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# Supramolecular Iron(III) Tetramesitylporphyrin Cluster Structure Assembled by Hydrogen Bonding with Sulfuric Acid

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We present here the first crystalline assembly of a supramolecular structure formed by iron(III) 5,10,15,20-tetrakismesitylporphyrin via hydrogen bonding with charge compensating hydrosulfate residues. Two additional molecules of sulfuric acid provide hydrogen bonding connection of four iron porphyrin units to form a fragment with interporphyrin void where two iron sites are situated at 9.52 Å distance. The insertion of two molecules of sulfuric acid into cavity formed by four Fe(III) porphyrin molecules led to the formation of the cluster structure with dihedral angle of 53.3° between adjacent porphyrin molecules  $Fe(1A)N_4/Fe(2A)N_4$  and parallel  $Fe(1A)N_4/Fe(1B)N_4$  and  $Fe(2A)N_4/Fe(2B)N_4$ planes. Such a supramolecular material, where four iron sites in the porphyrin ligand environment are strongly connected via network of the hydrogen bonds provides a new tool for exploring different applications involving multielectronic processes.

Keywords: Iron porphyrin, crystal structure, supramolecular associations, hydrogen bonding.

## Структура супрамолекулярного кластера, образованного тетрамезитилпорфиринатом железа(III) посредством водородных связей с серной кислотой

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Синтезирован первый кристаллический супрамолекулярный кластер, образованный 5,10,15,20-тетракисмезитилпорфиринатом железа(III) через водородные связи с гидросульфатными анионами, компенсирующими заряд. Две дополнительные молекулы серной кислоты обеспечивают связывание четырех молекул порфирина железа через водородные связи, что ведет к образованию организованной порфириновой структуры, где два иона железа находятся на расстоянии 9.52 Å. Внедрение двух молекул серной кислоты в полость, образованную четырьмя молекулами порфирината железа, ведет к образованию кластерной структуры, где две независимые молекулы  $Fe(1A)N_4/Fe(2A)N_4$  расположены под углом 53.3°, а макроциклы  $Fe(1A)N_4/Fe(1B)N_4$  и  $Fe(2A)N_4/Fe(2B)N_4$ параллельны друг другу. Подобный супрамолекулярный материал с четырьмя центрами железа в порфириновом лигандном окружении, связанными между собой через систему сильных водородных связей, представляет интерес для применения в различных областях, связанных с многоэлектронными процессами.

**Ключевые слова**: Порфиринат железа, кристаллическая структура, супрамолекулярные ассоциаты, водородные связи.

#### Introduction

Design and construction of phthalocyanine-[1] and porphyrin-based<sup>[2-4]</sup> structured materials is a rapidly expanding research area. Different structural and functional properties of supramolecular multiporphyrin assemblies can be used for the development of functional systems, e.g., light harvesting constructions, redox active materials and molecular electronic systems. These systems are also very attractive to create new materials, sensor devices and catalysts. Several synthetic strategies have been used to design organized systems composing of phthalocyanine and porphyrin fragments. Numerous covalent organic frameworks comprising phthalocyanine<sup>[5,6]</sup> and porphyrin<sup>[7,8]</sup> units have been prepared. These phthalocyanine and porphyrin network polymers with controlled porosity and a very high concentration of active site are believed to be useful for catalytic applications.<sup>[9-11]</sup> The preparation of multiporphyrinic cages with three-dimentional cavities has attracted considerable interest in view of the utilization of guest-host interactions in different applications.<sup>[12]</sup> Supramolecular systems including phthalocyanine<sup>[13,14]</sup> and porphyrin<sup>[15-18]</sup> ligands assembled onto solid supports have also been described.

