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Comparative study of reactions between μ-nitrido- or μ-oxo-bridged iron tetrasulfophthalocyanines and sulfur-containing reductants

ILIA A. DEREVEN'KOV[1], SVETLANA S. IVANOVA[1], EVGENY V. KUDRIK[1], SERGEI V. MAKAROV[1]*, ANNA S. MAKAROVA[2] and PAVEL A. STUZHIN[1]

[1]*State University of Chemistry and Technology, Engels Str. 7, 153000 Ivanovo, Russia and* [2]*G. A. Krestov Institute of Solution Chemistry of the RAS, Academicheskaya Str. 1, 153045 Ivanovo, Russia*

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Abstract: A comparative study of reactivity of μ-nitrido- and μ-oxo-dimers of iron tetrasulfophthalocyanine has been performed in aqueous solutions of various acidity. The substantially higher stability of the nitrido-bridged structure under both strongly acidic and strongly alkaline environments was demonstrated. The reactions of the complexes with sulfur-containing reductants (sodium dithionite, thiourea dioxide, sodium hydroxymethanesulfinate, L-cysteine) were studied. Differences in reduction processes were explained.

Keywords: μ-nitrido dimer, μ-oxo dimer, iron phthalocyanine, reduction.

INTRODUCTION

A selective low-temperature oxidation of hydrocarbons (especially of methane) is the challenging problem of great practical importance. The naturally occurring methane mono-oxygenase enzyme (MMO) converts methane to methanol in aqueous solutions under mild conditions.[1,2] The active site of the enzyme includes two non-heme iron atoms linked together by an oxygen bridge, and this structural feature determines the unique reactivity of MMO. μ-Oxo-dimers of iron complexes with tetrapyrrole macrocycles (porphyrins and phthalocyanines) have been intensively used in model reactions of hydrocarbon oxidation for a long time.[3,4] Their catalytic activity in the oxidation of unsaturated hydrocarbons and alkanes with active C–H bonds (tertiary, allyl and benzyl) was demonstrated.[5–9] In 2009, it was discovered that the μ-nitrido-dimer of iron phthalocyanine catalyzes the low-temperature oxidation of methane by hydrogen peroxide.[10] The authors showed that this complex reacts with hydrogen peroxide to

* Corresponding author. E-mail: makarov@isuct.ru
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form the strong oxidant $Fe^{IV}NFe^{V}O$ *via* heterolytic O–O bond cleavage in the peroxide and that the presence of the binuclear Fe–N–Fe motif is a prerequisite for an effective catalysis. Further possibilities of other substrate activations by μ-nitrido-dimers of iron phthalocyanines and porphyrins were evidenced later.[11–14]

Recent DFT calculations performed on the Fe-porphyrazine model[15] disclosed the fact that the unique catalytic activity of iron μ-nitrido-dimers may be connected with the ability of the nitrido-bridge (in contrast to the oxo-one) to bear an excessive charge in transient redox species in catalytic cycle and to stabilize their low-spin states.

Hence, as μ-nitrido(bis-iron phthalocyanines) are highly reactive in oxidations of organic substrates by hydrogen peroxide, it could be expected that oxygen activation is quite feasible *via* their mediation as well. The ability of Fe-porphyrazine μ-nitrido-dimer to bind reversibly dioxygen was proven earlier.[16] Dioxygen activation in the catalytic cycle obligatorily requires the participation of reductants in a fully reversible reduction step. In the case of μ-oxo-dimers applied as models of the MMO active site, the action of relatively weak reductants leads to the cleavage of the Fe–O bonds, with the formation of monomers.[17,18]

Recently, the first successful synthesis of the water-soluble sulfo-derivative of the μ-nitrido Fe-phthalocyanine dimer μ-N$(FeTSPc)_2$ was reported.[19] The synthesis was performed in two alternative ways: *i*) *via* the sulfonation of μ-nitrido-bridged Fe-phthalocyanine and *ii*) *via* the thermolysis of the azide complex of Fe-tetrasulfophthalocyanine in acetic acid.[19] This work presents a comparative analysis of the stability of μ-N$(FeTSPc)_2$ (**I**) and μ-O$(FeTSPc)_2$ (**II**) (Fig. 1) in aqueous solutions, as well as of reactivity in reduction processes with sulfur-containing compounds, *viz*., sodium dithionite, thiourea dioxide (TDO), sodium hydroxymethanesulfinate (HMS)[20] and L-cysteine.

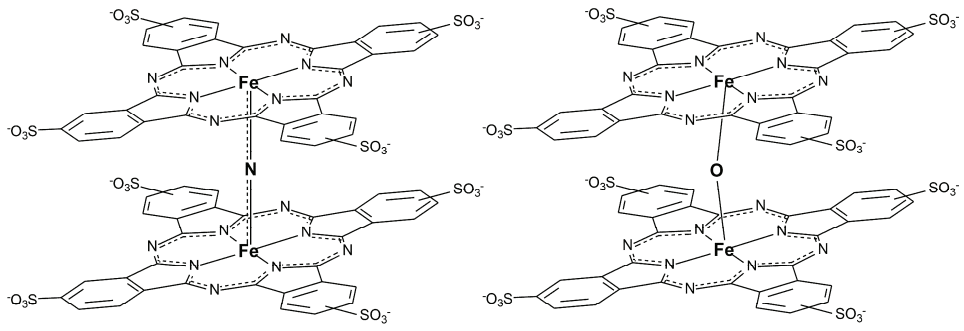


Fig. 1. The structures of the nitrido- and oxo-bridged complexes of iron tetrasulfophthalocyanine.

EXPERIMENTAL

Chemicals and methods

All reagents (Sigma–Aldrich) were used as received without further purification. Oxygen-free argon was used to deoxygenate the solutions. Britton–Robinson, phosphate and borate buffers were used to control the pH.

The IR-spectra were recorded on an Avatar 360 FT-IR spectrometer and the elemental composition of the complex was determined on a Flash EA CHNS-O Analyser. The UV–Vis spectra and kinetic traces were recorded on a thermostated Cary 50 spectrophotometer.

