Макрогетероциклы
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DOI: 10.6060/mhc150560s

1,2,5–Telluradiazoloporphyrazines. 2.[⊗] Direct Exchange of Te by Se and Conversion of 1,2,5–Telluradiazole Ring to Pyrazine Fragment

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Dedicated to Professor Andrej Fedorovich Mironov on the Occasion of his 80th Birthday

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Treatment of Mg^{II} complex of tert-butyl substituted 1,2,5-telluradiazolo[3,4-b]tribenzo[g,l,q]porphyrazine with SeO_2 in dichloromethane leads to direct substitution of Te by Se, while the reaction with diaminomaleonitrile in ethanol affords (5,6-dicyanopyrazino)[2,3-b]tribenzo[g,l,q]porphyrazines. The obtained results demonstrate that 1,2,5-telluradiazoloporphyrazines can be used as synthetic analogues of vicinal diamino-, diimino- and dioxoporphyrazines.

Keywords: Heterocyclic phthalocyanine analogues, fused porphyrazines, 1,2,5-telluradiazole, 1,2,5-selenadiazole, pyrazine, detelluration.

1,2,5–Теллурадиазолопорфиразины. 2.[⊗] Прямое замещение Te на Se и превращение 1,2,5–теллурадиазольного фрагмента в пиразиновый

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Посвящается профессору Андрею Фёдоровичу Миронову по случаю его 80–летнего юбилея

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При взаимодействии Mg^{II} комплекса трет-бутил-замещённого 1,2,5-теллурадиазоло[3,4-b]трибензо[g,l,q]-порфиразина с SeO_2 в дихлорметане наблюдается замещение атома теллура на селен, а реакция с диаминомалединитрилом в этаноле приводит к (5,6-дицианопиразино)[2,3-b]трибензо[g,l,q]порфиразинам. Полученные результаты показывают, что 1,2,5-теллурадиазолопорфиразины могут использоваться в качестве синтетических аналогов вицинальных диамино-, диимино- и диоксопорфиразинов.

Ключевые слова: Гетероциклические аналоги фталоцианина, порфиразины, 1,2,5-теллурадиазол, 1,2,5-селенадиазол, пиразин, детеллурирование.

Porphyrazines with annulated 1,2,5-thiadiazole and 1,2,5-selenadiazole rings have been actively studied over last two decades[1] and recently we have also reported first porphyrazines with fused 1,2,5-telluradiazole ring(s).[2,3] 1,2,5-Chalcogenodiazoles are known as strong electron-acceptor π-heterocycles[4] and their fusion to porphyrazine core leads to highly electron-deficient macroheterocyclic compounds[1,2a] which can be considered as perspective functional materials for design of organic electronic devices. Indeed, tetra(1,2,5-thiadiazolo)porphyrazine and its metal complexes were used as *n*-type organic semiconductors in the prototypes of field-effect transistors and photovoltaic cells.[5,6] The presence of 1,2,5-chalcogenodiazole

[⊗] Part 1 – see Ref. [2].

ring opens interesting synthetic possibilities for peripheral modification of porphyrazine macrocycle. Thus, it was demonstrated that 1,2,5-selenadiazoloporphyrazines can be considered as convenient precursors for unstable porphyrazines with vicinal amino groups in pyrrole ring(s).[7,8] They can be prepared *in situ* by reductive ring-opening of fused 1,2,5-selenadiazole fragment with H_2S in pyridine and used directly for further functionalization, *e.g.* for preparation of porphyrazines with attached formamide groups,[9] Schiff-base moieties,[10] fused pyrazine ring(s).[7,11] Oxidative scission of pyrrole ring in porphyrazinediamine occurring in the presence of oxygen allows the deeper transformation of the whole macrocyclic framework affording pyraziniporphyrazine, porphyrazinoid containing pyrazine ring instead of one of four pyrrole rings.[12] The Se atom in fused 1,2,5-selenadiazoles can be also directly exchanged by S when treated in the presence of pyridine with H_2S in $CHCl_3$[13] or with S_2Cl_2 in CH_3CN.[14] Direct exchange of O or S atoms by Se upon treatment of fused 1,2,5-oxa(thia)diazoles by SeO_2 in DMF or CH_3CN is also possible.[15] One can expect that fused 1,2,5-telluradiazole ring should be more reactive, but its detelluration reactions are still poorly studied.

