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First Water–Soluble μ–Nitrido Dimer of Iron Phthalocyanine

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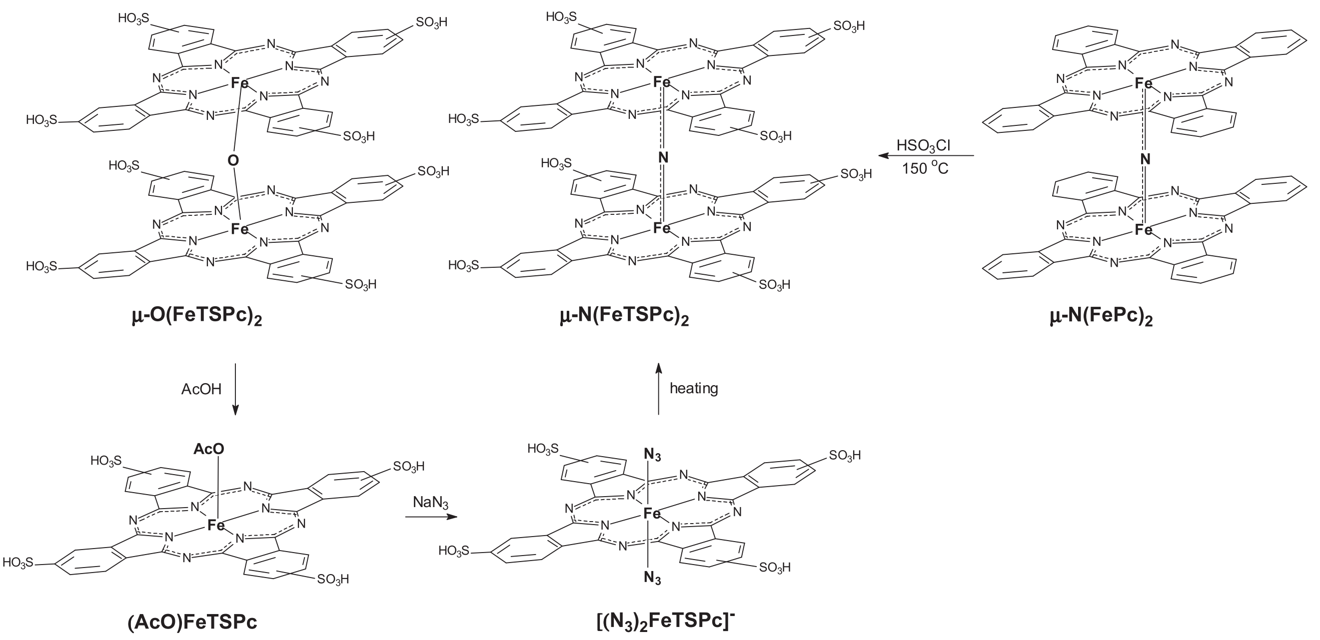
The first water soluble μ-nitridodimer of Fe-phthalocyanine μ-N(FeTSPc)$_2$ has been prepared by two alternative routes: (i) by thermolysis of bis-azidocomplex of iron(III) tetrasulfophthalocyanine [(N$_3$)$_2$FeTSPc]$^-$ in acetic acid, and (ii) by sulfontion of μ-nitridodiiron bisphthalocyanine μ-N(FePc)$_2$ with chlorosulfonic acid.

Keywords*:* Tetrasulfophthalocyanine, iron complex, μ-nitrido dimer.

The μ-nitrido dimer of Fe-phthalocyanine μ-N(FePc)$_2$ was first reported and actively studied in the middle of the 1980s.[1,2] Recently it was established that its *tert*-butyl substituted derivative μ-N(FePc^{t}Bu$_4$)$_2$ catalyses the oxidation of methane by H_2O_2 under very mild conditions (25-60°C),[3] and then a high catalytic activity was also demonstrated in the oxidation of other organic substrates.[4] It has been shown in theoretical work[5] that the ability of the μ-nitrido moiety to serve as a remarkable charge reservoir and to stabilise the lower spin-states can enhance the catalytic activity of μ-nitrido dimers of Fe-porphyrazines in comparison with the corresponding μ-oxo species. The water-soluble Fe^{III}-tetrasulfophthalocyanine in its μ-oxo form, μ-O(FeTSPc)$_2$, catalyses various redox-reactions in aqueous medium.[6] Among μ-nitrido dimers so far only μ-N(FePc^{t}Bu$_4$)$_2$ and other species well-soluble in organic solvents due to presence of alkyl residues were studied, including alkoxy[7] and alkylsulfonyl[8] substituted derivatives. We report here the synthesis of the first water-soluble derivative – the μ-nitrido dimer of Fe-tetrasulfophthalocyanine, μ-N(FeTSPc)$_2$, which was prepared by two alternative routes (Scheme 1).

