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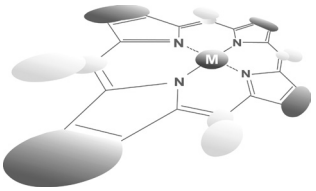

Synthesis and spectral study of tetra(2,3-thianaphtheno)-porphyrazine, its tetra-*tert*-butyl derivative and their Mg(II), Al(III), Ga(III) and In(III) complexes

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ABSTRACT: Starting from easily available thiophenols (PhSH (**1a**), 4-*tert*-butyl-PhSH (**1b**)) and oxalylchloride we have prepared 2,3-thianaphtenequinones **2a,b** which were then successively converted to thianaphthene-2,3-dicarboxylic acids **4a,b** their imides **10a**,**b**, diamides **9a,b** and finally to thianaphthene-2,3-dicarbonitriles **11a**,**b** — the key precursors for the series of novel porphyrazines bearing four 2,3-annulated thianaphthene moieties. The free-bases **12a**,**b** were obtained by cyclotetramerization of the dinitrile **11a**,**b** in the presence of lithium in *n*-pentanol, while the reaction with magnesium(II) butoxide in *n*-butanol leads to the Mg(II) complex **13a**. Complexes with Al(III) (**14a**,**b**), Ga(III) (**14a**,**b**) and In(III) (**14a**,**b**) were obtained by the template cyclotetramerization of the dinitriles **11a**,**b** in a melt with the corresponding (hydroxy)acetates. Tetra(2,3-thianaphtheno)porphyrazine **12a** and its metal complexes **13a**–**15a** are only sparingly soluble in common organic solvents, the solubility is enhanced for their *tert*-butyl substituted derivatives **12b**, **14b**–**16b**. The study of the electronic absorbtion spectra has revealed that the extension of the porphyrazine π-chromophore by fusion of four thianaphthene fragments due to the angular type of their annulation (similar to that found in 1,2-naphthalocyanines) and negative inductive effect of the sulfur atoms has an effect on its spectral properties which is less than in the case of the isoelectronic naphthalene rings fusion and is comparable with the influence of four benzene rings in phthalocyanines.

KEYWORDS: 2,3-thianaphthene derivatives, porphyrazines, tetra(2,3-thianaphtheno)porphyrazines, magnesium(II), aluminium(III), gallium(III), indium(III), electronic absorbtion spectra.

INTRODUCTION

Initially observed as unexpected byproducts [1, 2], now phthalocyanines, [MPc], are produced in million tons per year [3]. They are one of the major types of tetra-pyrrole derivatives showing a wide range of practical applications in various high technology fields such as nonlinear optics, photosensitizers, gas sensors, catalysis, liquid crystals, optical data storage, electrodes in fuel cell, photoelectric conversion materials and others [4–8]. A great number of promising applications of phthalocyanines arise from the presence of the unique 18π-electron conjugated aromatic porphyrazine (PA) core which determines their remarkable optic and coordination properties and endows them with high thermal and chemical stability. Useful properties of phthalocyanine materials can be tuned by structural modification of the periphery of the macrocyclic ligand. Along with introduction of different appendages in benzene rings of phthalocyanine, the growing attention is now given to heterocyclic phthalocyanine analogues containing aromatic heterocycles instead of the benzene