To construct these elaborated objects, porphyrin building blocks need to be functionalized to provide binding between porphyrin entities. This can be achieved by the introduction of different functional groups at the porphyrin moiety, *e.g.*, in the phenyl rings of the tetraphenylporphyrin scaffold<sup>[19]</sup> or in *meso*-positions.<sup>[20]</sup> A variety of useful synthetic approaches have been developed to design elaborated multiporphyrin and multiphthalocyanine arrays.<sup>[3,21]</sup>

On the other hand, non-covalent interactions including coordination, electrostatic interactions and hydrogen bonding allow for self-assembling of the functional macrocyclic units to multicomponent arrays. A 2D metal-organic network composing of zinc meso-polyphosphorylporphyrin was formed via P=O…Zn axial supramolecular coordination.<sup>[22]</sup> Self-organization of zinc  $\beta$ -(dialkoxyphosphoryl) porphyrins led to the solid dimeric species which were stable even in solution.<sup>[23]</sup> Unusual formation of a stable 2D copper porphyrin network where copper(II) sites are coordinated with two phosphoryl groups of adjacent porphyrin units was reported.[24] Weak intermolecular interactions play important role in supramolecular organization of Cd(II), Ni(II), Pd(II) and Pt(II) complexes 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyof rin.<sup>[25]</sup> Copper(II), nickel(II) and palladium(II) complexes of the same porphyrin in combination with dicopper paddlewheel tetrapivalate complex afforded a series of one-dimentional homo- and heterometallic coordination polymers.<sup>[20]</sup>

Porphyrinic supramolecular assemblies can be obtained using hydrogen bonds. For instance, three triaminotriazine compounds bearing two porphyrin units form a supramolecular assembly containing six porphyrins self-organized due to hydrogen bonds with three molecules of dialkylbarbituric acid.<sup>[26]</sup> The porphyrin units can be also assembled to linear arrays by hydrogen-hydrogen interactions between phenolic groups of 5,10,15,20-tetrakis(3,5-dimethyl-4-hydroxyphenyl)porphyrin and inner imino nitrogen atoms.<sup>[27]</sup> Stable *J*-aggregates of 2-*N*-methyl-5,10,15,20-tetrakis-(4'sulfophenyl)-2-aza-21-carbaporphyrin were formed due to hydrogen bonds between internal pyrrolic protons and sulfonic substituents.<sup>[28]</sup>

To the best of our knowledge, porphyrin metal complexes without functionalities at the porphyrin core, such as tetramesitylporphyrin (TMP), don't form supramolecular assemblies. The materials involving iron porphyrins are especially interesting since iron sites are responsible for catalytic properties of hemoprotein enzymes<sup>[29]</sup> and their biomimetic models.<sup>[30,31]</sup> In this context, assembling the iron porphyrin and phthalocyanine complexes in binuclear units provides catalysts with remarkable catalytic activity.[32-39] Although several crystal structures of iron(II) tetramesitylporphyrin complexes involving different pyridine and imidazole ligands,<sup>[40]</sup> 2-methylimidazole<sup>[41]</sup> as well as iron(III) tetramesitylporphyrin complexes with triphenyl- or triisopropylsilanethiolate,[42] 5-methylimidazole[43] and cyanide[44] ligands have been described, no supramolecular assemblies formed by iron tetramesitylporphyrin complex is available. Herein, we report X-ray structural studies of unusual supramolecular assembly consisting of four molecules of iron(III) tetramesitylporphyrin hydrosulfate complex [Fe(TMP)(OSO,H)] and two molecules of sulfuric acid formed due to intermolecular hydrogen bonding interactions during recrystallization of Fe(TMP)Cl from toluene/ H<sub>2</sub>SO<sub>4</sub> mixture.

#### **Experimental**

*Materials. meso*-Tetramesitylporphyrin ( $H_2TMP$ ) was prepared according to published procedure.<sup>[45,46]</sup> The insertion of iron into the  $H_2TMP$  ligand to obtain Fe(TMP)Cl was performed using literature method.<sup>[47]</sup> Spectral data were in agreement with those published in literature.

Preparation of crystals. The solution of Fe(TMP)Cl (500 mg, 0.71 mmol) in toluene (150 mL) was stirred at room temperature with 50 mL of concentrated sulfuric acid during 30 min. The organic phase was separated and ~100 mL of toluene was evaporated under reduced pressure at 60 °C. The concentrated iron porphyrin solution in toluene was left for crystallization at room temperature under aerobic conditions. After several days well shaped single crystals of the supramolecular complex [Fe(TMP)  $(OSO_3H]_2(H_2SO_4)$  (1) were grown. The crystals were separated by filtration, washed with methanol and air-dried. Yield 282 mg (49 %).