In the first approach Fe-tetrasulfophthalocyanine, which was prepared by cyclotetramerization of 4-sulfophthalic acid,[9] was used as a starting material. In neutral or basic water solutions this species exists as μ-oxodimer μ-O(FeTSPc)$_2$,[6] but its dissolution in acetic acid leads to the monomeric acetate complex (AcO)FeTSPc. This is evidenced by the UV-vis spectrum in acetic acid, in which along the *Q*-band at 652 nm the lower intensity charge-transfer band is seen at 840 nm (Figure 1, spectrum 2). Such spectrum is characteristic for five-coordinated Fe^{III} complexes of porphyrazines[10] and phthalocyanine[11] containing Fe^{III} in the intermediate spin



Scheme 1. Synthetic routes to μ-nitridodimer of Fe-tetrasulfophthalocyanine, μ-N(FeTSPc)$_2$.

state S=3/2. Thus for [(Cl)FePc] the Q-band at 655 nm (π-π^* transition) is accompanied by a charge transfer band (π-d_π) at 832 nm.[11] Addition of azide (NaN_3 or HN_3) leads to formation of a six-coordinated bisazido complex $[(N_3)_2FeTSPc]^-$ which can be followed by disappearance of the absorption bands of the pentacoordinated acetate complex at 652 and 840 nm and the appearance of a new very intense band at 673 nm (Figure 1, spectrum *3*). Six-coordinated pseudohalide complexes of Fe^{III}-phthalocyanine $[(X)_2FePc]^-$ exhibit similar spectral features with the Q-band at 670-690 nm. Refluxing of the solution of the bisazido complex $[(N_3)_2FeTSPc]^-$ leads to its thermolysis with formation of the μ-nitrido dimer, μ-N$(FeTSPc)_2$ (Figure 1, spectrum *4*), similarly as in the case of bisazido complexes of unsubstituted Fe^{III}-phthalocyanine.[2]

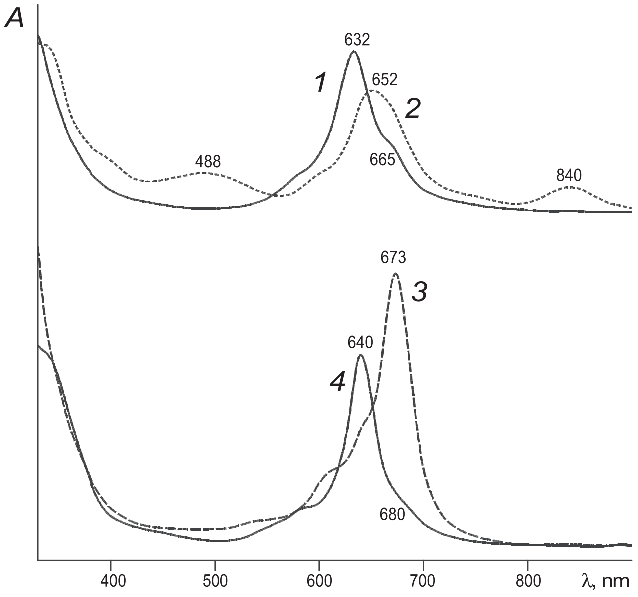


Figure 1. UV-Vis spectra of μ-oxo dimer μ-O$(FeTSPc)_2$ in water (*1*), acetate complex (AcO)FeTSPc formed in acetic acid (*2*); its conversion to bis azido complex $[(N_3)_2FeTSPc]^-$ (*3*)after addition of NaN_3, and to μ-nitrido dimer μ-N$(FeTSPc)_2$ (*4*) upon heating.