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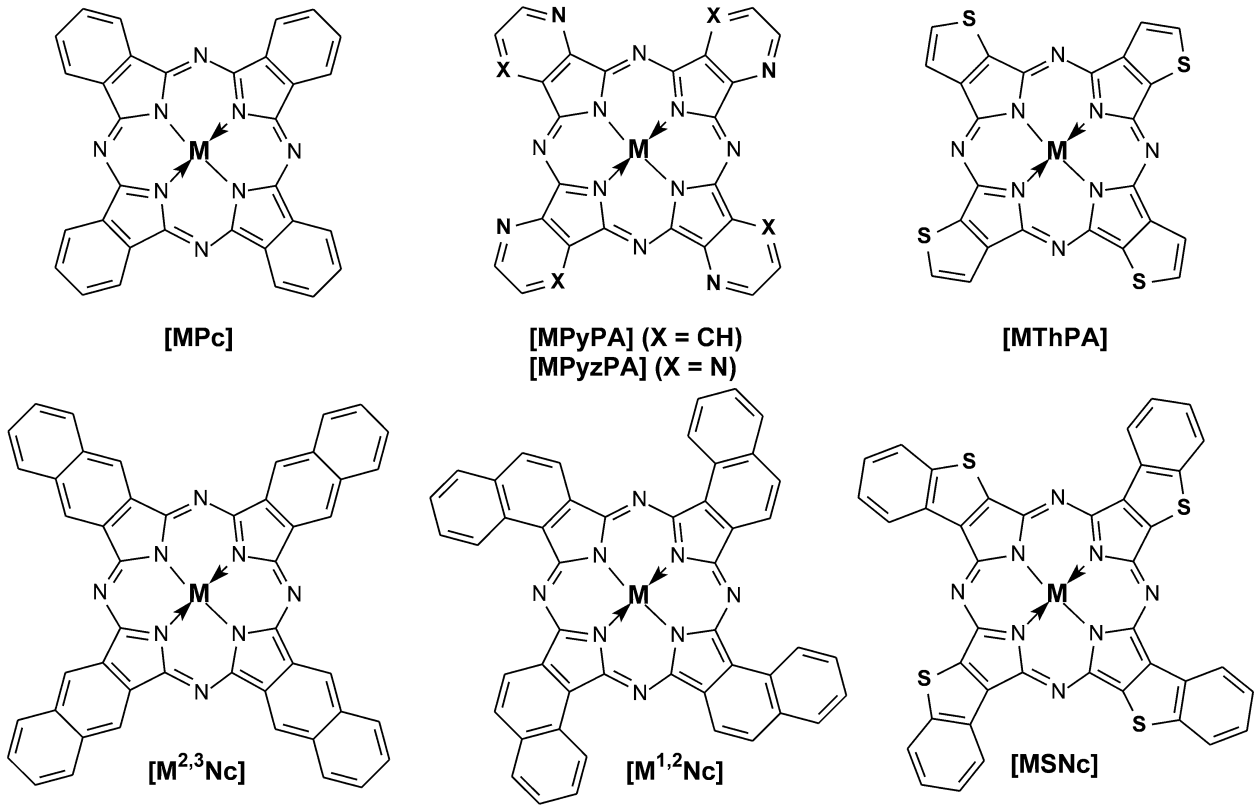


Chart 1. Molecular structures of metal phthalocyanines and its heterocyclic and π-extended analogues

rings [9, 10]. Azaanalogues of phthalocyanine containing 6-membered *N*-heterocycle (pyridine or pyrazine) fused to the porphyrazine core instead of benzene rings (*i.e.* tetrapyrido- and tetrapyrazinoporphyrazines, [MPyPA] and [MPyzPA]) and their benzohomologues containing quinoline and quinoxaline fragments are mostly well studied [9–13]. In the recent decade considerable advances have been also achieved in the synthesis and study of the chalcogen analogues of pyrazinoporphyrazines containing S or Se atom instead of the pyrazine C=C bond, *i.e.* porphyrazines with annulated 1,2,5-thiadiazole or 1,2,5-selenadiazole rings [14]. Thiaanalogues of phthalocyanine — porphyrazines with fused thiophene rings, [MThPA], which were first reported by Linstead in 1937 [15], since then have been only scarcerely studied [16–18]. Linstead and coworkers [15] have also observed formation of thiaanalogues of naphthalocyanine — upon melting of 2,3-thianaphthenedicarbonitrile with metallic reagents (CuCl, Cu, $AlCl_3$, Mg) green products were obtained. However, these species were not characterized and, to the best of our knowledge, since then no reports appeared on tetra(2,3-thianaphtheno) porphyrazine complexes [MSNc]. In our opinion, such porphyrazine macrocycles containing "mild" peripheral S-atoms with accessable *d*-sublevel might exhibit interesting and unusual properties and deserve more detailed investigation.

In this work, we report on the improved preparation of the precursors for tetra(2,3-thionaphtheno)porphyrazines and on the synthesis and characterization of Mg(II), Al(III), Ga(III) and In(III) complexes. The latter might be especially interesting for investigation of their nonlinear optical properties, since In(III) complexes of phthalocyanine and its analogues (porphyrazines, naphthalocyanines) often exhibit enhanced performance as optical limiting materials [19–22].