Experimental data were analyzed using the Origin 7.5 program. The rate constants were determined by fitting the absorbance *vs.* time curve to a single-exponential function implemented in the software. Calculations of equilibrium constants were performed by fitting the plots of absorbance *vs.* pH to sigmoidal (1) or double-sigmoidal (2) functions. The reported deviations are the calculated standard ones.

$$A = A_1 + \frac{A_1 - A_2}{1 + e^{(pH - pK_{a1})/d(pH)}} \quad (1)$$

$$A = A_1 + \frac{A_1 - A_2}{1 + e^{(pH - pK_{a1})/d(pH)}} + \frac{A_2 - A_3}{1 + e^{(pH - pK_{a2})/d(pH)}} \quad (2)$$

In these equations, A_1, A_2 and A_3 are the absorbance values of the dominating species at each pH value.

*Synthesis of μ-nitrido-bridged complex of iron tetrasulfophthalocyanine ammonium salt μ-N(FeTSPc)$_2$, **I***

μ-Nitrido-dimer of iron phthalocyanine μ-N(FePc)$_2$ (0.4 g), obtained according to a reported procedure,[21,22] was dissolved in chlorosulfonic acid (15 ml). The mixture was heated for four hours at 150 °C and after cooling, the solution was left standing overnight. Then the mixture was poured on ice (300 g). The formed precipitate was collected by filtration, washed with cold water until the filtrate was sulfate-ion free and hydrolyzed in distilled water (100 mL) at 80 °C until fully dissolved. The solution was evaporated on a water bath, the residue was dissolved in 5 % ammonia solution (50 mL) and half of the solvent was evaporated. The solution of octa-ammonium salt **I** was purified by column chromatography (Molselect G10, eluent – water) collecting the middle fraction of blue zone. After solvent evaporation, the hydrate of the octa-ammonium salt **I** (0.34 g) was obtained. Yield: 48 %; Anal. Calcd. for ($C_{64}H_{32}N_{17}S_8O_{24}Fe_2$)·8$NH_3$·5$H_2O$): C, 38.10; H, 3.30; N, 17.36; S, 12.71 %. Found: C, 37.8; H, 3.2; N, 17.1; S, 12.6 %; IR (KBr, cm^{-1}): 913 (ν_{as} FeNFe), 1028 (ν_s S=O), 1151 (ν_{as} S=O); UV–Vis (DMSO) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 336 (40800), 643 (43700).

Iron tetrasulfophthalocyanine was synthesized from 4-sulfophthalic anhydride as earlier proposed[23] and isolated as the μ-oxo-dimer μ-O(FeTSPc)$_2$, **II**. IR (KBr, cm^{-1}): 830 (ν_{as} FeOFe), 1029 (ν_s S=O), 1137, 1188 (ν_{as} S=O); UV–Vis (DMSO) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 334 (112200), 636 (114800).

RESULTS AND DISCUSSION

Stability in aqueous solutions

In the first step of the study, the stability of both complexes in aqueous aerobic solutions of various acidities was investigated. It was found that the

behavior of complexes **I** and **II** were substantially different in strongly acidic and strongly alkaline media.

Acidification of the μ-nitrido-dimer **I** solution resulted in a slight spectral change (Fig. 2a). During long storage in 0.1 M H_2SO_4, only a slow decrease at the initial absorption maxima was observed, which resulted from macrocycle destruction ($\tau_{1/2}$ = 15.5 h at 25 °C), while no changes resulting from complex monomerization were observed. On the contrary, after the acidification of the μ-oxo-dimer **II** solution, the UV–Vis spectra were significantly altered, *i.e.*, the intensity of the initial Q-band at 632 nm decreased, the Q-band split with maxima at 642 and 679 nm, a small peak at 817 nm appeared and the Soret band shifted from 327 to 336 nm. After long exposure of complex **II** to 0.1 M H_2SO_4, a slow absorption decay was observed, indicating chromophore decomposition ($\tau_{1/2}$ = = 12.5 h at 25 °C). It should be noted that this spectral picture (Fig. 2b) was fully reversible, which confirms the acid–base character of the process.

In aqueous media, μ-dimers **I** and **II** (μ-X[FeTSPc]$_2$) axially bind water molecules and exist as di-aqua complexes (Reaction (3)):

$$\mu\text{-X[FeTSPc]}_2 + 2H_2O \leftrightarrows \mu\text{-X[(H}_2\text{O)FeTSPc]}_2 \quad (3)$$

$$\mu\text{-X[(H}_2\text{O)FeTSPc]}_2 + 2H^+ \leftrightarrows \mu\text{-X[FeTSPc]}_2 + 2H_3O^+ \quad (4)$$

There are several possible explanations of observed spectral changes in acidic media in the case of complex **II**. First, axial water molecules under acidic environment can be protonated and removed from the coordination sphere, which may lead to the formation of a five-coordinated μ-oxo-dimer (Reaction (4)). Due to an increase in excitonic interaction, the Q-band maximum in the spectra of six-coordinated μ-oxo-dimers is hypsochromically shifted as compared to the maximum of five-coordinated μ-oxo-complexes.[24] The same effect was also observed during the formation of six-coordinate dimers of Fe(III)-octaphenylporphyrazine.[25]

Secondly, in acidic media, acid–base interactions with the *meso*-nitrogen atoms of the macrocycle become possible. The splitting of the Q-band observed in UV–Vis spectrum of the product of μ-oxo-dimer **II** transformations at low pH values may result from the lowering of the symmetry of the *meso*-protonated phthalocyanine π-chromophore.

Thirdly, the protolytic dissociation of μ-dimers is possible in acidic media as previously observed, for example, in the case of Fe(III) μ-oxo-dimers of porphyrins, azaporphyrins and porphyrazines.[26–28] The monomerization of iron μ-oxo-porphyrazines and μ-oxo-phthalocyanines was also shown to proceed in the presence of bases.[17] Nevertheless, data on the monomerization of μ-nitrido--dimers is still unknown.

It should be noted that five-coordinated monomers of iron phthalocyanines are characterized by a single Q-band at 655–660 nm and an additional long-

wavelength band at ≈830 nm, but in the case of six-coordinated Fe-phthalocyanines, the Q-band is usually located at ≈680 nm in the UV–Vis spectrum.[29] The spectrum of an acidic solution of complex **II** includes peaks of all the above-mentioned species that may result from monomerization of complex **II**, giving a mixture of five- and six-coordinated iron tetrasulfophthalocyanines.