We have studied reactions of Mg^{II} complex of *tert*-butyl substituted 1,2,5-telluradiazolo[3,4-*b*]tribenzo[*g,l,q*]-porphyrazine (**1**) with selenium(IV) dioxide and with diaminomaleonitrile (Scheme 1) and found that 1,2,5-telluradiazoloporphyrazines can be used as synthetic analogues of vicinal diamino-, diimino- and dioxoporphyrazines.

The Mg^{II} complex of *tert*-butyl substituted 1,2,5-telluradiazolo[3,4-*b*]tribenzo[*g,l,q*]porphyrazine (**1**)[2] (5 mg, 0.006 mmol) and SeO_2 (1 mg, 0.01 mmol) were dissolved in CH_2Cl_2 (5 ml) in the presence of few drops of pyridine and refluxed for 30 min. The reaction process was monitored spectrophotometrically by disappearance of the double Q-band of the Te-containing Mg^{II} complex **1** (λ_{max}= 677 and 722 nm) and appearance of the new maxima at 672 and 709 nm (Figure 1).

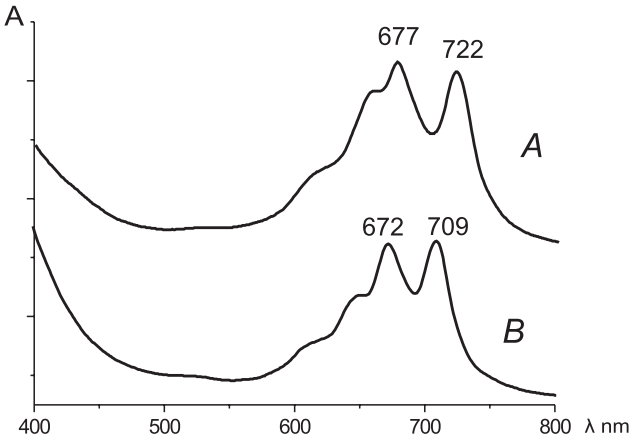
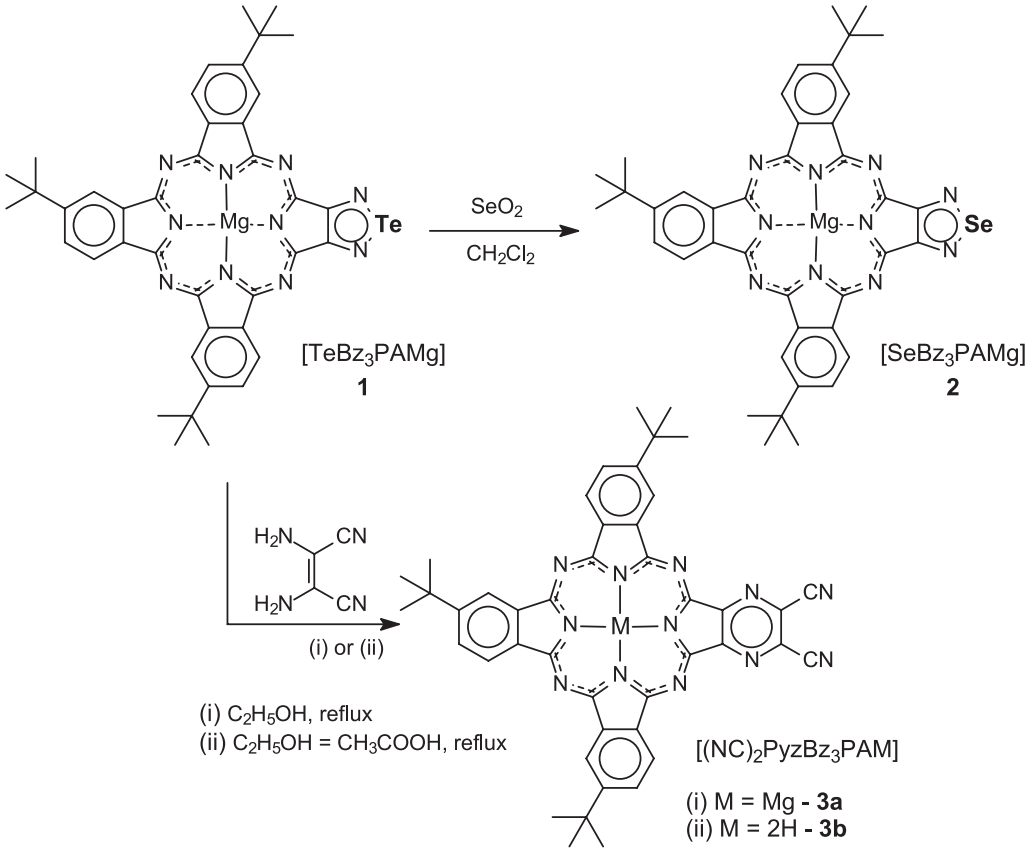