EXPERIMENTAL

General

All chemicals were commercially available reagent grade species (Aldrich, Merck, Reakhim, Vecton, Technolog) and used without further purification otherwise specified. Solvents such as *n*-butanol, DMF and pyridine were distilled before use. Infrared spectra were measured on IR-spectrometer AVATAR 360 FT-IR in KBr pellets, UV-vis spectra were recorded with Perkin Elmer spectrometer Lambda 20, elemental analyses were performed on a CHN analyser Flash EA 1112. Mass-spectrometric measurents were carried out by mass-spectrometer Saturn 2000R (Varian Chrompack) for porphyrazine precursors and MALDI-TOF Bruker Ultraflex spectrometer for porphyrazines. The melting points for porphyrazine precursors were determined using Buchi Melting Point B-540 apparatus.

Preparation of precursors

4-*tert*-butylbenzenesulfonyl chloride. It was synthesized as described elsewhere [23]. Yield *ca*. 80%, mp 78–80 °C (lit. data 79–80 °C [24]). Anal. calcd. for $C_{10}H_{13}SO_2Cl$ (%): C, 51.61; H, 5.63; S, 13.78; O, 13.76. Found (%): C, 49.94; H, 6.10; S, 13.58; O, 13.95. IR (KBr): ν, cm^{-1} 3070w and 3030w ($\nu(CH)_{Ar}$), 2970s and 2872m ($\nu(CH)_{tBu}$), 1926w, 1793w, 1664w, 1589s, 1477m, 1462m, 1402s, 1373vs ($\nu(SO_2Cl)$), 1298m, 1269m, 1236m, 1201s, 1176vs ($\nu(SO_2Cl)$), 1111s, 1080s, 1012m, 835m, 752m, 615s, 575s, 534s. MS: *m/z* 217 (100%, $[M]^+$). ^1H NMR ($CDCl_3$): δ, ppm 8.00 (2H, m, Ar*H*), 7.60 (2H, m, Ar*H*), 1.36 (9H, s, *t*Bu).

4-*tert*-butylbenzenethiol (1b). Zinc dust (22 g, 0.336 mol) was added to a mixture of chopped ice (125 g) and concentrated sulfuric acid (35 mL) under intensive stirring in a three-neck flask. Then 4-*tert*-butylbenzenesulfonyl chloride (15 g, 0.06 mol) was immersed in small portions. Reaction mixture was stirred for 3 h and then refluxed 2 h on the water bath. The resulting suspension was cooled and the product was extracted in chloroform or ether. Extract was purged with water to neutrality, dried with $CaCl_2$ and after evaporation of the solvent 4-*tert*-butylbenzenethiol was obtained as yellow oil. Yield 9.1 g (85%), bp 120–122 °C at 20 mmHg (lit. data 112–114 °C at 15 mmHg [24]). Anal. calcd. for $C_{10}H_{14}S$ (%): C, 72.23; H, 8.49; S, 19.28. Found (%): C, 71.54; H, 7.99; S, 19.18. IR (KBr): ν, cm^{-1} 3080w and 3030w ($\nu(CH)_{Ar}$), 2962vs, 2904m and 2868m ($\nu(CH)_{tBu}$), 2550w (ν(SH)), 1492s, 1398m, 1362m, 1267m, 1117s, 990s, 823s, 551m. MS: *m/z* 166 (45%, $[M]^+$). ^1H NMR ($CDCl_3$): δ, ppm 7.54 (2H, m, Ar*H*), 7.37 (2H, m, Ar*H*), 3.37 (1H, s, -S*H*), 1.29 (9H, s, *t*Bu).