*Instrumentation.* UV-Vis spectra were recorded on a Agilent 8453 spectrophotometer. ESI-MS spectra were collected using a Bruker micrOTO-QII spectrometer.

X-Ray data collection and structure refinement. The measurements were made on a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromator, Mo-K $\alpha$  radiation,  $\lambda$ =0.71073 Å,  $\omega$ -scanning). The semi-empirical method SADABS was applied for the absorption correction. <sup>[48]</sup> The structures were solved by direct methods and refined by the full-matrix least-squares technique against F<sup>2</sup> with the anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms in the complex 1 were placed geometrically and included in the structure factors calculation in the riding motion approximation. The carbon atom of the methyl group of toluene solvate is disordered in two positions with a multiplicity of 0.5. All the data reduction and further calculations were performed using the SAINT and SHELXTL-97.[49,50] CCDC reference number is CCDC 1456002. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data\_request/cif. Brief crystal data are listed in Table 1.

Table 1. Crys	stal data and	structure refinement	nt for <b>1</b>
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Empirical formula	$C_{119}H_{116}Fe_2N_8O_{12}S_3$	
f.w.	2058.07	
Colour	brown	
Temperature (K)	150(2)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions (Å, deg)	<i>a</i> =17.5209(15)	
	<i>b</i> =19.4972(17)	
	<i>c</i> =20.1876(17)	
	α=63.1650(10))	
	β=80.1330(10)	
	γ=72.8590(10)	
$V(Å^3)$	5874.3(9)	
Ζ	2	
d (calculated) (mg/m <sup>3</sup> )	1.164	
Abs coeff (mm <sup>-1</sup> )	0.0360	
F(000)	2164	
Crystal size (mm)	0.28×0.26×0.2	
$\theta$ range for data collection (deg)	2.19 to 29.88	
Index ranges	-24<=h<=24, -27<=k<=27, -28<=1<=28	
Refins collected	33822	
Independent refins	17397 [R(int)=0.0566]	
data / restraints / params	17397 / 0 / 1334	
Goodness-of-fit on F <sup>2</sup>	0.983	
<sup>a</sup> Final <i>R</i> indices [I>2sigma(I)]	<i>R1</i> =0.0622, <i>wR2</i> =0.1363	
<sup>a</sup> <i>R</i> indices (all data)	<i>R1</i> =0.1502, <i>wR2</i> =0.1877	
<sup>b</sup> Largest diff. peak and hole (e.A <sup>-3</sup> )	0.603 and -0.727	

 ${}^{a}R_{i} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|; wR_{2} = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma w(F_{o}^{2})^{2}\}^{1/2}$ b'In all structures the largest diff. peak is observed in the vicinity of heavy atom.

\*) Two independent molecules.

#### **Results and Discussion**

Iron tetramesitylporphyrin has been widely used in many studies on cytochrome P-450 modelling<sup>[29-31]</sup> and several crystal structures of the Fe(TMP) complexes mostly bearing nitrogen ligands have been published.<sup>[40-44]</sup> However, to the best of our knowledge, no crystal structure of Fe<sup>III</sup>(TMP)X (X=anion) is available. We have found that the addition of sulfuric acid to toluene solution of Fe(TMP)Cl at room temperature followed by separation

of the organic phase and slow evaporation of the solvent during five days resulted in the formation of brown monocrystals of  $[Fe^{III}(TMP)(OSO_3H]_2(H_2SO_4)$  (1) with a 49 % yield. According to X-ray diffraction data for 1 (Figure 1, Table 1), an  $HSO_4^-$  anion is located in the axial position of the complex with Fe(1)-O(1) 1.8915(19) Å, Fe(2)-O(5) 1.893(2) Å, S(1)-O(1) 1.514(2) Å, S(2)-O(5) Å 1.515(2) distances in two independent molecules. The Fe-Np distances are practically equivalent, within 2.051(2)-2.060(2) Å and 2.049(2)-2.062(2) Å, respectively. It should be noted that pyrrolic nitrogen atoms are situated practically in the same plane with  $\pm 0.0115$  Å and  $\pm 0.0046$  Å deviations. The iron atom displacements from the macrocycle plane are 0.451 Å and 0.468 Å, respectively. The dihedral angles between the four mesityl rings and the mean porphyrin plane are 77.1, 81.9, 84.1 and 86.0° showing similar deviation pattern with that of previously published  $[Fe(TMP)(5-MeHIm)_2]ClO_4$  structure with the dihedral angles of 80.9, 82.0, 84.2 and 84.3°.<sup>[43]</sup>