Figure 1. UV-VIS spectra of Mg^{II} complex **1** (*A*) in CH_2Cl_2 and its change after heating with SeO_2 leading to formation of the Se-analogue **2** (*B*).

After isolation the product of the reaction was characterized also by mass-spectrometry and by IR spectroscopy, which indicate that treatment of Mg^{II} porphyrazine **1** with SeO_2 leads to direct substitution of Te by Se and formation of the Se-containing Mg^{II} porphyrazine **2**.§ The MALDI-TOF



Scheme 1.

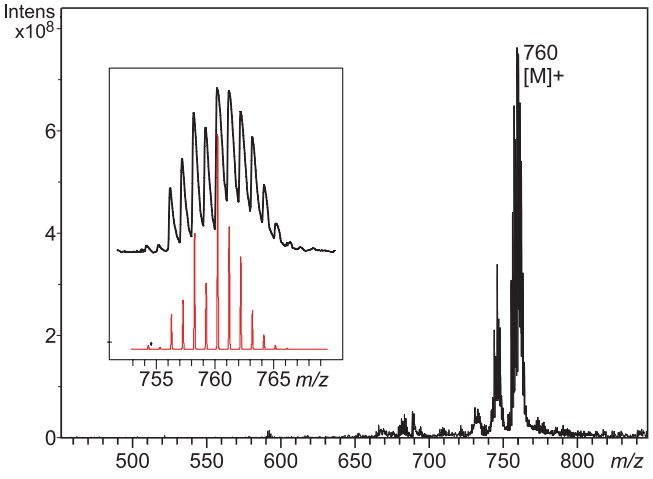


Figure 2. MALDI-TOF mass-spectrum of the reaction product obtained upon heating of Mg^{II} complex **1** with SeO_2 in CH_2Cl_2.

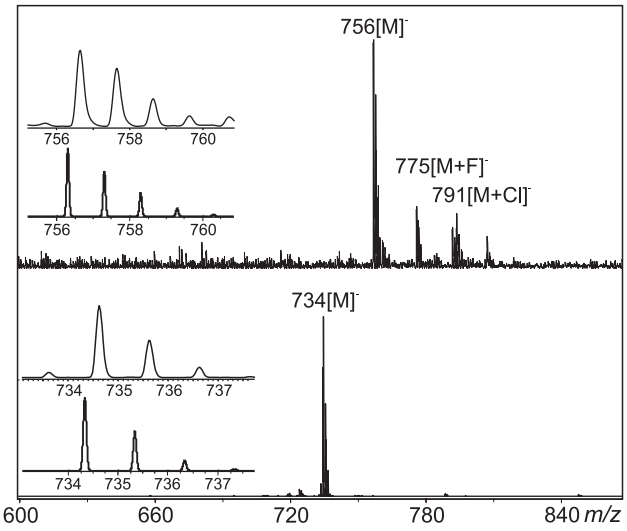


Figure 3. MALDI-TOF mass-spectrum of pyrazine fused porphyrazines **2a** (top) and **2b** (bottom) obtained upon interaction of Mg^{II} complex **1** with diaminomaleodinitrile.

mass-spectrum of the obtained product (Figure 2) contains the intense peak of the molecular ion with *m/z* = 760 and isotopic distribution pattern characteristic for the Se-analogue **2** (calc. for $C_{40}H_{36}MgN_{10}Se$ *m/z* = 760.2).