The second approach is based on our finding that the μ-nitrido dimer of Fe-phthalocyanine μ-N$(FePc)_2$, prepared as described elsewhere,[1a,2] unlike the μ-oxo-dimer μ-O$(FePc)_2$, is very stable even in very strongly acidic media and can be chlorosulfonated with hot HSO_3Cl (4 h at 150°C). After overnight staying of the reaction mixture the chlorosulfonic derivative μ-N$(FePc(SO_2Cl)_4)_2$ was isolated by pouring on ice and then hydrolysed with water at 80°C to give μ-N$(FeTSPc)_2$. Treatment of the sulfochloride μ-N$(FePc(SO_2Cl)_4)_2$ with dibutylamine gives the sulfamide derivative μ-N$(FePc(SO_2NBu_2)_4)_2$. Elemental analysis and ESI mass-spectroscopy show the presence of four sulfonyl groups per Fe-phthalocyanine unit.

The UV-Vis spectrum of the obtained μ-nitrido dimer μ-N$(FeTSPc)_2$ in acetic acid contains a broadened Q-band with a maximum at 640 nm and a shoulder at 680 nm (Figure 1, spectrum *4*). The spectrum in water is shown in Figure 2 (left panel). Such spectral pattern is typical for single-atom μ-bridged dimeric Fe-phthalocyanines with exciton coupling between two adjacent π-chromophores. In comparison with the μ-oxodimer μ-O$(FeTSPc)_2$ the Q-band and the Soret bands in the UV-vis spectrum of μ-N$(FeTSPc)_2$ are bathochromically shifted (632 → 640 and 326 → 336 nm, respectively, Figure 2, left panel). Interestingly, the maximum of the Q-band in μ-N$(FeTSPc)_2$ has a similar position to that observed in dichlorometane solutions of alkylsulfonyl substituted derivatives μ-N$(FePc(SO_2Alk)_4)_2$ (Alk = *tert*-butyl, hexyl, λ_Q ~ 638 nm) and dibutylsulfonylamide μ-N$(FePc(SO_2NBu_2)_4)_2$ (λ_Q = 634 nm). The difference in the electron-withdrawing properties of various sulfonyl groups is relatively small and the peripheral substituents in the phthalocyanine macrocycle have only weak influence on the spectral properties, which are more sensitive to the coordination mode and electronic structure of the metal center. The close position of the Q-band for the obtained sulfonated μ-nitrido dimer of Fe-phtalocyanine (~635-640 nm) with the non-oxidised μ-nitrido dimers bearing other sulfonyl substituents is indicative of their similar electronic structure.

The μ-nitrido dimers of Fe-phthalocyanine can contain two equivalent iron atoms either in the oxidation state +3.5 ($Fe^{III½}\cdots N\cdots Fe^{III½}$) or +4 ($Fe^{IV}=N^+=Fe^{IV}$).[1,2] In the case of the unsubstituted derivative μ-N$(FePc)_2$ the oxidation to cationic species $[\mu\text{-}N(FePc)_2]^+$ containing two Fe^{IV} occurs already at $E^{½}$=0.00 V and requires very mild oxidation agents such as ferrocenium cation, tetracyanoquinodimethane[1] or even iodine, while stronger oxidants, *e.g.* bromine, nitric acid or trifluoroacetic acid in air, lead to further oxidation involving macrocycle[2] yielding red-brown coloured complexes of Fe^{IV} with phthalocyanine cation-radical - $[\mu\text{-}N((X)FePc^{+\cdot})_2]^+(X)$ (X = Br^-, CF_3COO^-, NO_3^-). Upon oxidation of the μ-bridge from ($Fe^{III½}\cdots N\cdots Fe^{III½}$) to ($Fe^{IV}=N^+=Fe^{IV}$) the Q-band maximum is shifted bathochromically by 10-20 nm,[1b,8] while further oxidation of the macrocycle leads to red-brown species[2] due to appearance of absorption in the 500-550 nm region characteristic for cation-radicals.

