Molecular Structure, Optical and Magnetic Properties of Iron Tetra(2,3–quinoxalino)porphyrazine
\[[(N–MeIm)_2Fe\{T(2,3–Q)Pz\}^{3–}]^{2–}\] Radical Dianions

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Iron(II) tetra(2,3-quinoxalino)porphyrazine, \(\text{Fe}^{II}T(2,3-Q)\text{Pz}\), was obtained using diaminomaleonitrile and o-phenylenediamine as starting materials. Reduction of \(\text{Fe}^{II}T(2,3-Q)\text{Pz}\) by sodium fluorenone ketyl in the presence of cryptand[2.2.2] and N-methylimidazole followed by precipitation of crystals leads to crystalline salt \([\text{cryptand[2.2.2]}(\text{Na}^+)\cdot\{(\text{N-MeIm})_2\text{Fe}^{II}\{T(2,3-Q)\text{Pz}\}^{3–}\}^{2–}\cdot\text{3C}_6\text{H}_4\text{Cl}_2\cdot\text{2H}_2\text{O}\) (1). Molecular structure and properties of the \([(\text{N-MeIm})_2\text{Fe}^{II}\{T(2,3-Q)\text{Pz}\}^{3–}\}^{2–}\) radical dianions have been studied. Reduction of \(\text{Fe}^{II}T(2,3-Q)\text{Pz}\) is accompanied by strong blue shift of Soret band in spectrum of 1 but Q-band has close position to that in the spectrum of neutral macrocycle. There is an alternation of the C-N meso bonds in the macrocycle in 1, the difference between short and long C-N meso bonds of 0.017 Å supports the formation of radical trianionic \{T(2,3-Q)Pz\}^{3–} macrocycle. Coordination of N-methylimidazole molecules to iron (I) atoms with the Fe–N(imidazole) distance of 1.999(7) Å is observed. Both FeI atom and radical trianionic \{T(2,3-Q)Pz\}^{3–} macrocycle contribute to the EPR signal of 1, which is well interpreted as the superposition of Lorentzian shaped lines with \(g_1=2.0917\), \(g_2=2.0679\), \(g_3=2.0292\), \(g_4=1.9991\) and \(g_5=1.9922\). The lines with higher g-factor (\(g_1\) and \(g_2\)) value can be attributed to low spin (\(S=1/2\)) \(\text{Fe}^{II}\) whereas the lines with lower g-factor (\(g_3\) and \(g_4\)) values can be attributed to the radical trianionic \{T(2,3-Q)Pz\}^{3–} macrocycle. The line with intermediate g-factor value (\(g_5\)) can originate from the contribution of both components. The value of effective magnetic moment at 300 K (2.32 µ\(_B\)) indicates a contribution of two non-interacting \(S=1/2\) spins from iron(I) atoms and radical trianionic \{T(2,3-Q)Pz\}^{3–} macrocycle. These spins weakly antiferromagnetically interact with Weiss temperature of –3 K.

Keywords: Tetrapyrazinoporphyrazines, crystal structure, optical and magnetic properties, reduction, coordination.

Молекулярная структура, оптические и магнитные свойства дианион–радикальной соли тетра(2,3–хиноксалино)порфиразина железа \([(N–MeIm)_2Fe\{T(2,3–Q)Pz\}^{3–}]^{2–}\)
The addition of benzo-groups to TPyzPzs by linear pounds of tetrapyrazinoporphirazines were obtained till additional chains [22] or closely packed electron density delocalized over macrocycle which can of these macrocycles lead to the appearance of unpaired acceptor properties in comparison with Pc macrocycle.

In this work we synthesized iron(II) tetra(2,3-quinoxalino)porphyrin, Fe(II)(T(2,3-Q)Pz), and study the reduction of this porphyrin in the presence of cryptand[2.2.2] and N-methylimidazole with following precipitation of diaminomaleonitrile (DAMN) as described in ref. [35] 2,3-Dicyanoquinodimethane (electrochemical oxidation of 2,3-dicyanoquinoline, Sigma-Aldrich, 98 %), 4,7,13,16,21,24-hexaoxa-1,10-diazeno-1,4-benzoquinone (Sigma-Aldrich, 98 %), iron(II) acetate (Acros, 98 %), sodium fluorenone (Fluka, 99 %), tetrafluoroboric acid (Acros, 99 %), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Sigma-Aldrich, 98 %), trifluoroacetic acid (Acros, 99 %), and dialkyl; hydrogen-1,1,1,2,2,2-hexafluoroacetone (Acros, 99 %). The solvents were distilled over Na/benzophenone, benzyl chloride (C 6H 5Cl 2) was distilled over CaH 2, hexane was distilled over Na/benzophenone under reduced pressure. The solvents were stored at −5 °C.