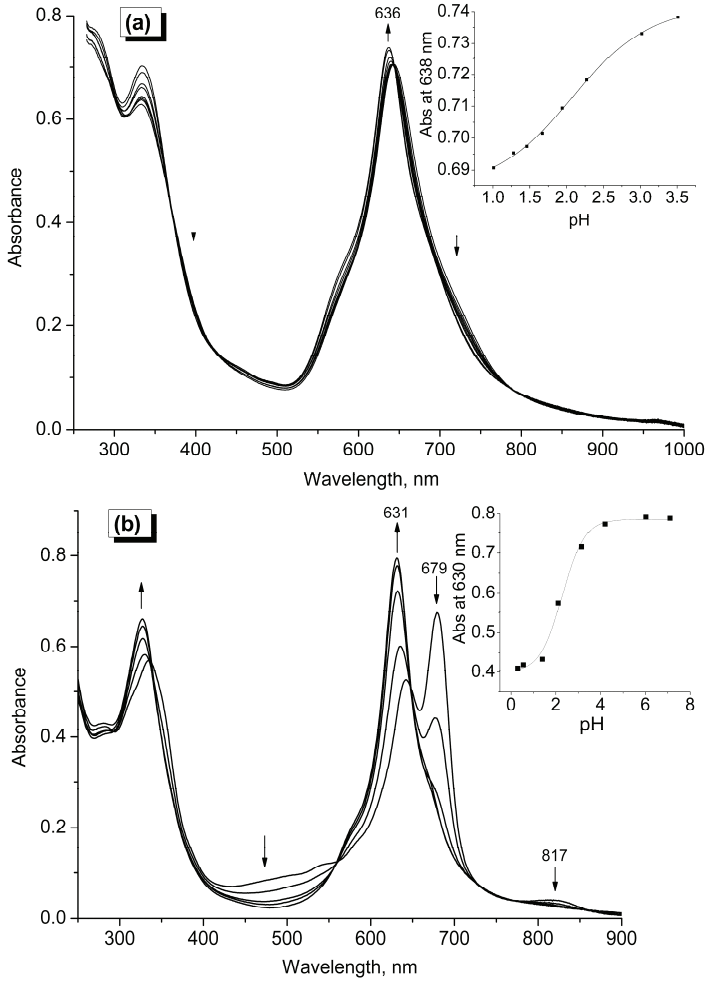


Fig. 2. UV–Vis spectral changes accompanied the pH-titration of both complex **I** ($c_{0,I}$ = = 1.4×10^{-5} M) (a) and **II** ($c_{0,II}$ = 6.1×10^{-6} M) (b) during the titration from acidic media to neutral. Insets: pH-titration curves of both complex **I** and **II** at 25 °C, ionic strength = 0.2 M (ClO_4^-), aerobic conditions.

This suggestion is supported by the following experiments. The titration of complex **II** with thiocyanate in acidic media (pH 1.7) leads to a shift from a spec-

trum with the split Q-band to a spectrum with the single band at 679 nm (Fig. 3a). Simultaneously, the long-wave band at 817 nm, typical for five-coordinates iron(III) phthalocyanines, disappears. In the process, only one thiocyanate molecule became coordinated ([NCS^-] ≤ 0.1 M). Probably, the mixture of five- and six-coordinate Fe-tetrasulfophthalocyanine complexes after the addition of thiocyanate is transformed to a mixture of six-coordinated complexes. It is important to note that in weakly acidic media the addition of thiocyanate to complex **II** solution induces only slight spectral changes (Fig. 3b), which may be connected

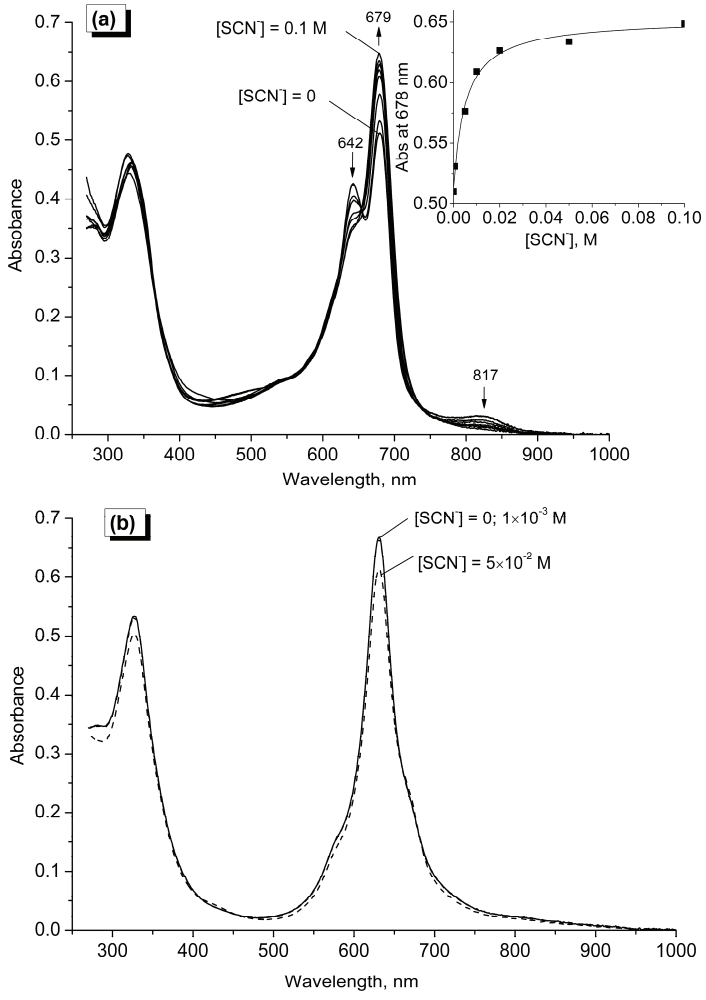


Fig. 3. UV–Vis spectral changes occurring during the titration of complex **II** ($c_{0,II}$ = = 5.1×10^{-6} M) by thiocyanate at pH 1.7 (a) and at pH 6.0 (b). Inset: titration curve of complex **II** by thiocyanate under aerobic conditions at pH 1.7, 25 °C, I = 0.2 M (ClO_4^-).

with difficulties in the substitution of an axial water in the oxo-dimer, as well as with the high stability of oxo-bridged structures to dissociation under the given conditions.

The observed value of $pK_{a(obs)}$ determined during pH-titration of complex **II** (6.07×10^{-6} M) in acidic media and ionic strength 0.2 M was 2.29±0.11 at 25 °C. After the addition of thiocyanate (0.1 M) to the mixture during the pH-titration in acidic media, a change of spectrum from one with a single Q-band at 679 nm to one with a single maximum at 631 nm was found. In the latter experiment, the $pK_{a(obs)}$ value was increased up to 3.19±0.02. Thus, thiocyanate promotes oxo-dimer dissociation to monomeric species of Fe-tetrasulfophthalocyanine.