2,3-thianaphthenequinone [2,3-dihydrobenzo[b] thiophene-2,3-dione] (2*a*). Oxalyl chloride (14.6 mL, 0.144 mol) was added to thiophenol (**1a**) (15.0 mL, 0.144 mol) under vigorous stirring which was continued till solidification of the reaction mixture. Then carbon disulfide (45 mL) was added, solution was cooled to 0–5 °C and anhydrous $AlCl_3$ (38.5 g, 0.288 mol) was immersed in portions to regulate acylation reaction. Stirring was continued for further 10 min and then the solvent was evaporated by heating on a water-bath at 42–45 °C. Dark residue was mixed with ice and kept overnight. The orange precipitate was filtered and treated with saturated aqueous $NaHCO_3$ solution. Filtrate was collected and carefully acidified by concentrated HCl solution until complete precipitation of the bright orange product (yield 53%), mp 119–121 °C. Anal. calcd. for $C_8H_4SO_2$ (%): C, 58.54; H, 2.41; S, 19.51; O, 19.51. Found (%): C, 58.03; H, 2.27; S, 19.95; O, 19.81. IR (KBr): ν, cm^{-1} 1726m, 1714s (ν(C=O)), 1589m, 1468s, 1452m, 1360s, 1342s, 1282s, 1242m, 1147s, 1108s, 1060m, 962m, 843s, 748m, 449m.

5-*tert*-butyl-2,3-thianaphthenquinone [5-*tert*-butyl-2,3-dihydrobenzo[b]thiophene-2,3-dione] (2*b*). It was prepared similarly to unsubstituted quinone **2a**. Yield 7.6 g (63%), mp 103–105 °C. Anal. calcd. for $C_{12}H_{12}SO_2$ (%): C, 65.43; H, 5.49; S, 14.56; O, 14.53. Found (%): C, 64.78; H, 4.88; S, 13.69; O, 13.98. IR (KBr): ν, cm^{-1} 3409s (ν(COOH)), 3072m ($\nu(CH)_{Ar}$), 2964s, 2871m ($\nu(CH)_{tBu}$), 1708vs (ν(C=O)), 1596s, 1562m, 1477s, 1365m, 1288m, 1257m, 1201m, 1110m, 1004m, 919m, 850m. ^1H NMR ($CDCl_3$): δ, ppm 7.84 (1H, m, Ar*H*), 7.69 (1H, m, Ar*H*), 7.39 (1H, m, Ar*H*), 1.33 (9H, s, *t*Bu).

2-oxalylphenylthioglycolic acid [2-(2-carboxymethylsulfanylphenyl)-2-oxoacetic acid] (3a). It was prepared by modification of the earlier reported procedure [25]. Solutions of 2,3-thionaphthenequinone **2a** (5 g, 30.5 mmol) and chloroacetic acid (2.88 g, 30.5 mmol) each in 20 mL of 10% aqueous $NaHCO_3$ were mixed together, heated for 10–15 min and cooled to 5 °C. Addition of conc. aqueous HCl leads to precipitation of **3a** as yellow product, which was filtered and dried. Yield 6.95 g (95%), mp 164–168 °C. Anal. calcd. for $C_{10}H_8SO_5$ (%): C, 50.00; H, 3.33; S, 13.33; O, 33.3. Found (%): C, 48.31; H, 3.15; S, 13.65; O, 30.94. IR (KBr): ν, cm^{-1} 3414m (ν(OH)), 1711s (ν(COOH)), 1676s (ν(C=O)), 1612s (ν(C=O)), 1591m, 1554vs, 1522vs, 1493vs, 1458s, 1412s, 1373m, 1333m, 1290s, 1271vs, 1244s, 1142m, 1107s, 1014w, 974m, 891w, 802m, 789s, 762vs, 723s, 689s, 638m, 575m, 480m, 446vs, 426s. ^1H NMR (DMSO-d_6): δ, ppm 3.89 (2H, s, -S-CH_2-COOH), 7.36 (1H, t, Ar*H*), 7.49 (1H, d, Ar*H*), 7.67 (1H, t, Ar*H*), 7.79 (1H, dd, Ar*H*).