Recently it was shown that in salts obtained by reduction, FeI{T(2,3-Q)Pz} + and Fe(II) tetra(2,3-quinoxalino)porphyrin, Fe(II)(T(2,3-Q)Pz). The synthesis was performed in a glove box. KBr pellets for IR- and UV-Visible-NIR measurements were also prepared in the glove box. EPR and SQUID measurements were performed on polycrystalline samples of 1 sealed in 2 mm quartz tubes under 10−5 Torr.

Synthesis

Iron(II) tetra(2,3-quinoxalino)porphyrin, Fe(II)(T(2,3-Q)Pz), was synthesized according to procedure in ref.[34] with some modifications.

Diaminosuccinonitrile (DISN) was synthesized by oxidation of diaminomalenitrile (DAMN) as described in ref.[34] 2,3-Dicyanoquinoxaline was synthesized by condensation of DISN and o-phenylenediamine according to ref.[34] 2,3-Dicyanoquinoxaline (1 g, 5.6 mmol) was added to solution of n-butanol (50 mL) with dissolved magnesium (140 mg, 5.8 mmol) (dissolution was initiated by iodine crystal) and the stirred mixture was refluxed for 6 h. Solvent was evaporated under reduced pressure. After this the obtained Mg2 complex was demetalated by dissolution in CF3COOH (15 %). Acid was evaporated,
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the residue was washed with water, methanol and dried. The obtained crude metal-free macroheterocycle, \( H[T(2,3-Q)Pz] \), and iron(II) acetate (500 mg) were refluxed in pyridine for 3 h under argon. After cooling the reaction mixture was poured into water, filtered, and carefully washed with water, methanol and toluene. Powder was dried at 100 °C in a vacuum for 2 hours to remove pyridine and water to give Fe\(^{II}[T(2,3-Q)Pz]\) (60 % yield). Anal. found: C 62.57, N 29.30, H 2.04 %. Calcd. for C\(_{40}\)H\(_{16}\)N\(_{16}\)Fe: C 62.68, N 29.24, H 2.10. IR (KBr) ν cm\(^{-1}\): 2366w, 2920w, 2972m, 3063w. UV-Vis (KBr pellet) λ\(_{\text{max}}\) nm: 348, 763s, 881w, 1050m, 1080w, 1111m, 1132s, 1203m, 1229s, 1322w, 1394w, 1561w, 2608w, 2920w, 2972m, 3063w. UV-Vis (KBr pellet) λ\(_{\text{max}}\) nm: 348, 478, 551, 714 nm.

**Synthesis of crystalline salt 1.** Salt [cryptand[2.2.2] (Na\(^{+}\))]\(_2\)[(N-MeIm)Fe\(^{II}[T(2,3-Q)Pz]\)\(^{2-}\)]. 3C\(_6\)H\(_4\)Cl\(_2\)H\(_2\)O (1) was obtained by reduction of 31.9 mg of Fe\(^{II}[T(2,3-Q)Pz]\) (0.042 mmol) by excess of sodium fluorenone ketyl (50 mg, 0.247 mmol) in the presence of two equivalents of cryptand[2.2.2] (31.6 mg, 0.084 mmol) and 0.5 ml of N-methylimidazole by stirring overnight at 100 °C till complete dissolution of parent macrocycle and the formation of deep-violet solution. The reaction solution of salt 1 was filtered in a 50 mL glass tube of 1.8 cm diameter. The solvent was decanted from the crystals and they were washed with \( n \)-hexane. Metallic dark black blocks of 1 were obtained in 31 % yield.

The composition of 1 was determined from X-ray diffraction on single crystals. The analysis of the obtained crystals under microscope in a glove box as well as testing of several single crystals from each synthesis by X-ray diffraction showed that only one crystalline phase is formed. Elemental analysis cannot be used to determine the composition of the obtained crystals due to their high air sensitivity and an addition of oxygen during the procedure of elemental analysis.