Thus, the above-mentioned differences in reactivity under environments of different acidities as well as spectral characteristics of the produced species indicate that complex **II** dissociates at low pH values giving a mixture of five- and six-coordinated Fe-tetrasulfophthalocyanine monomers (Reactions (5) and (6)):

$$\mu\text{-O}[(H_2O)\text{FeTSPc}]_2 + H^+ \leftrightarrows \mu\text{-H}^+\text{O}[(H_2O)\text{FeTSPc}]_2 \rightarrow$$
$$\rightarrow [(H_2O)\text{FeTSPc}]^+ + [(H_2O)(HO)\text{FeTSPc}] \quad (5)$$
$$[(H_2O)(HO)\text{FeTSPc}] + H^+ \leftrightarrows [(H_2O)_2\text{FeTSPc}]^+ \quad (6)$$

The value of $pK_{a(obs)}$ can be recalculated using Eq. (7) to produce pK_a = = –3.10±0.11, corresponding to Reaction (5):

$$pK_a = pK_{a(obs)} + \log (2/3[\mathbf{II}]_0) \quad (7)$$

UV–Vis spectra recorded during the stage shown in Fig. 2a indicate relatively slight change in the structure of complex **I** after reaction with protons. The value of pK_a 2.09±0.03 probably reflects both the protonation of the axial water molecule and its further dissociation (Reaction (4), protonation of the first water molecule).

Reactions of the oxo- and nitrido-dimers of iron tetrasulfophthalocyanine with hydroxide ions in alkaline media leads to the formation of aquahydroxo- and dihydroxocomplexes (Reactions (8) and (9)):

$$\mu\text{-X}[(H_2O)\text{FeTSPc}]_2 + OH^- \leftrightarrows \mu\text{-X}\{[(H_2O)\text{FeTSPc}][(HO^-)\text{FeTSPc}]\} + H_2O \quad (8)$$
$$\mu\text{-X}\{[(H_2O)\text{FeTSPc}][(HO^-)\text{FeTSPc}]\} + OH^- \leftrightarrows \mu\text{-X}[(HO^-)\text{FeTSPc}]_2 + H_2O \quad (9)$$

Complex **I** is relatively stable at pH 13 (the decrease in concentration was 3.7 % in 4 h at 25 °C), but a maximum at 667 nm, typical for Fe^{II}TSPc,[30] slowly appeared in the UV–Vis spectrum of complex **II** (observed rate constant is $k_{obs.}$ = = $(9.97\pm0.30)\times10^{-5}$ s^{-1} at pH 13 and 25 °C) simultaneously with the decay of $(Fe^{III}TSPc)_2O$ peak (631 nm) (Fig. S-1 of the Supplementary material to this paper). The latter fact presumably resulted from reduction of complex **II** to Fe^{II}TSPc (Reactions (10) and (11)). At the same time, the depletion of the oxo-bridged structure without electron transfer cannot be excluded, since the spectra of the six-coordinated Fe^{III}TSPc and Fe^{II}TSPc complexes are similar. This pro-

cess proceeds without chromophore decomposition under anaerobic conditions, but noticeable decomposition of the complex occurs in the presence of oxygen.

$$\mu\text{-O}[(HO^-)Fe^{III}TSPc]_2 + H_2O \rightarrow 2[(HO^-)Fe^{II}TSPc] + 2HO^\bullet \quad (10)$$

$$[(HO^-)Fe^{II}TSPc] + OH^- \rightarrow [(HO^-)_2Fe^{II}TSPc] \quad (11)$$

The pH-titration of complex **I** in alkaline media revealed the presence of two consecutive steps accompanied by weakly intensive but distinctly different spectral changes (Fig. S-2 of the Supplementary material to this paper). Probably, these steps correspond to the transformation of the nitrido-dimer to mono- and dihydroxo-species (Reactions (8) and (9), respectively, where X = N). The pK_a values of these equilibria were found to be 10.5±0.1 and 12.9±0.1 at 25 °C, respectively. These values were expectedly higher than those reported for Fe(III) complexes of octakis(benzenesulfonato)porphyrazine (7.5 and 11.16 at 25 °C[31]) and porphyrins (*e.g.*, for *meso*-tetrakis(4-*N*-methylpyridiniumyl)porphyrin, the pK_a values are of 5.0 and 11.9 at 25 °C[32]), which results from the lesser propensity of the nitrido-dimer to bind axial ligands.

Reactions with reductants

To date, the study of μ-N(FePc)$_2$ reduction in pyridine solution was the subject of only one paper.[22] Particularly, it was shown that this complex can be involved in three reversible reduction steps, but at potentials lower than –1.29 V, the dimer structure is destroyed giving two reduced monomer moieties per one nitrido-dimer unit. Earlier reported data,[22] summarized in Table I, demonstrates the substantial stabilization of high-valent iron ions in the nitrido-dimer as compared to corresponding monomer. The transfer of the first electron on the iron ion in the +3.5 formal oxidation state occurs in the potential region near to that of Fe^{2+} phthalocyanine monomer reduction. It is also known that the two-electron reduction of the Fe^{3+} phthalocyanine oxo-dimer proceeds fully irreversibly, leading to the decay of the dimer structure.[33]

TABLE I. Potentials of reduction stages of (FePc)$_2$N and FePc[22]

Redox stage	$E_{1/2}$ / V	
	(FePc)$_2$N	FePc
0/–1	–0.83	–0.96
–1/–2	–1.02	–1.29
–2–3	–1.29	–

It should be noted that above-mentioned study of μ-N(FePc)$_2$ reduction was performed in the strongly coordinating solvent pyridine, which may facilitate the monomerization of dimers. Thus, some questions remain open, such as how fast does the decomposition of the nitrido-dimer to iron(II) phthalocyanine occur during its reduction in water and can complex **I** form more reduced states?