5-*tert*-butyl-2-oxalylphenylthioglycolic acid {5-*tert*-butyl-2-[(carboxymethyl)thio]phenyl}(oxo)acetic acid (3b). It was prepared from quinone **2b** similarly to unsubstituted acid **3a**. After acidification of the reaction mixture with aqueous HCl, the product was extracted with chloroform to give **3b** as a ductile yellow liquid. Yield 8.5 g (83%). Anal. calcd. for $C_{14}H_{16}SO_5$ (%): C, 56.74; H, 5.44; S, 10.81. Found (%): C, 50.64; H, 5.71; S, 8.85. IR (KBr): ν, cm^{-1} 2964s, 2906m, 2868w ($\nu(CH)_{tBu}$), 1708vs (ν(C=O)), 1596s, 1477m, 1468m, 1396m, 1363m, 1288m, 1263m, 1207m, 1169m, 1004m, 921m, 851m, 585m. ^1H NMR ($CDCl_3$): δ, ppm 8.56 (1H, m, Ar-*H*), 8.10 (1H, m, Ar*H*), 7.72–7.54 (1H, m, Ar*H*), 3.73 (2H, s, -S-CH_2-COOH), 1.33 (9H, s, *t*Bu).

Thianaphthene-2,3-dicarboxylic acid [benzo[b] thiophene-2,3-dicarboxylic acid] (4a). It was prepared by modification of the earlier reported procedure [25]. Acid **3a** (6.95 g, 0.029 mol) was dissolved in 30% aqueous NaOH solution (30 mL) with heating. After transformation of the red solution to dense gruel of beige color, distillated water (40 mL) was added to dissolve the precipitate. Then the solution was cooled and acidified with conc. aqueous HCl to precipite the acid **4a** which was filtered and dried. Yield 5.21 g (81%), mp 248–252 °C. Anal. calcd. for $C_{10}H_6O_4S$ (222.21) (%): C, 54.05; H, 2.7; S, 14.41; O, 28.83. Found (%): C, 53.21; H, 2.41; S, 13.92; O, 27.45. IR (KBr): ν, cm^{-1} 1675m (ν(COOH)), 1554m, 1492s, 1263s, 1243m, 1106m, 802s, 761m.

^{1}H NMR (DMSO-d_6): δ, ppm 7.45–7.60 (2H, m, Ar*H*), 8.00–8.15 (2H, m, Ar*H*).

5-*tert*-butylthianaphthene-2,3-dicarboxylic acid [5-*tert*-butylbenzo[b]thiophene-2,3-dicarboxylic acid] (4*b*). It was prepared similarly to the unsubstituted acid **4a**, but the reaction time was increased to 1 h. Yield 5.2 g (65%), mp 132–137 °C with decomposition. Anal. calcd. for $C_{14}H_{14}SO_4$ (%): C, 60.43; H, 5.07; S, 11.51; O, 22.99. Found (%): C, 58.50; H, 4.87; S, 11.25; O, 20.11. IR (KBr): ν, cm^{-1} 2965s, 2927m, 2871m (ν(CH)$_{t\text{Bu}}$), 2366w, 1841w, 1708vs (ν(COOH)), 1596s, 1562m, 1477s, 1467m, 1413m, 1398m, 1365m, 1299m, 1288m, 1259m, 1207m, 1110m, 1089m, 1047m, 1004m, 921m, 906w, 879w, 850w, 836w, 775w, 755w, 730w, 709w, 690w, 667w, 588w, 543w, 497w, 449w, 418vw. MS: *m/z* 277 (40%, [M]$^+$). ^{1}H NMR ($CDCl_3$): δ, ppm 7.89 (2H, m, COO*H*), 7.70 (1H, m, Ar-*H*), 7.46 (1H, m, Ar-*H*), 7.39 (1H, m, Ar-*H*), 1.33 (9H, s, *t*Bu).

Thianaphthene-2,3-dicarboxylic acid anhydride [1,3-dihydrobenzo[4,5]thieno[*2,3-c*]furan-1,3-dione] (6a). It was obtained following the procedure of Linstead [15] by refluxing of acid **3a** in acetic anhydride for 1 h with yield *ca*. 95%, mp 171–173 °C. IR (KBr): ν, cm^{-1} 3088w (ν(CH)$_{arom}$), 1832vs and 1762vs (ν(-CO-O-CO-)), 1597m, 1563m, 1522s, 1470s, 1419m, 1394m, 1324m, 1267s, 1170m, 1151s, 1119s, 1050m, 1006m, 961w, 890s, 830s, 785s, 757s, 719s, 700m, 661m, 632m, 563m, 492m, 425m. Anal. calcd. for $C_{10}H_5O_3S$ (204.19) (%): C, 58.82; H, 1.96; S, 15.69; O, 23.53. Found (%): C, 57.91; H, 1.68; S, 14.18; O, 21.82.