We have studied the action of oxidants on the spectral properties of the obtained μ-nitridodimer of Fe-tetrasulfophthalocyanine. In the presence of hydroperoxide (H_2O_2 in basic medium) no changes were observed in its UV-vis spectrum in aqueous solution. Addition of bromine to its solution in acetic acid leads only to some broadening of the Q-band, while the position of its maximum remains changed. The Q-band at ~635-640 nm in μ-N$(FeTSPc)_2$ can be associated with the presence of the ($Fe^{III½}\cdots N\cdots Fe^{III½}$) bridge, since in the cationic oxidised species, containing ($Fe^{IV}=N^+=Fe^{IV}$), it should be observed at longer wavelength (650-665 nm). Thus, for the oxidised alkylsulfonyl derivatives $[\mu\text{-}N(FePc(SO_2Alk)_4)_2]^+$ the Q-band is shifted from 638 to 647-657 nm,[8] and the addition of Br_2 to solution of sulfamide derivative μ-N$(FePc(SO_2NBu_2)_4)_2$ in CH_2Cl_2 shifts the Q-band from 634 to 664 nm and broadens it. The electron-withdrawing sulfonyl groups presumably stabilise the phthalocyanine macrocycle to oxidation by bromine.

The ESR spectrum of μ-N$(FeTSPc)_2$ aqueous solution (Figure 2, right panel) confirms the presence of the ($Fe^{III½}\cdots N\cdots Fe^{III½}$) bridge. It contains the characteristic triplet at $g_\perp$=2.13, which is typical for μ-nitrido dimers of Fe-porphyrins[12] and Fe-porphyrazines[13] and originates from the hyperfine interaction of the unpaired electron with ^{14}N nucleus on the μ-nitrido-bridge ($A^N_\perp$=2.60 mT). The complicated ESR pattern in the g~1.9-2.9

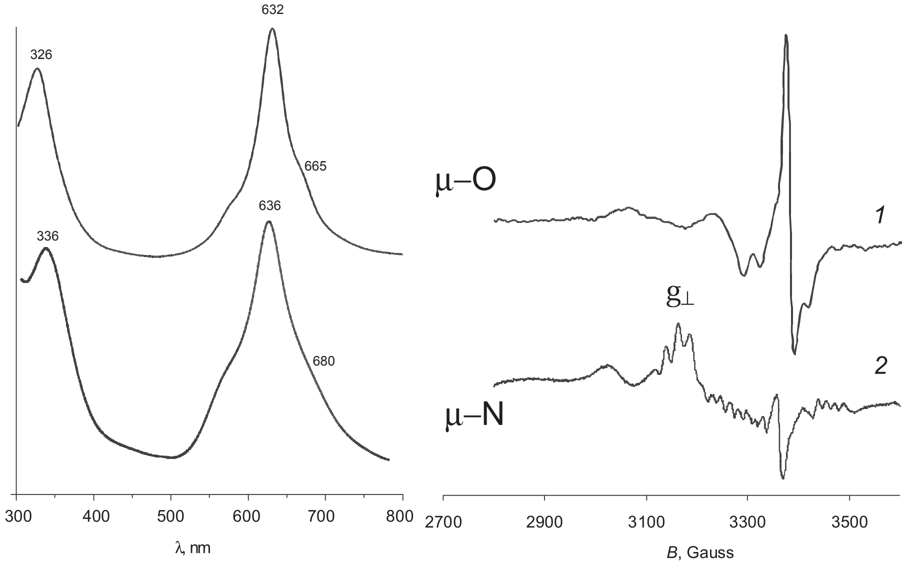


Figure 2. UV-Vis (left) and ESR (right) spectra of μ-oxo (*1*) and μ-nitrido (*2*) dimers of Fe-tetrasulfophthalocyanine in water.

region might be connected with the additional interaction with the nitrogen atoms of the phthalocyanine macrocycle and coordination of oxygen as was observed for μ-nitrido dimer of Fe-porphyrazine.[13] The ESR spectrum exhibits also minor signals of the monomeric impurities, containing $\mathrm{Fe^{III}}$ in the spin states $S = 1/2$ and $3/2$ (g_3 at 2.3 and $g_\perp \sim 4.3$, respectively), which can not be seen in UV-Vis spectrum

The value of the magnetic moment of μ-N$(\mathrm{FeTSPc})_2$ in water solution $\mu_{\mathrm{eff}} = 2.14\mu_\mathrm{B}$ at 298 K (Evans method) also corresponds to the value expected for a system with one unpaired electron and is consistent with the data reported for the dimeric μ-nitrido Fe-complexes of other tetrapyrrolic macrocycles – μ-N$(\mathrm{FePc})_2$ (μ_{eff}=$2.13\mu_\mathrm{B}$),[1] Fe-octaphenylporphyrazine ($2.24\mu_\mathrm{B}$)[13] and Fe-tetraphenylporphine (μ_{eff}=$2.04\mu_\mathrm{B}$).[14]

