-vis (CH₂Cl₂) $\lambda_{\max}$ nm (rel. intensity): 341 (0.481), 680 (1.00).

Heterometallic μ -nitridodimer μ -(MnNFe)(^tBuPc)₂, **4**. Compound **3** (0.03 g, 37 μ mol) and complex **1** (0.04 g, 54 μ mol) were dissolved in 5 ml of xylene. The resulting solution was heated at 140°C during 4 h under argon. The dimer **4** was purified using column chromatography (SiO₂). The impurities were removed



Scheme 1.

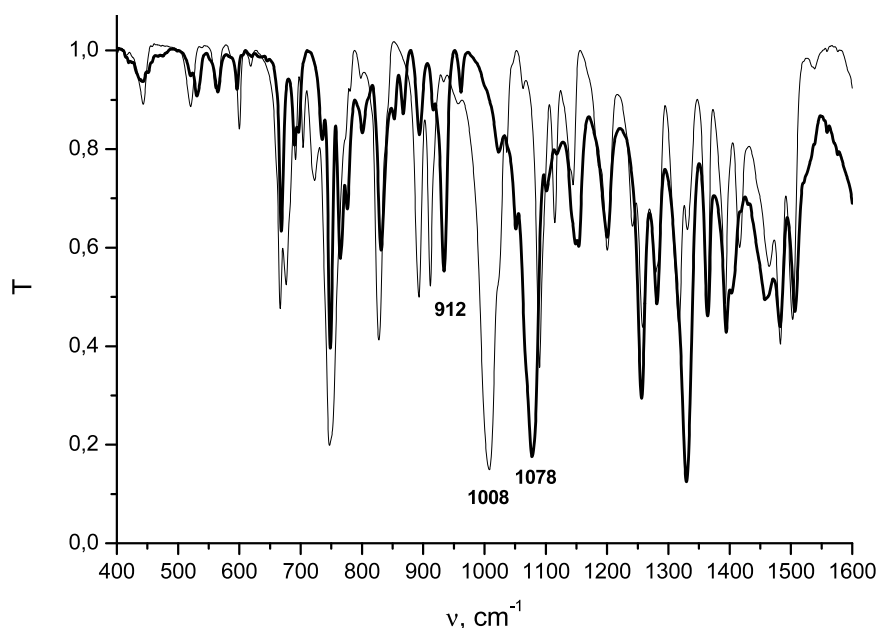


Figure 1. IR spectra of compounds **3** (bold line) and **4** (1 % in KBr).

with $\text{CH}_2\text{Cl}_2\text{:MeOH}$ (10:1) mixture and compound **4** was eluted using THF. Yield of **4** 0.038 g (64 %). m/z (ESI) (%) 1598.8 (100) $[(M)^+]$. IR (KBr) ν_{max} cm^{-1} : 1008 ($\nu_{\text{Mn=N}}$), 912 ($\nu_{\text{as Fe-N-Mn}}$), 676 ($\nu_{\text{Fe-N}}$). UV-vis (CH_2Cl_2) λ_{max} nm: 317, 453, 603, 657, 846; (EtOH) λ_{max} nm: 335, 662; (C_6H_6) λ_{max} nm: 329, 361, 599, 660, 685, 832.

Results and Discussion

The key step in the synthesis of the compound **4** is the preparation of nitrido(tetra-4-*tert*-butyl-phthalocyaninate) manganese(V) (**3**). Nitrido complexes of manganese(V) are generally synthesized by the oxidation of Mn^{III} derivatives by chlorine or sodium hypochlorite in the presence of ammonia or by photolysis of corresponding Mn^{III} azido complexes.^[19,20] In the current study the complex **3** could in fact be prepared by reacting the appropriate acetatomanganese(III) complex with an excess of sodium azide in high-boiling solvents, like xylene or α -chloronaphthalene. This approach allows significantly milder and more practical reaction conditions than those traditionally employed (no strong oxidants or UV light). The reaction takes place *via* intermediate formation of corresponding azido complex which undergoes thermal decomposition to give the complex **3** with high yield. For example, in α -chloronaphthalene at 230°C the complex **3** was formed with almost quantitative yield after 30 min.

The heterometallic complex **4** was synthesized with high yield by heating **3** with an excess of $^t\text{BuPcFe}^{\text{II}}$ (**1**) in xylene (Scheme 1). It should be noted that it is necessary to use Fe^{II} phthalocyanine. When we used $^t\text{BuPcFe}^{\text{III}}$ complex no formation of **4** was observed as evidenced from UV-vis and TLC data. Initially blue colour of solution of **4** changed to green colour during the purification by column chromatography. ESI-MS and IR spectral data confirm the formation of **4**.

Only one similar complex was previously described in the literature.^[21] The heterometallic Fe-N=Mn complex with octaphenyltetraazaporphine ligand have been synthesized by interaction of corresponding Mn^{V} nitrido and intermediate spin Fe^{III} complexes in benzene at room temperature. It

should be noted that spectral properties of this compound were significantly different than those obtained for complex **4**. It could probably be due to the influence of nature of ligand or Fe-N bond order (covalent vs. coordination).