In the present study, the reduction of both complexes **I** and **II** with thiourea dioxide (TDO, $(NH_2)_2CSO_2$) was studied under anaerobic conditions. The reactions were accompanied by significant UV–Vis spectral changes and occurred at relatively low rates at pH 7.8. The latter is caused by the moderate rate of TDO decomposition in weakly alkaline solutions giving the strong reducing agent – sulfoxylate, SO_2H^- (SO_2^{2-}) (reaction (12)):[34]

$$NH_2NHCSO_2^- + H_2O \rightarrow (NH_2)_2CO + SO_2H^- \quad (12)$$

During the first reduction step of complex **I**, a sharp isosbestic point was observed at 498 nm that supports the presence in system of only two absorbing species; a slight shift of the Q-band from 636 to 631 nm also occurred. The second reduction step was accompanied by substantial changes in UV–Vis spectrum, *i.e.* a decrease in the intensity of the Q-band, the appearance of a new band at 500 nm and an absorption increase in the near-IR region (Fig. 4a). During the third step, both an increase of the absorption band at 655 nm and a decay of the band at 483 nm were observed (not shown). The same picture emerges during the use of either dithionite ($S_2O_4^{2-}$) or hydroxymethanesulfinate ($HOCH_2SO_2^-$) as the reductant under moderately alkaline conditions. The highest reduction rate was observed in the case of sulfoxylate (SO_2H^- has been obtained after TDO "aging" under strongly alkaline anaerobic conditions for four hours[35]); a slower reaction proceeded when dithionite is used while the slowest reaction rates were observed using hydroxymethanesulfinate as the reductant. Moreover, the reaction rates at the final step had the highest values in neutral and weakly alkaline media and were substantially retarded at higher pH values, which was probably due to the transformation of the nitrido-dimer into the inert dihydroxocomplex.

The reduction of complex **II** included two consecutive stages (Fig. 4b): an increase in the UV–Vis maximum at 668 nm with a simultaneous absorption decrease at 631 nm and the subsequent appearance of a new band at 490 nm with a simultaneous decay of peak at 668 nm. These stages corresponded to the reduction of $(Fe^{III}TSPc)_2O$ to $Fe^{II}TSPc$ and the reduction of $Fe^{II}TSPc$ to the Fe^{II}-anion-radical of tetrasulfophthalocyanine, respectively.[30] The use of sulfoxylate enabled the occurrence of the following electron transfers, which resulted in the formation of the formally Fe(0) state. According to DFT data, the most probable electromer of the latter species is the Fe^{II}-anion-biradical.[30,36] Note, the latter process did not occur when dithionite or hydroxymethanesulfinate were added.

The distinct difference in UV–Vis changes during the reduction of complexes **I** and **II** is the absence in the first case of a species absorbing at ≈670 nm, which corresponds to $Fe^{II}TSPc$. To gain further insight into this fact, a titration of complex **I** with dithionite was performed. It is well known that dithionite serves as a two-electron reductant; thus, its application allows the exact number

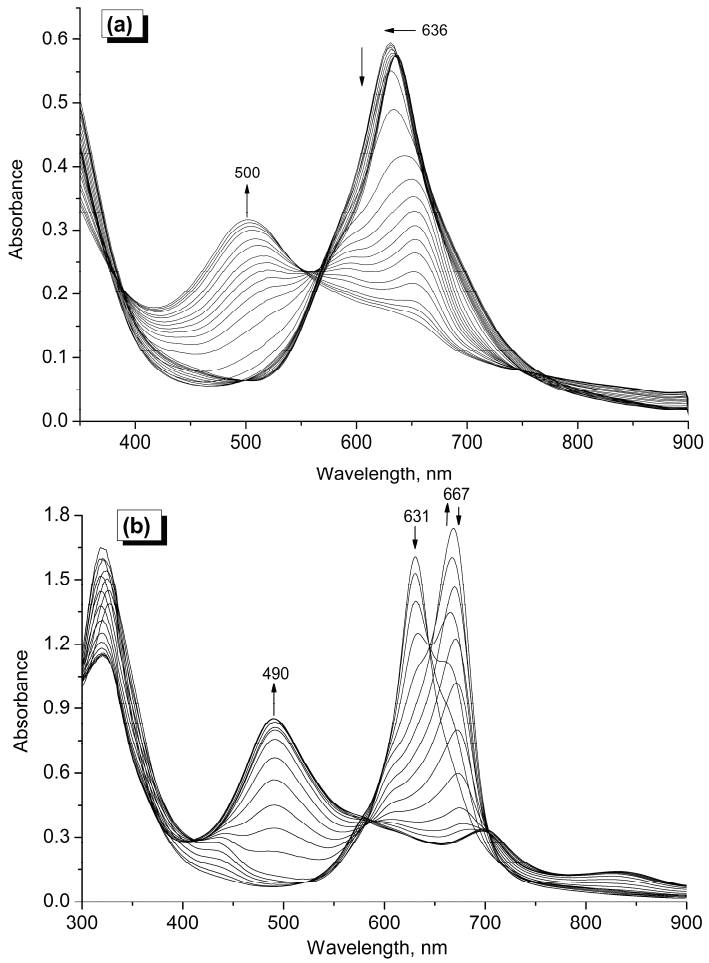


Fig. 4. Changes in the UV–Vis spectra during the reduction of complex **I** ($c_{0,I}$ = 1.1×10^{-5} M, τ = 90 min) (a) and complex **II** ($c_{0,II}$ = 1.3×10^{-5} M, τ = 70 min) (b) by TDO (5×10^{-4} M) at pH 7.8, 25 °C.

of electrons received by the complex during the reduction to be established. Moreover, dithionite possesses a significant reactivity in this process (reduction by dithionite at concentrations comparable with that of the nitrido-dimer occur in a few seconds or tens of minutes, depending on pH). The dithionite concentration can be exactly determined from the absorption at 315 nm (extinction coefficient is 8043 M^{-1} cm^{-1}).[37]

The titration of complex **I** with dithionite (Fig. 5a) resulted in UV–Vis spectra different from those observed in the course of reaction between nitrido-dimer and excess of TDO. The transfer of the first electron from the added dithionite to the complex gave TSPcFe^{III}···N···Fe^{III}TSPc, which was accompanied by a slight

blue shift of the Q-band (similar to that observed during first reduction stage of complex **I** by TDO). However, the transfer of two or more electrons to the nitrido-dimer resulted in the appearance in the spectra of bands at 667 nm that were absent during reduction by excess TDO. It should be emphasized that the appearance of these bands in the UV-Vis spectrum corresponds to electron transfer(s) on the nitride-dimer and its further decomposition to monomer (*vide infra*). The UV–Vis spectrum of the final product formed after the three-electron reduction of TSPcFe$^{III1/2}$···N···Fe$^{III1/2}$TSPc coincides with the spectrum of Fe^{II}TSPc. The spectra of two- and four-electron reduced TSPcFe$^{III1/2}$···N···Fe$^{III1/2}$TSPc complexes include peaks of the corresponding monomers.