**Figure 1.** Structure of one of two independent molecules of iron tetramesitylporphyrin in the complex **1**. Displacement ellipsoids are drawn at a 30 % probability level. Hydrogen atoms are omitted for clarity.

Axial position of Fe<sup>III</sup>TMP cation is occupied by HSO<sub>4</sub> anion balancing the positive charge. Two independent Fe(TMP)HSO<sub>4</sub> molecules are connected by hydrogen bonds between two  $\text{HSO}_4^-$  residues to form a dimeric structure (Figure 2).

Two porphyrin molecules forms dihedral angle of  $53.3^{\circ}$  with Fe(1) – Fe(2) distance of 9.250 Å. This dimeric associate is formed due to the short intermolecular hydrogen bonds between two axial hydrosulfate anions having following bond lengths: S(1)-O(2) 1.555(2) Å, S(1)-O(3) 1.500(2) Å, S(1)-O(4) 1.574(2) Å, S(2)-O(7) 1.507(2) Å, S(2)-O(8) 1.550(2) Å, S(2)-O(6) 1.565(2) Å at the O(2)-O(7) 2.606(3), O(3)...O(8) 2.629(3) Å distances. The unusual lengths of the S-O bonds in coordinated HSO, anions with respect to the S-OH and S=O bonds of sulfuric acid, 1.574 and 1.442 Å, respectively, occurs due to the formation of very strong intermolecular hydrogen bonding. The only published structure of iron porphyrin with anions of sulfuric acid represents a binuclear complex  $(Fe^{III}TPP)_{2}(\mu-SO_{4})$ where two iron tetraphenylporphyrin units are connected via one SO<sub>4</sub> anion bridge with bond distances: Fe-O=1.894 Å, Fe-N=2.058-2.074 Å and S-O<sub>Fe</sub>=1.513 Å.<sup>[51]</sup>



**Figure 2.** Hydrogen bonding between two  $Fe(TMP)HSO_4$  molecules forming the supromolecular complex 1.

Additional hydrogen bonding with two molecules of sulfuric acid results in the supramolecular structure containing four Fe(TMP) cations, four HSO<sub>4</sub> anions and two  $H_2SO_4$  molecules situated within the interporphyrin voids with elongated S-O distances: S(3)-O(11)=1.5103(19) Å, S(3)-O(10)=1.541(2) Å, S(3)-O(12)=1.542(2) Å, S(3)-O(9)=1.543(2) Å (Figure 3). The tetramer structure shows following O-O distances between solvate sulfuric acid molecules and coordinated HSO, anions: O(10)... O(7A)=2.545, O(10)...O(9)=2.507, O(9)...O(11A)=2.590, O(11)...O(4)=2.790, O(11)...O(6A)=2.790, O(11)... O(4)=2.758,O(11)...O(9)=2.518, O(11)...O(9A)=2.590, O(12)...O(3)=2.582, O(12)...O(3)=2.582. As a consequence of the insertion of two molecules of sulfuric acid into cavity formed by four porphyrin molecules, the cluster structure with dihedral angle of 53.3° between adjacent porphyrin molecules  $Fe(1A)N_4/Fe(2A)N_4$  and parallel  $Fe(1A)N_4/Fe(1B)$  $N_4$  and Fe(2A) $N_4$ /Fe(2B) $N_4$  planes is formed (Figure 3).