The UV-VIS and IR spectra of the reaction product correspond to the spectra of the Mg^{II} complex **2** obtained alternatively by co-cyclotetramerization of 1,2,5-selenadiazolo-3,4-dicarbonitrile and 4-*tert*-butylphthalodinitrile.[16]§ The maximum of the long-wave component of the Q-band for the Se-containing porphyrazine **2** (709 nm) has an intermediate position between the S-analogue (682 nm[17]) and Te-analogue **1** (722 nm). This is indicative that the stabilization effect of the 1,2,5-chalcogenodiazole fragment on the highest occupied molecular orbital (HOMO) is strengthened along with the increase of electronegativity in the series Te < Se < S. Vibration bands appearing in the IR spectrum of **2** at 1235, 696 cm^{-1} can be assigned to the stretching (CN/CC and SeN) and at 432 cm^{-1} to the torsion vibrations of the 1,2,5-selenadiazole ring.[18] Since 1,2,5-selenadiazoles are usually obtained by treatment of *vic*-diamines with SeO_2,[4] the observed formation of the Se-containing porphyzine **2** by reaction between SeO_2 and the Te-analogue **1**, allows to consider the latter as protected (hidden) form of porphyrazine with vicinal diamine moiety.

On the other hand, the easy detelluration of 1,2,5-telluradiazole ring indicates its structural similarity to diimines. Indeed, according to DFT calculations of Mg^{II} complexes of tetra(1,2,5-chalcogenodiazolo)porphyrazines the double bond character of the CN bonds adjacent to chalcogen atom is increased in the order S(1.507) < Se(1.610) < Te(1.678), while the NX bond order is decreased S(1.211) > Se(1.107) > Te(1.008).[19] Reaction between diimines (or α-diketones) and the vicinal diamines can be directly used for the synthesis of pyrazine ring, *e.g.* reaction with diaminomaleodinitrile provides pyrazine-2,3-dicarbonitrile – precursors for pyrazinoporphyrazines.[20] We have conducted the reaction between Te-containing Mg^{II} porphyrazine **1** (8 mg, 0.01 mmol) and diaminomaleodinitrile (4 mg, 0.04 mmol) in anhydrous ethanol (5 ml) upon reflux (4 h) and observed that it leads to detelluration and formation of the Mg^{II} complex of 2,3-dicyanopyrazino[2,3-*b*]tribenzo[*g,l,q*]porphyrazine **3a**.¶

When the reaction was accomplished in the mixture of ethanol and acetic acid (3:1) the corresponding metal free species **3b**# was obtained.

In the negative region MALDI-TOF mass-spectra of **3a** the molecular ion peak is observed at *m/z*=756 (100%, $[M]^-$) which is followed by peaks at 775 Da (28%) and 791 Da (25%) corresponding to the stable anions $[M+F]^-$ and $[M+Cl]^-$ formed by axial coordination to central Mg atom of fluoride and chloride, respectively. In the case of metal free porphyrazine **3b** the molecular ion peak $[M]^-$ is observed at *m/z*=734 Da.

UV-VIS spectra of the pyrazine fused porphyrazines **3a,b** (Figure 4) are typical for low-symmetry tribenzoporphyrazines with one annulated heterocycle[16,17] and contain a split *Q*-band with maxima at 665 and 705 nm for **3a** and 688 and 725 nm for **3b**. The bathochromic shift of the long-wave component of the *Q*-band in **3b** as compared to tribenzoporphyrazines with fused 1,2,5-thiadiazole and 1,2,5-selenadiazole rings[16,17] indicates the stronger polar-

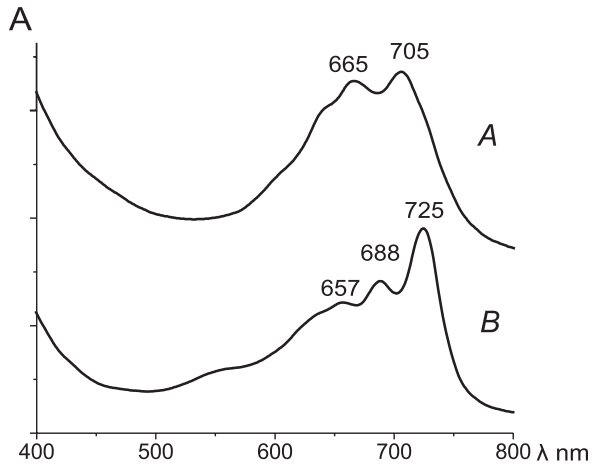


Figure 4. UV-VIS spectra of Mg^{II} complex **3a** (*A*) and corresponding metal free porphyrazine **3b** (*B*) in CH_2Cl_2 containing 1 % of MeOH.

ization of the porphyrazine π-chromophore by dicyano substituted pyrazine fragment.