**General**

UV-Visible-NIR spectra were measured in KBr pellets on a Perkin Elmer Lambda 1050 spectrometer in the 250-2500 nm range. FT-IR spectra were obtained in KBr pellets with a Perkin-Elmer Spectrum 400 spectrometer (400–7800 cm\(^{-1}\)). EPR spectra were recorded on polycrystalline samples of \( \alpha \)-azaleonitrile (DAMN) by two stages as described in ref. [35,36]. 2,3-Dicyanoquinoxaline was synthesized from diaminomethane in the presence of magnesium butoxide in \( n \)-butanol.

2,3-Dicyanoquinoxaline is the most suitable precursor to obtain tetra(2,3-quinoxalino)porphyrine macrocycle. \(^{[34]}\) Iron(II) tetra(2,3-quinoxalino)porphyrine, Fe\(^{II}[T(2,3-Q)Pz]\)\(_4\), was synthesized by metatation of corresponding metal-free macrocycle which was obtained by demetallation of corresponding Mg\(^{II}[T(2,3-Q)Pz]\) complex. Mg\(^{II}[T(2,3-Q)Pz]\) was obtained by tetramerization of 2,3-quinoxaline in the presence of magnesium butoxide in \( n \)-butanol.

2,3-Dicyanoquinoxaline was synthesized from diaminonaleonitrile (DAMN) by two stages as described in ref. [35,36] (Scheme 1).

**Results and Discussion**

2,3-Dicyanoquinoxaline is the most suitable precursor to obtain tetra(2,3-quinoxalino)porphyrine macrocycle. \(^{[34]}\) Iron(II) tetra(2,3-quinoxalino)porphyrine, Fe\(^{II}[T(2,3-Q)Pz]\)\(_4\), was synthesized by metatation of corresponding metal-free macrocycle which was obtained by demetallation of corresponding Mg\(^{II}[T(2,3-Q)Pz]\) complex. Mg\(^{II}[T(2,3-Q)Pz]\) was obtained by tetramerization of 2,3-quinoxaline in the presence of magnesium butoxide in \( n \)-butanol. 2,3-Dicyanoquinoxaline was synthesized from diaminonaleonitrile (DAMN) by two stages as described in ref. [35,36] (Scheme 1).

Obtained iron(II) tetra(2,3-quinoxalino)porphyrine was used in the synthesis without further purification due to extremely low solubility of this porphyrine. It

\[
\text{Fe}^{III}[T(2,3-Q)Pz]^{-2} \cdot 3C_6H_4Cl_2\cdot 2H_2O (1)
\]

\[
\{\text{cryptand}[2.2.2](Na^+))_2\}[(N-MeIm)\text{Fe}^{II}[T(2,3-Q)Pz]^{-3-}]^{-2} \cdot 3C_6H_4Cl_2\cdot 2H_2O (1)
\]
was reduced by an excess of sodium fluorenone ketyl and an excess of N-methylimidazole in o-dichlorobenzene. N-methylimidazole was added to increase the solubility of the salt in dichlorobenzene which is only partially soluble in this solvent without N-methylimidazole. In this case reduction results in complete dissolution of neutral FeII(T(2,3-Q)Pz) and deep-violet solution is formed. Slow case reduction results in complete dissolution of neutral soluble in this solvent without the salt in dichlorobenzene which is only partially removed from the sample even under vacuum.

Earlier it was shown that reduction of titanyl tetra-(acenaphthenopyrazino)porphyrizine (TiIVO=AcETPrzPz) which has larger macrocycle by sodium fluorenone ketyl also leads to the formation dianionic species O=TiIV(AcETPrzPz)−·−·2.[31] At the same time appearance of distortions of the macrocycle in the visible range with the maximum at 662 nm.[22] FeII(T(2,3-Q)Pz) shows one broad band in the visible range with the maximum at 662 nm,[22] FeII(T(2,3-Q)Pz) shows larger number of bands in the UV-Visible-NIR range. The Soret band has maximum at 348 nm, the split Q-band is manifested at 478, 551 and 714 nm (Figure 1). The formation of I is accompanied by blue shift of Soret band to 318 nm, but Q-band in the spectrum of I has close position to that in the spectrum of neutral macrocycle and is observed as split band at 481, 563 and 717 nm. In spite of a close position contribution of the bands at 481 and 563 nm is essentially increases in comparison with the spectrum of pristine FeII(T(2,3-Q)Pz) (Figure 1).