In the crystal packing the Fe(1) porphyrin molecules are situated in the parallel head-to-head fashion with close contacts between methyl groups of mesityl substituents (Figure 4). Due to this interaction, the Fe(1)-Fe(1A) distance of 8.451 Å is significantly shorter than the distance between Fe(2)-Fe(2A) head-to-head fragments without contacts between methyl groups (12.749 Å). A disordered solvate molecule of toluene doesn't form any notable contacts with other molecules of the crystal packing.

This structure differs from the only related structure of iron porphyrin complex in the presence of sulfuric acid reported so far. Scheidt and co-workers prepared ( $\mu$ -sulfato)bis[*meso*-tetraphenylporphinato)iron(III)] complex with monodentate bridging sulfate ligand using 1 M H<sub>2</sub>SO<sub>4</sub> in benzene solution.<sup>[51]</sup> Consequently, using of the concentrated H<sub>2</sub>SO<sub>4</sub> appears to be important factor for the formation of cluster structure in our case. The crystals suitable for X-ray diffraction studies were



Figure 3. Supramolecular structure formed by two fragments of the complex 1.

obtained by layering a saturated chloroform solution of (FeTPP)<sub>2</sub>SO<sub>4</sub> on 50 % H<sub>2</sub>SO<sub>4</sub> and allowing *n*-pentane to diffuse into the two-layered mixture. The dihedral angle between the two porphyrin moieties was 24° and the axial Fe-O bond distance was 1.894 Å. In turn, intramolecular Fe-Fe separation was 6.049 Å. The crystal structures of multiporphyrin assemblies formed from Mn(III) complex of 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin and phosphoric acid via hydrogen bonding were also different.<sup>[52]</sup> Phosphate anions act as bridges between porphyrin moieties via hydrogen bonding with peripheral carboxyl groups of the Mn(III) porphyrin molecules rather than via coordination with manganese sites. This resulted in open square-grid-type layers with alternating porphyrin and phosphate components.<sup>[52]</sup> Thus, strong hydrogen bonding via network of molecules of sulfuric acid provides assembling of iron(III) tetramesitylporphyrin fragments into unprecendented cluster-like supramolecular structure.

### Conclusions

The simple synthetic procedure described here led to the formation of unusual cristalline material. Four iron tetramesitylporphyrin molecules have been assembled in the cluster *via* strong hydrogen bonding provided by four hydrosulfate axial ligands and two molecules of sulfuric acid. The interesting feature of the crystal structure is an absence of  $\pi$ -stacking of porphyrin moieties. It should be noted that organized porphyrin materials have usually



Figure 4. Views of the crystal packing in 1.

been prepared from elaborated porphyrin units bearing different functional groups at the periphery of the porphyrin ligand via covalent, coordination or electrostatic interactions. Supramolecular self-organization of simple porphyrin assemblies resulted mostly in linear structures involving axial coordination of the metal sites via bidentate ligands.[53] However, the structural parameters of such assemblies have been rarely published. Here, we used unfunctionalized tetramesitylporphyrin ligand which can be readily available. The system shows the important role of hydrogen bonding interactions occuring between the metal site and sulfate anions to stabilize this specific structure. Previously, the role of protonated water aggregates for assembling non-metalated porphyrin molecules to dimers has been reported on the basis IR and SEM data.<sup>[54,55]</sup> In this work, we have shown that hydrogen bonding can be successfully used for the preparation of much more elaborated organized

systems which were structurally characterized. Although a great number of supramolecular materials involving porphyrin complexes of different metals have been prepared and characterized,<sup>[2-4]</sup> iron porphyrin-based structures are still rare.<sup>[11]</sup> Taking into account redox properties of iron porphyrins and available axial position in each of four Fe(TMP) molecules forming the supramolecular cluster, this structure might be suitable for catalytic applications involving multielectronic processes.