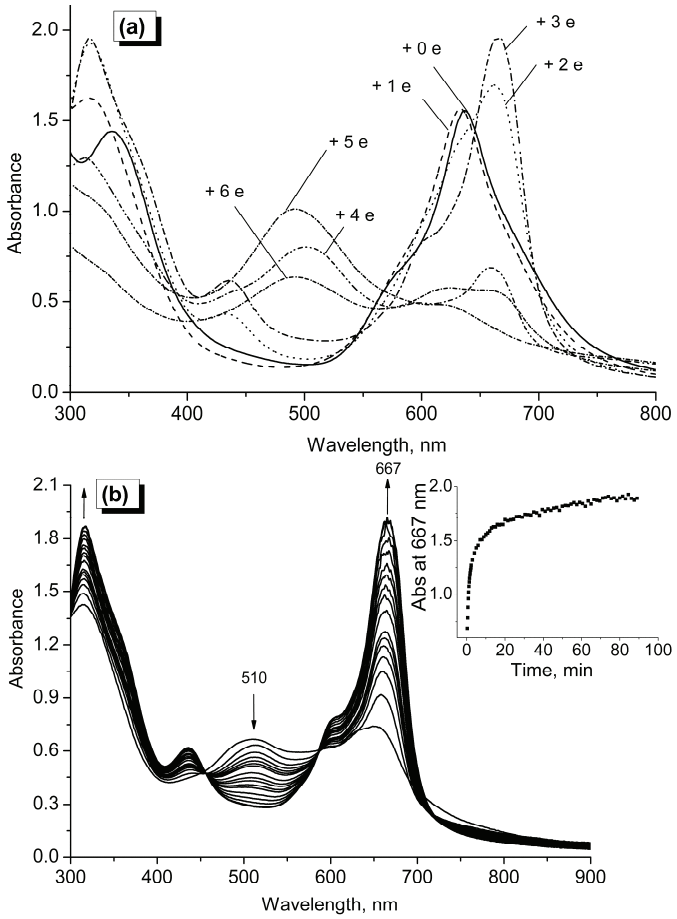


Fig. 5. UV–Vis spectra of dithionite reduced species of complex **I** recorded one hour after mixing the reagents (a) and the spectral changes during the decay of the three-electron reduced complex **I** ($c_{0,I}$ = 2.9×10^{-5} M) (b) at pH 8.8, 25 °C. Inset: kinetic trace corresponding to the stage shown in Fig. 5b.

The addition of 1.5-fold excess of dithionite to complex **I** in weakly alkaline media resulted in a rapid spectral change (Fig. 5b, first spectrum) that likely resulted from the transfer of three electrons to the nitrido-dimer. Probably, the electrons are received in this case predominantly by the macrocycles since the UV–Vis spectrum of the product includes an absorption maximum at ≈500 nm, observed in the spectra of metallophthalocyanine anion-radicals.[38–40] It is likely that $N(Fe^{III}TSPc^{\bullet})_2$ is formed during the three-electron transfer. The nitrido-dimer existing in this state is unstable and further decomposes to $Fe^{II}TSPc$. The rate constant of the decay stage was found to be $(1.18\pm0.05)\times10^{-2}$ s^{-1} (25 °C, pH 8.8). This value again indicates higher stability of the nitrido-dimer, since the oxo-dimer decomposition after achievement of the Fe^{II}-state proceeds much faster. The latter implies an important feature of the nitrido-dimer: in the presence of excess reducing agent, the fast reduction of unstable species and the achievement of lower oxidation states (being potentially more stable) become possible.

A comparative study of formally Fe^{I}-complexes produced after reduction of nitrido- and oxo-dimers was performed. Electromerism of tetrapyrroles existing in this oxidation state was the subject of some studies.[41,42] DFT calculations performed on iron porphyrins models revealed evidence of macrocycle reduction in the course of electron transfer onto Fe^{II}, albeit electromerism remains possible depending on the nature of the axial and equatorial ligands. Phthalocyanines possess stronger electron-withdrawing properties than porphyrins used in above-mentioned calculations. Moreover, sulfo-groups result in a further increase of the electron-withdrawing properties of phthalocyanine. In addition, Fe^{I}-phthalocyanines have absorption maxima in the UV–Vis spectra at approximately 500 nm, *i.e.*, in the region of absorption maxima of phthalocyanines and porphyrins anion-radicals.[38–40] Thus, the data mentioned above allows the conclusion that the formally Fe^{I}-oxidation state of tetrasulfophthalocyanines corresponded to the Fe^{II}--phthalocyanine-anion-radical structure.

The UV–Vis spectra of the Fe^{II}-anion-radicals of complexes **I** and **II** obtained after reduction by sodium dithionite are distinctly different. The spectrum of Fe^{II}--radical of nitrido-dimer significantly depended on the pH value of the solution, *i.e.*, in neutral media, the UV–Vis spectrum included one small intensity maximum at 480 nm, while in strongly alkaline media, intensive maxima at 330, 485 and 707 nm were observed (Fig. 6a). The same situation existed after use of TDO and HMS as reducing agents. The spectra of the Fe^{II}-anion-radicals obtained after reduction of the oxo-dimer by dithionite and TDO were pH-independent in neutral and alkaline media (Fig. 6b).