It was shown that reduction of unsubstituted tetrapyrazinoporphyrizine H,TTPyzPz led to appearance of new intense absorption NIR band with maximum at 822 nm.[30] Characteristic for the reduced macrocycle absorption band in the NIR range is also observed in spectrum of (PPN)2 [(O=TiIV(AcETPrzPz))−·−·solv] at 963 nm.[30] At the same time reduction of iron(II) phthalocyanine and iron(II) hexadeca-chlorophthalocyanine is metal-centered and is accompanied by the formation of iron(I) and iron(0) species without electron transfer to the phthalocyanine macrocycle.[22-24] As a result, the formation of [FeII(Pc)(−2)]+, [FeII,Cl4,Pc(−2)]− and [FeII,Cl,Pc(−2)]+ anions in solid state does not provide the appearance of new bands in the NIR range.[22-24] Absorption is also observed in the spectrum of I in the NIR range (shown by arc in Figure 1) but this absorption is not appeared as a separate band.

**Figure 1.** UV-Visible-NIR spectra of pristine FeII(T(2,3-Q)Pz) and salt 1 in KBr pellets prepared for 1 in anaerobic conditions.

**Molecular Structure of [(N-MeIm)FeII(T(2,3-Q)Pz)]−·−·2− and Crystal Structure of 1**

Salt 1 contains one independent half of radical dianions [(N-MeIm)FeII(T(2,3-Q)Pz)]−·−·2−, one independent cryptand[2.2.2](Na+) cation, one half o-dichlorobenzene molecule and one water molecule. The cryptand[2.2.2](Na+) cation is disordered between two positions with 0.529(8) and 0.471(8) occupancies. Water molecule is positioned close to the hydrogen atom of the N-methylimidazole ligand and forms short hydrogen bond with it of 2.45 Å length.

Tetrapyrazinoporphyrizine macrocycle initially has stable aromatic 18 π-electron system. Its reduction is accompanied by the formation of less stable 19 π-electron system providing partial disruption of aromaticity of the macrocycle. That results in the alternation of the C-N meso bonds. Studying of molecular structure of 1 shows that alternation of the C-N meso bonds is observed in the [(N-MeIm)FeII(T(2,3-Q)Pz)]−·−·2− radical dianions (Figure 2a). Four shorter and four longer C-N meso bonds belong to two oppositely located isoindole units in 1. The average difference between short and long bonds is 0.398 Å. Redistribution of the length of other bonds at the reduction is also observed. The average difference between short and long C-N meso bonds is 0.012 Å. The average difference between short and long bonds C-N meso bonds in the {O=TiIV(AcETPrzPz)−·−·2−}+ and H,TTPyzPz−·−·2− dianions containing tetranionic and protonated dianionic macrocycles of 0.060 Å[31] and 0.092 Å[30] is essentially larger. Thus, disruption of aromaticity is less pronounced for the macrocycle in 1 compared with tetranionic and protonated dianionic TPrzPzs macrocycles. Nevertheless, the appearance of distortions of the macrocycle in 1 confirms formation of radical trianionic T(2,3-Q)Pz−·−· macrocycles.

Macrocycle in 1 has saddle-like conformation, two benzozyprazine groups lie almost in 24-atom porphyrizine plane, but two other oppositely located groups come out above and below plane with displacement of atoms up to 0.398 Å. Iron(I) atoms lie exactly in 24-atom porphyrizine plane, the average distance Fe-Nmeso, is 1.962 Å. Coordination of N-methylimidazole molecules to iron(I) atoms is observed with the average N(imidazole)-Fe distance of 1.999(7) Å (Figure 2a).

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In whole, salt 1 has a structure (Figure 2b) with one-dimensional chains formed by the \([(N\text{-MeIm})_2Fe^\text{i}(T(2,3-Q)Pz)^\text{I}^\text{-}]^\text{-}\) radical dianions, each macrocycle has four side-by-side van der Waals (vdW) C···C contacts in these chains with neighboring ones of 3.435Å (are shown by green dashed lines in Figure 2b). These chains have perpendicular arrangement relative to each other as shown in Figure 2b. There is no short van der Waals contacts between the chains due to their isolation by bulky cryptand[2.2.2](Na\text{+}) cations and solvent C\text{6H}4Cl\text{2} molecules (are not shown in Figure 2b).