So far the low-symmetry porphyrazines bearing one fused dicyanopyrazine fragment were only prepared starting from Cu^{II} and Ni^{II} complexes of 2,3-dihydroxy-7,8,12,13,17,18-hexapropylporphyrazine by trapping their unstable oxidation products – vicinal dioxoporphyrazines with diaminomaleonitrile.[21] Our approach to dicyanopyrazinoporphyrazines by one stage modification of 1,2,5-telluradiazoloporphyrazines has an advantage over their preparation from vicinal dihydroxyporphyrazines, which can be obtained only in multistage procedure.[21]

In conclusion, we have demonstrated that 1,2,5-telluradiazoloporphyrazines can be considered as protected form of porphyrazines with vicinal amino, imino or oxo groups. Porphyrazines **3a,b** containing fused dicyanopyrazine fragment might be quite interesting synthetic precursors for binuclear bisporphyrazines joined by the pyrazine bridge.

Acknowledgements. This work was supported by Russian Foundation of Basic Research (grant 13-03-0902a).

Notes and References

§ Mg^{II} porphyrazine **2**. *Method A*. From **1** and SeO_2. Yield 80 %. *Method B*. From 1,2,5-selenadiazolo-3,4-dicarbonitrile and 4-*tert*-butylphthalodinitrile.[16] Yield 3 %. R_f=0.65 (CH_2Cl_2+5%MeOH). MALDI-TOF MS *m/z* = 760 $[M]^+$ (calcd for $C_{40}H_{36}MgN_{10}Se$ - 760.21). UV-VIS (CH_2Cl_2) λ_{max} nm (lgε): 353 (4.85), 520(3.58), 612 (4.03), 651 (4.33), 671 (4.65), 707 (4.66). IR (KBr) ν cm^{-1}: 2957s, 2802m, 2866m, 1613m, 1487s, 1393m, 1326m, 1256m, 1235w, 1158m, 1084s, 1046m, 832w, 752m, 696m, 432w. Anal. Found: C, 61.24; H, 4.98; N, 18.30%. Calcd. for $C_{40}H_{36}MgN_{10}Se{\cdot}H_2O$ (778.22) C, 61.68; H, 4.92; N, 17.99%.

¶ Mg^{II} porphyrazine **3a**. The reaction mixture was filtrated and the residue after evaporation of the solvent was chromatographed on silica (eluent – CH_2Cl_2 + 5% MeOH). Yield 40 %. R_f=0.5 (CH_2Cl_2 +5%MeOH). MALDI-TOF MS (negative) *m/z* = 756 $[M]^-$ (100%, calcd for $C_{44}H_{36}MgN_{12}$ – 756.30), 775 $[M+F]^-$ (28%), 791 $[M+Cl]^-$ (25%).

Porphyrazine **3b**. The residue after evaporation of the solvent was dissolved in acetone, passed through alumina and then chromatographed on silica (eluent – CH_2Cl_2+ 2% MeOH). Yield 30 %. R_f=0.75 (CH_2Cl_2+1%MeOH). MALDI-TOF MS (negative) *m/z* = 734 $[M]^-$ (100%, calcd for $C_{44}H_{38}N_{12}$ – 734.33).