Thianaphthene-2,3-dicarboximide [2,3-dihydro-1H-benzo[4,5]thieno[*2,3-c*]pyrrole-1,3-dione] (10a). *Method A.* Dry NH_3 was bubbled through a stirred solution of the anhydride **6a** (2 g, 0.01 mol) in $CHCl_3$ for 2–3 h at room temperature. This leads to precipitation of amidoacids **8a**, which were filtered, dried, dissolved in DMF (10 mL) and treated with $POCl_3$ (2.6 mL, 0.03 mol) in an ice bath overnight. The precipitate formed after pouring of the reaction mixture into water was filtered, dried and sublimed to give 0.98 g of the imide **10a** (yield *ca*. 50%). *Method B.* Dicarboxylic acid **4b** (5.79 g, 0.0261 mol) was refluxed with thionyl chloride (40 mL, 0.56 mol) for 6 h. Excess $SOCl_2$ was removed under reduced pressure, the residue (see remark below) was dissolved in chloroform (40 mL) and dry ammonia gas was bubbled through the solution for 2–3 h. The obtained suspension was kept in a closed flask overnight. The precipitate containing a mixture of amidoacids **8a** and diamide **9a** (mp 178–192 °C, yield 3.1 g, 54%) was filtered, dried and dissolved in DMF (20 mL). The solution was cooled in an ice bath to 0–5 °C and $POCl_3$ (5.14 mL, 0.056 mol) was added in portions to keep the temperature at 5–7 °C. The stirring of the reaction mixture was continued for another 3 h and then it was left overnight. Precipitate formed upon pouring of the reaction mixture on ice was filtered, dried and washed with $CHCl_3$. Evaporation of the extract gave 0.48 g (10%) of dinitrile **11a** (see characterization details below). Sublimation of the insoluble residue gave the imide **10a** as yellow crystals. Yield 2.1 g (39.5%), mp 235–240 °C. Anal. calcd. for $C_{10}H_5NO_2S$ (203.21) (%): (C 59.10% H 2.48% N 6.89% O 15.75% S 15.78%). Found (%): (C, 59.73; H, 2.56; N, 7.42, O, 13.11; S, 16.34). IR (KBr): ν, cm^{-1} 3242s (ν(NH)), 3066m (ν(CH)$_{Ar}$); 1834m, 1768s 1730s and 1709s (ν(imide), 1597w, 1520m, 1473m, 1429m, 1392m, 1329s, 1306s, 1259m, 1194m, 1173w, 1063m, 1047s, 995s, 947w, 899w, 856w, 841m, 787m, 752s, 721, 665m, 644m, 565m, 519m, 496m, 428s. MS: *m/z* 203 (100%, [M]$^+$). ^{1}H NMR ($CDCl_3$): δ, ppm 7.5–7.6 (2H, m, Ar*H*), 7.95–8.00 (1H, m, Ar*H*), 8.2–8.3 (1H, m, Ar*H*). *Remark.* The residue obtained after the reaction of dicarboxylic acid **4a** with thionyl chloride is a mixture consisting from anhydride **6a** (*m/z* = 204) and easily hydrolizable dichloroanhydride **7a** (*m/z* = 259). mp 64 (partly) and 156–159 °C (completely). IR (KBr): ν, cm^{-1} 3579m (ν(OH)), 3082m (ν(CH)$_{Ar}$), 2093m, 1837vs and 1756vs (ν(-CO-O-CO-)), 1662s, 1633w, 1597s, 1562m, 1522vs, 1470vs, 1419s, 1394s, 1325s, 1267vs, 1218w, 1203w, 1171s, 1149vs, 1118vs, 1049m, 1005s, 960m, 891vs, 831vs, 785vs, 756vs, 731s, 719s, 700s, 661s, 633m, 563m, 513m, 487m, 484m, 426s. Anal. found (%): C, 53.24; H, 1.77; S, 15.00; O, 17.49. Calcd. (%) for $C_{10}H_4SO_3$ (204.19): C, 58.82; H, 1.96; S, 15.69; O, 23.53; for $C_{10}H_4ClSO_2$ (259.10) C, 46.36; H, 1.56; S, 12.37; O, 12.35. Separation of this mixture is wasteful and it was used as obtained in further ammonolysis.