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#### References

- de la Torre G., Claessens C.G., Torres T. Chem. Commun. 2007, 2000–2015.
- Drain C.M., Varotto A., Radivojevic I. Chem. Rev. 2009, 109, 1630–1658.
- 3. de la Torre G., Bottari G., Sekita M., Hausmann A., Guldi D.M., Torres T. *Chem. Soc. Rev.* **2013**, *42*, 8049–8105.
- Beletskaya I., Tyurin V.S., Tsivadze A.Y., Guilard R., Stem C. Chem. Rev. 2009, 109, 1659–1713.
- 5. Spitler E.L., Dichtel W.R. Nat. Chem. 2010, 2, 672-677.
- Bezzu G., Helliwell M., Warren J.E., Allan D.R., McKeown N.B. Science 2010, 327, 1627–1630.
- Gao W-Y., Chrzanowski M., Ma S. Chem. Soc. Rev. 2014, 43, 5841–5866.
- Fateeva A., Clarisse J., Pilet G., Grenèche J-M., Nouar F., Abeykoon B.K., Guegan F., Goutaudier C., Luneau D., Warren J.E., Rosseinsky M.J., Devic T. *Cryst. Growth Des.* 2015, 15, 1819–1826.
- 9. Sorokin A.B. Chem. Rev. 2013, 113, 8152-8191.
- Mackintosh H.J., Budd P.M., McKeown N.B. J. Mater. Chem. 2008, 18, 573–578.
- Abeykoon B., Devic T., Grenèche J-M., Fateeva A., Sorokin A.B. Chem. Commun. 2018, 54, 10308–10311.
- 12. Durot S., Taesh J., Heitz V. Chem. Rev. 2014, 114, 8542-8578.
- 13. Bottari G., de la Torre G., Torres T. *Acc. Chem. Res.* 2015, *48*, 900–910.
- Bottari G., de la Torre G., Guldi D.M., Torres T. Chem. Rev. 2010, 110, 6768–6816.
- 15. Fuhrhop J-H. Langmuir 2014, 30, 1–12.
- 16. D'Souza F., Ito O. Chem. Commun. 2009, 4913-4928.
- Ermakova E.V., Enakieva Yu.Yu., Zvyagina A.I., Gorbunova Yu.G., Kalinina M.A., Arslanov V.V. *Macroheterocycles* 2016, 9, 378–386.
- Ermakova E.V., Enakieva Yu.Yu., Meshkov I.N., Baranchikov A.E., Zvyagina A.I., Gorbunova Yu.G., Tsivadze A.Yu., Kalinina M.A., Arslanov V.V. *Macroheterocycles* 2017, 10, 496–504.
- Samaroo D., Soll C.E., Todaro L.J., Drain C.M. Org. Lett. 2006, 8, 4985–4988.
- Uvarova M.A., Sinelshchikova A.A., Golubnichaya M.A., Nefedov S.E., Enakieva Y.Y., Gorbunova Y.G., Tsivadze A.Y., Stern C., Bessmertnykh-Lemeune A., Guilard R. Cryst. Growth Des. 2014, 14, 5976–5984.
- 21. Ragoussi M-E., Torres T. Chem. Asian J. 2014, 9, 2676–2707.
- Enakieva Y.Y., Bessmertnych A.G., Gorbunova Y.G., Stern C., Rousselin Y., Tsivadze A.Y., Guilard R. Org. Lett. 2009, 11, 3842–3845.
- Vinogradova E.V., Enakieva Y.Y., Nefedov S.E., Birin K.P., Tsivadze A.Y., Gorbunova Y.G., Bessmertnykh-Lemeune A.G., Stern C., Guilard R. *Chem. Eur. J.* 2012, *118*, 15092– 15104.
- Sinelshchikova A.A., Nefedov S.E., Enakieva Y.Y., Gorbunova Y.G., Tsivadze A.Y., Kadish K.M., Chen P., Bessmertnykh-Lemeune A., Stern C., Guilard R. *Inorg. Chem.* 2013, 52, 999–1008.
- Zubatyuk R.I., Sinelshchikova A.A., Enakieva Y.Y., Gorbunova Y.G., Tsivadze A.Y., Nefedov S.E., Bessmertnykh-Lemeune A., Guilard R., Shishkin O.V. *CrystEngComm* 2014, *16*, 10428–10438.