It was found that the Fe^{II}-radical of complex **I** participates in two acid–base equilibria in an alkaline environment. The pK_a of the first transformation (8.3±0.3) was found with a considerable degree of uncertainty because of an interference of a subsequent process. The pK_a of the second equilibrium (10.01±0.05) was found

by spectrophotometric titration at 707 nm where the influence of the first process is minimal. It is likely that during these stages, mono- (reaction (13)) and dihydroxo-species (reaction (14)) are formed. These transformations are supported by a significant reaction rate decrease of the subsequent reduction step in the case of both dithionite and HMS in strongly alkaline media, since hydroxo-species of metallo complexes are less reactive in redox processes as compared to their aqua forms:

$$\mu\text{-N}[(H_2O)Fe^{II}TSPc^{\bullet}]_2 + HO^- \leftrightarrows$$
$$\leftrightarrows \mu\text{-N}\{[(H_2O)Fe^{II}TSPc^{\bullet}][(HO^-)Fe^{II}TSPc^{\bullet}]\} + H_2O \quad (13)$$
$$\mu\text{-N}\{[(H_2O)Fe^{II}TSPc^{\bullet}][(HO^-)Fe^{II}TSPc^{\bullet}]\} + OH^- \leftrightarrows$$
$$\leftrightarrows \mu\text{-N}[(HO^-)Fe^{II}TSPc^{\bullet}]_2 + H_2O \quad (14)$$

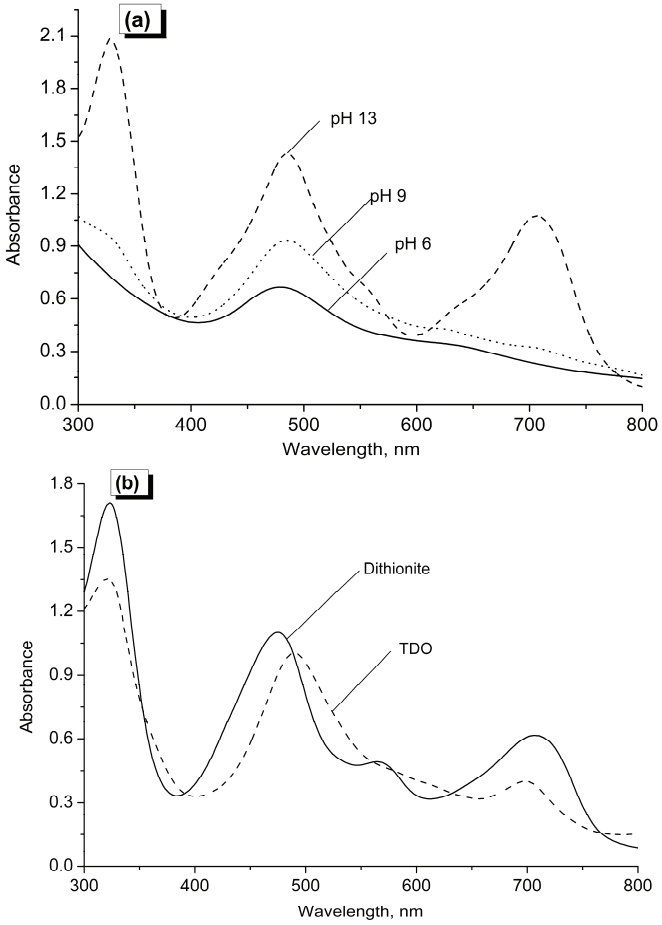


Fig. 6. UV–Vis spectra of Fe^{II}-phthalocyanine-radicals of complexes **I** (a) and **II** (b). $c_{0,I} = 2.7\times10^{-5}$ M; $c_{0,II} = 1.3\times10^{-5}$ M.

The noticeable difference in the UV–Vis spectra of the Fe^{II}-radicals of complexes **I** and **II** results from the inequality of their structures. In addition, the formed species possess different acid–base properties; the nitrido-dimer is capable of receiving one extra electron from both dithionite and HMS in contrast to the oxo-one. Perhaps, the strong reductant readily donates electrons to the nitrido-complex transiently existing in the unstable Fe^{II}-state and shifts it to the more stable Fe^{II}-anion-radical form.

Fe^{II}-anion-radicals are known to be potent reducing agents.[30,43] The oxidation by air of Fe^{II}-anion-radicals prepared by the reaction between complex **II** and sulfur-containing reductants leads to Fe^{II}TSPc and further complex bleaching. Fe^{III}-state regeneration in this case is unfeasible. Bleaching in this case is likely to be connected with the formation of SO_5^-, being a strong oxidant produced by the reaction of sulfite with dioxygen (or reactive oxygen species)[43,44] that is capable of destroying the macrocycle. In the presence of relatively mild oxidants (*e.g.*, nitrite), the Fe^{II}-anion-radical is oxidized to Fe^{II}TSPc without chromophore depletion. The oxidation of Fe^{II}-anion-radical of complex **I** by air also results in macrocycle destruction. Its oxidation by nitrite or iodine gives Fe^{II}-complexes spectrally similar to that of Fe^{II}TSPc and no complex bleaching in this case occurs. However, the latter oxidation process includes two-stages proceeding at different rates (*e.g.*, during the oxidation by nitrite at pH 7.8, 25 °C k_1 = 0.21±0.01 and k_2 = 0.054±0.002 M^{-1} s^{-1}), in contrast to the one-step oxidation of the Fe^{II}-anion-radical prepared from complex **I**. Probably, the first constant in this reaction corresponds to electron transfer from metallocomplex to the oxidant while the second is connected with the monomerization of dimer (reactions (15) and (16), respectively).

$$\mu\text{-N}[Fe^{II}TSPc^{\bullet}]_2 + Ox \rightarrow \mu\text{-N}\{[Fe^{II}TSPc^{\bullet}][Fe^{II}TSPc]\} + Ox^- \quad (15)$$

$$\mu\text{-N}\{[Fe^{II}TSPc^{\bullet}][Fe^{II}TSPc]\} + Ox + 3H^+ \rightarrow 2[Fe^{II}TSPc] + Ox^- + NH_3 \quad (16)$$

where Ox = oxidant.

The use of L-cysteine as a reductant of complex **I** and of complex **II** did not lead to the formation of any strongly reduced states. The UV–Vis spectra of the final reaction products are shown in Fig. 7. The same spectra could be obtained after careful aerial oxidation of a corresponding Fe^{II}-anion-radicals followed by L-cysteine addition. These complexes can be formed under both anaerobic and aerobic conditions, although in the latter case, the reaction proceeded much slower, that may have been be caused either by aerial metallocomplex oxidation or by oxidative cysteine conversion to cystine. Apparently, the products of these processes were Fe^{II}-dithiolate complexes spectrally similar to other hexacoordinated complexes of Fe^{II}-phthalocyanines[45,46] and porphyrazines.[47] An interaction of the complexes with nitrite resulted in their rapid relegation giving spec-

tra identical to those of the corresponding nitrite-oxidation product of the Fe^{II}-anion-radical.

Based on the herein presented experimental results and published data,[22,33] two schemes for the reduction of complex **II** and of complex **I** are proposed (Scheme 1 and 2, respectively).