**Magnetic Properties**

Magnetic properties of 1 were studied by EPR and SQUID techniques on a polycrystalline sample in anaerobic conditions.

Effective magnetic moment of salt 1 at 300 K is 2.32 \(\mu_B\) that approximately corresponds to the contribution of two non-interacting \(S = 1/2\) spin per formula unit (Figure 3a). These spins can originate from radical dianions \([(N\text{-MeIm})_2Fe^\text{i}(T(2,3-Q)Pz)^\text{I}^\text{-}]^\text{-}\) containing iron(I) atoms with \(S = 1/2\) spin state and radical trianionic \(T(2,3-Q)Pz^\text{I}^\text{-}\) macrocycle also with \(S = 1/2\) spin state. Reciprocal magnetic susceptibility follows the Curie-Weiss law allowing the Weiss temperature to be estimated as \(-3\) K (Figure 3b) indicating weak antiferromagnetic coupling of spins localized on Fe\text{I} atom and delocalized over the macrocycle. Previously was even shown that such coupling between central paramagnetic metal atom and radical trianionic macrocycle can be rather weak.\(^{[13,14]}\) Magnetic moment decreases slightly at cooling (Figure 3a) most probably due to weak antiferromagnetic coupling of spins.

Salt 1 manifests EPR signal which can be fitted well by five lines with Lorentzian line shape. Lines with \(g_1 = 2.0679\) and \(g_2 = 2.0917\) and the linewidth \((\Delta H)\) of 5.61 and 3.69 mT, respectively, were attributed to Fe\text{I} with low \((S = 1/2)\) spin state. Earlier it was shown that Fe\text{I} with \(S = 1/2\) spin state in generally manifests EPR signals with \(g\)-factor smaller than 2.3.\(^{[22-24]}\) Narrower lines with \(g_4 = 1.9991\) \((\Delta H = 1.17\) mT) and \(g_5 = 1.9922\) \((\Delta H = 3.11\) mT) were attributed to the radical trianionic \(T(2,3-Q)Pz^\text{I}^\text{-}\) macrocycle, such asymmetric signals are generally characteristic for the reduced macrocycles.\(^{[13,14]}\) There is also broad line with intermediate \(g\)-factor of 2.0292 \((\Delta H = 7.83\) mT). This \(g\)-factor is intermediate between those characteristic for Fe\text{I} and radical trianionic macrocycles\(^{1+}\) and, therefore,
this component can be attributed to the contribution from both components. Thus, EPR spectra unambiguously show the presence of both paramagnetic species in 1. The 5-line EPR spectrum of 1 is preserved down to 4.2 K. All components have nearly temperature independent g-factors and weakly temperature dependent linewidths as shown in Figure S2.

Conclusions

Thus, iron(II) tetra(2,3-quinoxalino)porphyrizine (Fe\textsuperscript{II}T(2,3-Q)Pz) was obtained using dianimomaleonitrile and o-phenylenediamine as starting materials. Reduction of Fe\textsuperscript{II}T(2,3-Q)Pz followed by precipitation of crystals leads to crystalline salt 1. That allows us to study molecular structure and properties of the [(N-Melm),Fe\textsuperscript{II}(T(2,3-Q)Pz)\textsuperscript{2-}]\textsuperscript{2-} radical cations. Reduction of Fe\textsuperscript{II}T(2,3-Q)Pz is accompanied by strong blue shift of Soret band \(\Delta\mu\) and the appearance of weak NIR absorption in spectrum 1. Thus, iron(II) phthalocyanine has metal-centered first reduction and only third and forth reduction is centered not only on the iron atoms but the macrocycle as well. Reduction of other iron(II) macrocycles in presence of different coordination ligands can yield ions with different value of charge transfer between iron atoms and the macrocycle and this work is now in progress.

Acknowledgements. The work was supported by Russian Science Foundation (project № 17-73-10199).

References

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Received 30.04.2019
Accepted 15.05.2019