1. Donzello M.P., Ercolani C., Stuzhin P.A. *Coord. Chem. Rev.* **2006**, *250*, 1530–1561.
2. Stuzhin P.A., Mikhailov M.S., Yurina E.S., Bazanov M.I., Koifman O.I., Pakhomov G.L., Travkin V.V., Sinelshchikova A.A. *Chem. Comm.* **2012**, 10135–10137.
3. Svec J., Zimcik P., Novakova L., Rakitin O.A., Amelichev S., Stuzhin P.A., Novakova V. *Eur. J. Org. Chem*. **2015**, 596–604.
4. Lonchakov A.V., Rakitin O.A., Gritsan N.P., Zibarev A.V. *Molecules* **2013**, *18*, 9850–9900.
5. (a) Miyoshi Y., Kubo M., Fujinawa T., Suzuki Y., Yoshikawa H., Awaga K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5532–5536; (b) Fujimoto T., Miyoshi Y., Matsushita M.M., Awaga K. *Chem. Commun*. **2011**, 5837–5839; (c) Miyoshi Y., Fujimoto T., Yoshikawa H., Matsushita M.M., Awaga K., Yamada T., Ito H. *Organic Electronics* **2011**, *12*, 239–243; (d) Miyoshi Y., Takahashi K., Fujimoto T., Yoshikawa H., Matsushita M.M., Ouchi Y., Kepenekian M., Robert V., Donzello M.P., Ercolani C., Awaga K. *Inorg. Chem*. **2012**, *51*, 456–462.
6. (a) Stuzhin P.A., Mikhailov M.S., Travkin V.V., Gudkov E.Y., Pakhomov G.L. *Macroheterocycles* **2012**, *5*, 162-165 [DOI: 10.6060/mhc2012.120573p]; (b) Stuzhin P.A., Mikhailov M.S., Travkin V.V., Pakhomov G.L. In: *Recent Developments in Coordination, Bioinorganic, and Applied Inorganic Chemistry,* Vol. 11 [Melnik M., Segl'a P., Tatarko M., Eds.], Bratislava, Press of Slovak University of Technology, **2013**. 318–323. [ISBN 978-80-227-3918-4; ISSN 1335-308X. DOI: 10.13140/2.1.2341.3761]
7. Bauer E., Ercolani C., Galli P., Popkova I., Stuzhin P.A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 371–379.
8. Kozlov A.V., Stuzhin P.A. *Russ. J. Org. Chem*. **2013**, *49*, 913–921.
9. Ul-Haq A., Stuzhin P.A. *Macroheterocycles* **2008**, *1*, 82–84 [https://macroheterocycles.isuct.ru/ru/system/files/08MHC_82-84.pdf].
10. Zhao M., Stern C., Barrett A.G.M., Hoffman B.M. *Angew. Chem*., *Int. Ed*. **2003**, *42*, 462–465.
11. (a) Onay H., Esat B., Öztürk R. *Polyhedron* **2010**, *29*, 1314-1316; (b) Baum S.M., Trabanco A.A., Montalban A.G., Micallef A.S., Zhong C., Meunier H.G., Suhling K., Phillips D., White A.J.P., Williams D.J., Barrett A.G.M., Hoffman B.M. *J. Org. Chem.* **2003**, *68*, 1665–1670.
12. Kozlov A.V., Stuzhin P.A. *Macroheterocycles* **2014**, *7*, 170–173.
13. Ul-Haq A., Donzello M.P., Stuzhin P.A. *Mendeleev Commun.* **2007**, *17*, 337–339.
14. Konstantinova L.S., Knyazeva E.A., Rakitin O.A. *Molecules* **2015**, *20*, 14522–14532.
15. Konstantinova L.S., Knyazeva E.A., Nefyodov A.A., Camacho P.S., Ashbrook S.E.M., Woollins J. D., Zibarev A.V., Rakitin O.A. *Tetrahedron Letters* **2015**, *56*, 1107–1110.
16. Solovyov K.N., Stuzhin P.A., Kuzmitsky V.A., Volkovich D.I., Knyukshto V.N., Borisevich E.A., Ul-Haque A. *Macroheterocycles* **2010**, *3*, 51–62. [http://macroheterocycles.isuct.ru/sites/default/files/MHC2010_t03n01_51-62.pdf]
17. Gaberkorn A.A., Donzello M.-P., Stuzhin P.A. *Russ. J. Org. Chem*. **2006**, *42*, 929–935 (Engl. transl.) [*Zh.Org. Khim*. **2006**, *42*, 946–952 (in Russ.)].
18. El-Azhary A.A. *Acta Chem. Scand*. **1995**, *49*, 11–19.
19. Zhabanov Yu.A., Tverdova N.V., Stuzhin P.A., Girichev G.V. Theoretical study of the molecular structure of magnesium tetrakis(chalocogenadiazolo)porphyrazines. In: *Proceedings of VI Russian Youth School Conference "Quantum-Chemical Calculations: Structure and Reactivity of Organic and Inorganic Molecules*. Ivanovo, ISUCT: **2013**. pp. 410–413 (in Russ.) [http://www.isuct.ru/qc6/Man_qc6.pdf].
20. Donzello M.P., Ercolani C., Novakova V., Zimcik P., Stuzhin P.A. *Coord. Chem. Rev*. **2015**, DOI: 10.1016/j.ccr.2015.09.006.
21. Bellec N., Montalban A.G., Williams D.B.G., Cook A.S., Anderson M.E., Feng X.D., Barrett A.G.M., Hoffman B.M. *J. Org. Chem*. **2000**, *65*, 1774–1779.

Received 05.05.2015
Accepted 18.06.2015