The IR spectrum of **3** contained very strong absorbance at 1078 cm^{-1} (Figure 1) which is assigned to the $\text{Mn}\equiv\text{N}$ valence vibration. This is close to that observed in the $\text{PcMn}^{\text{V}}\text{N}$.^[22] In the case of μ -nitrido bridged dimer **4** this band transformed to $\text{Mn}=\text{N}$ and shifted to the 1008 cm^{-1} . A new strong absorption at 912 cm^{-1} appears which is typical for M-N-M antisymmetric stretching vibrations. These observations indicate that the complex **4** can be characterized as system with localized unpaired electron in comparison with similar diiron compounds and asymmetrical bond distribution in $\text{Mn}^{\text{IV}}=\text{N}-\text{Fe}^{\text{III}}$ centre. In principal, the complex **4** should be EPR-silent due to antiferromagnetic coupling between Fe^{III} and Mn^{IV} centers. Unexpectedly, the EPR spectrum of solid **4** showed symmetric strong and narrow (14 G width) signal

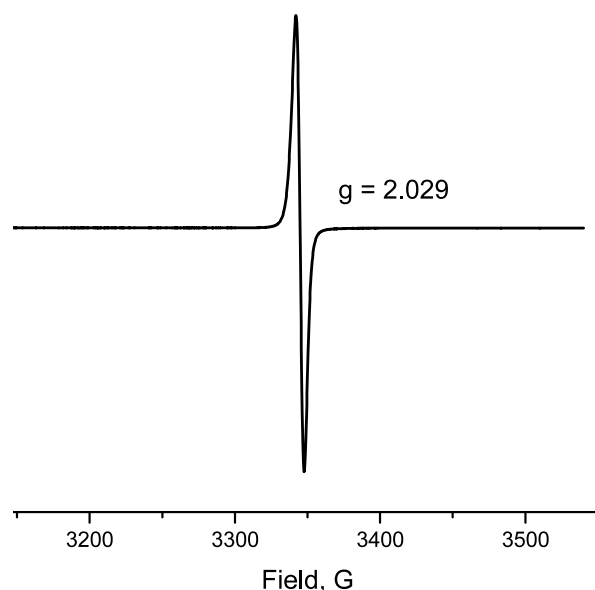


Figure 2. EPR spectrum of compound **4** (solid, 77 K).

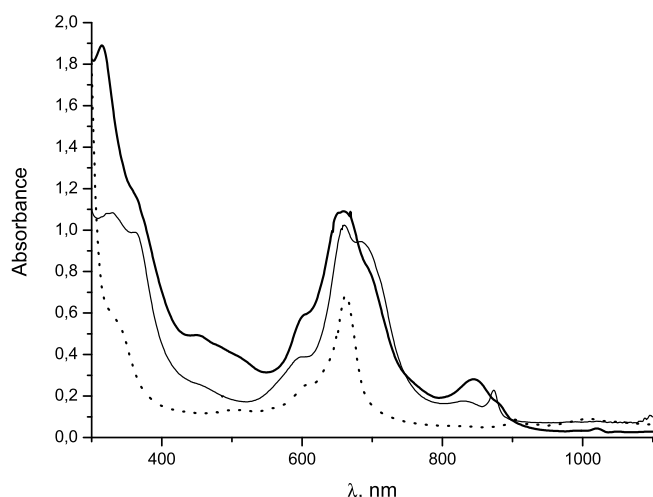


Figure 3. UV-vis spectra of compound **4** (CH₂Cl₂ – bold line, benzene – thick line, EtOH – dot line).

without hyperfine structure with *g* value close to that of electron (Figure 2), which is typical for organic radicals. The same spectrum was also recorded in CH₂Cl₂ solution. Such a spectrum is characteristic of phthalocyanine cation-radical.^[21] This spectrum can be explained by possible oxidation of mixed dimer by dioxygen to form stable phthalocyanine cation-radical during isolation and purification of the complex **4**. A similar EPR signal was observed for the stable phthalocyanine cation radical obtained by the oxidation of (BuPcFe)₂N by tBuOOH in halogenated solvents.^[14]

UV-vis spectroscopy is one of the most useful methods for investigation of phthalocyanines and their metal complexes. The spectra of these compounds strongly depend on the nature of ligand and metal, aggregation in solutions, axial coordination, *etc.* The optical absorption spectra of compound **4** are dependent on the solvent used (Figure 3). The complex **4** show two strong absorption bands typical for phthalocyanines: an ultraviolet Soret (*B*) band around 330 nm and a visible *Q* band around 660 nm. The complex **4** is green in aprotic solvents and its UV-vis spectrum contains two new less intense broad bands at 450–460 nm and 820–850 nm which are typical for phthalocyanine cation-radicals.^[23] The colour of solution changed to blue after addition of EtOH or hydrazine and bands in the region of 450–460 and 820–850 nm completely disappears probably due to reduction of phthalocyanine cation radical. The spectrum of **4** in EtOH typical for metal phthalocyanines and close to the spectrum of neutral (BuPcFe)₂N with *Q* band bathochromically shifted at 25 nm. The UV-vis data are in full agreement with EPR and clearly demonstrate that complex **4** is the rare example of stable phthalocyanine cation radical which is formed through oxidation of neutral Mn^{IV}=N-Fe^{III} by oxygen.

Conclusion

In this work the synthesis of new heterometallic PcFeMnPc (Pc – tetra-*tert*-butylphthalocyanine) by

interaction of nitrido(tetra-4-*tert*-butyl(phthalocyaninato)manganese)(V) with tetra-4-*tert*-butyl(phthalocyaninato)iron(II) was described. This complex **4** was characterized by FT-IR, EPR and UV-visible spectroscopies. In solution, the complex **4** showed rapid colour changes upon addition of weak reductants. As evidenced by spectral data the complex **4** is the rare case of the stable phthalocyanine cation radical complexes. These preliminary results demonstrate the great potential of this compound as a material for chemical sensors, nonlinear optics as well as for catalytic oxidation reactions.

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