In the NMR spectrum, the aromatic protons of the benzene rings are observed as overlapping multiplets in the region typical for diamagnetic phthalocyanines (7.6-8.7 ppm), implying negligible delocalization of the unpaired electron from the d_{z^2} orbital onto the phthalocyanine macrocycle.[15]

In conclusion, we have prepared the μ-nitrido dimer of Fe-tetrasulfophthalocyanine, μ-N$(\mathrm{FeTSPc})_2$ – the first water-soluble μ-nitrido dimer, and provide evidence that it contains an $(\mathrm{Fe^{III\frac{1}{2}}}\cdots\mathrm{N}\cdots\mathrm{Fe^{III\frac{1}{2}}})$ bridging moiety. Further studies of this complex, including its redox properties and catalytic activity in aqueous solution, are in progress.

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References

1. (a) Goedken V.L., Ercolani C. *J. Chem. Soc., Chem. Comm.* **1984**, 378-379. (b) Bottomley L.A., Gorce J.-N., Goedken V.L., Ercolani C. *Inorg. Chem.* **1985**, *24*, 3733-3737. (c) Ercolani C., Gardini M., Pennesi G., Rossi G., Russo U. *Inorg. Chem.* **1988**, *27,* 422-427.
2. Kennedy B.J., Murray K.S., Homborg H., Kalz W. *Inorg. Chim. Acta* **1987**, *134*, 19-21.
3. Sorokin A.B., Kudrik E.V., Bouchu D. *Chem. Commun*. **2008**, 2562-2564.
4. Kudrik E.V., Sorokin A.B. *Macroheterocycles* **2011**, *4*, 154-160 (http://dx.doi.org/10.6060/mhc2011.3.02).
5. Silaghi-Dumitrescu R., Makarov S.V., Uta M.-M., Dereven'kov I.A., Stuzhin P.A. *New J. Chem*. **2011**, *35*, 1140-1145.
6. (a) Hadasch A., Sorokin A., Rabion A., Meunier B. *New J. Chem.* **1998**, *22*, 45-51. (b) Beyrhouty M., Sorokin A.B., Daniele S., Hubert-Pfalzgraf L.G. *New J. Chem.* **2005**, *29*, 1245-1248. (c) Kudrik E.V., Makarov S.V., Zahl A., van Eldik R. *Inorg. Chem*. **2005**, *44*, 6470-6475.
7. Kudrik E.V., Afanasiev P., Bouchu D., Sorokin A.B. *J. Porphyrins Phthalocyanines* **2011**, *15*, 583-591.
8. (a) İşci Ü., Afanasiev P., Millet J.-M.M., Kudrik E.V., Ahsen V., Sorokin A.B. *Dalton Trans*. **2009**, 7410-7420. (b) Afanasiev P., Bouchu D., Kudrik E.V., Millet J.-M.M., Sorokin A.B. *Dalton Trans*. **2009**, 9828-9836.
9. Weber J.N., Busch D.H. *Inorg. Chem*. **1965**, *4*, 469.
10. Stuzhin P.A. *Macroheterocycles* **2009**, *2*, 114-129 (http://macroheterocycles.isuct.ru/sites/default/files/MHC2009t02n02_114–129_0.pdf).
11. (a) Kalz W., Homborg H. *Z. Naturforsch*. **1983**, *38b*, 470-484. (b) Kennedy B.J., Murray K.S., Zwack P.R., Homborg H., Kalz W. *Inorg. Chem*. **1986**, *25*, 2539-2545.
12. Bottomley L.A., Garrett B.B. *Inorg. Chem*. **1982**, *21*, 1260-1263.
13. Stuzhin P.A., Latos-Grazynski L., Jezierski A. *Transition Met. Chem*. **1989**, *14*, 341-346.
14. Summerville D.A., Cohen I.A. *J. Am. Chem. Soc.* **1976**, *98*, 1747-1752.
15. Tatsumi K., Hoffmann R. *J. Am. Chem. Soc*. **1981**, *103*, 3328-3341.

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