- 26. Drain C.M., Russell K.C., Lehn J-M. Chem. Commun. 1996, 337–338.
- Hill J.P., Wakayama Y., Akada M., Ariga K. J. Phys. Chem. C 2007, 111, 16174–16180.
- 28. Sheinin V.B., Kulikova O.M., Aleksandriiskii V.V., Koifman O.I. *Macroheterocycles* **2016**, *9*, 353–360.
- 29. Ortiz de Montellano P.R. Chem. Rev. 2010, 110, 932-948.
- 30. Costas M. Coord. Chem. Rev. 2011, 255, 2912-2932.
- Che C-M., Kar-Yan L., Zhou C.Y., Huang J-S. Chem. Soc. Rev. 2011, 40, 1950–1975.
- Kudrik E.V., Afanasiev P., Alvarez L.X., Blondin G., Clémancey M., Latour J.-M., Bouchu D., Albrieux F., Nefedov S.E., Sorokin A.B. *Nat. Chem.* 2012, *4*, 1024–1029.
- Colomban C., Kudrik E.V., Afanasiev P., Sorokin A.B. J. Am. Chem. Soc. 2014, 136, 11321–11330.
- İşci Ü., Faponle A.S., Afanasiev P., Albrieux F., Briois V., Ahsen V., Dumoulin F., Sorokin A.B., de Visser S.P. *Chem. Sci.* 2015, 6, 5063–5075.
- Alvarez L.X., Kudrik E.V., Sorokin A.B. Chem. Eur. J. 2011, 17, 9298–9301.
- Afanasiev P., Sorokin A.B. Acc. Chem. Res. 2016, 49, 583–593.
- 37. Kudrik E.V., Sorokin A.B. *Macroheterocycles* **2011**, *4*, 154–160.
- Kudrik E.V., Sorokin A.B. J. Mol. Catal. A: Chem. 2017, 426, 499–505.
- Kudrik E.V., Afanasiev P., Bouchu D., Millet J.M.M., Sorokin A.B. J. Porphyrins Phthalocyanines 2008, 12, 1078–1089.
- 40. Safo M.K., Nesset M.J.M., Walker A., Debrunner P.G., Scheidt W.R. J. Am. Chem. Soc. **1997**, 119, 9438–9448.
- Hu C., Noll B.C., Schulz C.E., Scheidt W.R. *Inorg. Chem.* 2005, 44, 4346–4358.
- 42. Meininger D.J., Caranto J.D., Arman H.D., Tonzetich Z.J. Inorg. Chem. 2013, 52, 12468–12476.
- Munro O.Q., Serth-Guzzo J.A., Turowska-Tyrk I., Mohanrao K., Shokhireva T.K., Walker F.A., Debrunner P.G., Scheidt W.R. J. Am. Chem. Soc. 1999, 121, 11144–11155.
- Li J., Noll B.C., Schulz C.E., Scheidt W.R. Inorg. Chem. 2007, 46, 2286–2298.
- Wagner R.W., Lawrence D.S., Lindsey J.S. *Tetrahedron Lett.* 1987, 28, 3069–3070.
- 46. Lindsey J.S., Wagner R.W. J. Org. Chem. 1989, 54, 828-836.
- Adler A.D., Longo F.R., Kampus F., Kim J. J. Inorg. Nucl. Chem. 1970, 32, 2443–2445.
- Sheldrick G., Bruker AXS Inc., Madison, WI-53719, USA. 1997.
- Bruker SAINT: Area-Detector Integration Sofware, 2012, Madison, Wisconsin, USA, 2012.
- 50. SHELX-97, Program for the Refinement of Crystal Structures, University of Göttingen: Göttingen, Germany, **1997**.
- Scheidt W.R., Lee Y.J., Bartzcak T., Hatano K. *Inorg. Chem.* 1984, 23, 2552–2554.
- 52. George S., Goldberg I. Cryst. Growth Des. 2006, 6, 755-762.
- Khodov I.A., Nikiforov M.Yu., Alper G.A., Mamardashvili G.M., Mamardashvili N.Zh., Koifman O.I. J. Mol. Struct. 2015, 1081, 426–430.
- Udal'tsov A.V., Bolshakova A.V., Vos J.G. J. Mol. Struct. 2015, 1080, 14–23.
- Udal'tsov A.V., Bolshakova A.V., Vos J.G. J. Mol. Struct. 2014, 1065-1066, 170–178.

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