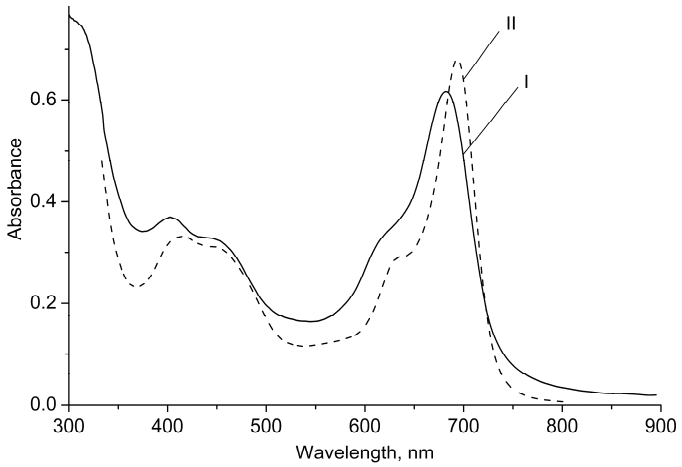
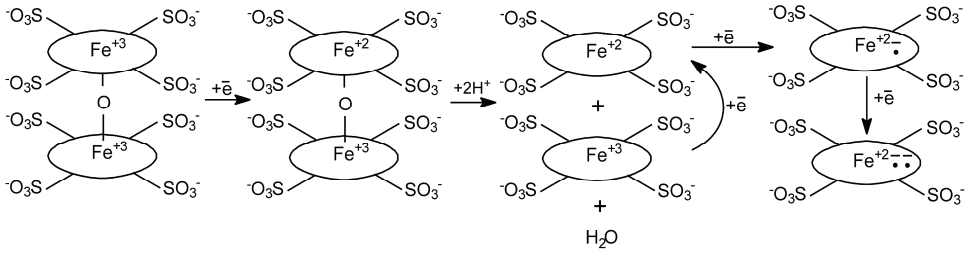
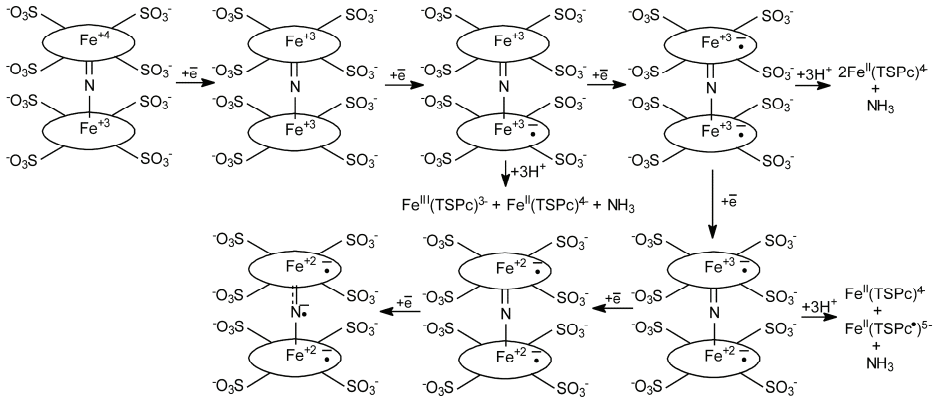


Fig. 7. UV–Vis spectra of L-cysteine (0.15 M) reduced complexes **I** ($c_{0,I}$ = 1.2×10^{-5} M) and **II** ($c_{0,II}$ = 0.9×10^{-5} M) at pH 10, 25 °C.



Scheme 1. Reduction of the μ-oxo-dimer of iron tetrasulfophthalocyanine.

To summarize, an investigation of reduction reactions of complexes **I** and **II** by sulfur-containing reductants demonstrated the low stability of Fe^{II}-dimers. It was established that stability of Fe^{II}-dimer with the nitrido-bridge was noticeably higher in comparison to oxo-one. Apparently, the nitrido-bridge provides the possibility for **I** to accept additional electrons without dimer structure decay in the presence of excess reductant. A comparison of the UV–Vis spectral data, acid–base properties and reactivity of the Fe^{II}-anion-radicals produced during the reduction of complexes unambiguously manifests their structural difference.



Scheme 2. Reduction of the μ-nitrido-dimer of iron tetrasulfophthalocyanine.

CONCLUSIONS

A comparative study of water-soluble μ-oxo- and μ-nitrido-dimers of iron tetrasulfophthalocyanine in aqueous media of various pH values has been presented. The higher stability of the nitrido-bridged structure in comparison to oxo-dimer in strongly acidic and strongly alkaline environments was demonstrated. The involvement of the nitrido-bridged complex in three reversible acid–base interactions was revealed. For the first time, the ability of a nitride-dimer to accept six electrons from strong reductants (*viz.*, dithionite, thiourea dioxide and hydroxymethanesulfinate) was evidenced. It was proved that both reduced dimers containing iron in +2 oxidation state possess low stability. The structural difference of Fe^{II}-anion-radicals was stressed. It was shown that the μ-nitrido-dimer moiety stabilizes iron cations in high oxidation states.

SUPPLEMENTARY MATERIAL

Figures S-1 and S-2 are available electronically at http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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И З В О Д

ИСПИТИВАЊЕ РЕАКЦИЈА ИЗМЕЂУ μ-НИТРИДО- И μ-ОКСО-ГВОЖЂЕ--ТЕТРАСУЛФОФТАЛОЦИЈАНИНА И РЕДУКЦИОНИХ СРЕДСТАВА КОЈА САДРЖЕ СУМПОР

ILIA A. DEREVEN'KOV[1], SVETLANA S. IVANOVA[1], EVGENY V. KUDRIK[1], SERGEI V. MAKAROV[1], ANNA S. MAKAROVA[2] и PAVEL A. STUZHIN[1]

[1] *State University of Chemistry and Technology, Engels Str. 7, 153000 Ivanovo, Russia и* [2] *G. A. Krestov Institute of Solution Chemistry of the RAS, Academicheskaya Str. 1, 153045 Ivanovo, Russia*

У овом раду је упоређивана реактивност μ-нитридо- и μ-оксо-димера гвожђе-тетрасулфофталоцијанина у воденој средини при различитим pH вредностима. Утврђено је да

је комплекс са нитридо-мосним лигандом знатно стабилнији у киселој и у базној средини. Испитиване су реакције одговарајућих комплекса са редукционим средствима која садрже сумпор (натријум-дитионит, тиоуреа-диоксид, натријум-хидроксиметансулфинат и L-цистеин) и објашњене разлике у одговарајућим редокс процесима.

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