5-*tert*-butylthianaphthene-2,3-dicarboximide [2,3-dihydro-7-*tert*-butyl-1H-benzothieno[*2,3-c*]pyrrole-1,3(2H)-dione (10b). The synthetic method of substituted imide is the same as described above for **10a** (*method B*). Yield 1.5 g (31%), mp 179–181 °C. Anal. calcd. for $C_{14}H_{13}SNO_2$ (%): C, 64.84; H, 5.05; S, 12.36; N, 5.40; O, 12.34. Found (%): C, 64.30; H, 5.09; S, 12.13; N, 5.46. IR (KBr): ν, cm^{-1} 3444m, 3211m (ν(NH)), 3058m (ν(CH)$_{At}$), 2964m (ν(CH)$_{t\text{Bu}}$), 2904m, 2865m, 1765s, 1734vs (ν(C=O)$_{imide}$), 1637m, 1545w, 1519m, 1459m, 1433m, 1394m, 1357m, 1331m, 1294s, 1255m, 1184m, 1103m, 1068m, 1039m, 997m, 883m, 819m, 740m, 725m, 704m, 681m, 640m, 519m, 451w, 428w. ^{1}H NMR ($CDCl_3$): δ, ppm 8.20 (1H, s, Ar-*H*), 8.01 (1H, m, -CO-N*H*-CO-), 7.89 (1H, d, Ar*H*), 7.65 (1H, m, Ar*H*), 1.43 (9H, s, *t*Bu).

Thianaphthene-2,3-dicarboxylic acid diamides (9). [Benzo[b]thiophene-2,3-dicarboxamides] (*9a*). Imide **10a** or **10b** (3.69 mmol) was suspended in the saturated ammonia solution (0.88 g/cm^3, 30–40 mL). On the next day, the white precipitate of diamides **9a** or **9b** was filtered and dried. **Diamide 9a.** Yield 0.68 g (84%), mp 221–225 °C (lit. mp 204–205 °C [15]). Anal. calcd. for $C_{10}H_8N_2O_2S$ (220.24) (%): C, 54.54; H, 3.64; S, 14.55; N, 12.73. Found (%): C, 54.84; H, 3.35; S, 14.61; N, 11.65. IR (KBr): ν, cm^{-1} 3381s and 3269m (ν(NH$_2$)), 3059w (ν(CH)$_{Ar}$), 1668vs and 1616s (ν(C=O)$_{amide}$), 1567s, 1519m, 1456w, 1404s, 1381w, 1313m, 1252w, 1147m,

1117m, 1103m, 1051m, 937m, 881m, 800m, 733s, 704s, 667s, 648s, 636s, 471m, 434m, 407m. ^{1}H NMR (DMSO-d_6): δ, ppm 8.37 (2H, s, CON*H*$_2$), 8.18 (2H, s, CON*H*$_2$), 8.0–8.1 (1H, m, Ar*H*), 7.9–8.0 (1H, m, Ar*H*), 7.45–7.55 (2H, m, Ar*H*). **Diamide 9b.** Yield 1.3 g (81%), mp 221–225 °C with decomposition. Anal. calcd. for $C_{14}H_{16}SN_2O_2$ (%): C, 60.85; H, 5.84; S, 11.60; N, 10.14. Found (%): C, 60.93; H, 5.63; S, 11.78; N, 9.35. IR (KBr): ν, cm^{-1} 3332s and 3197s (ν(NH$_2$)), 2963s and 2869m (ν(CH)), 1764m, 1722m, 1658vs and 1612s (ν(C=O)$_{amide}$), 1525m, 1442s, 1398m, 1363m, 1325m, 1292m, 1259m, 1201m, 1160m, 1105m, 979w, 914w, 879w, 810w, 646m, 586m, 526w, 441w. ^{1}H NMR (DMSO-d_6): δ, ppm 8.42 (1H, s, Ar-*H*), 8.15–8.12 (2H, s, CON*H*$_2$), 7.98 (1H, d, Ar*H*), 7.87 (2H, s, CON*H*$_2$), 7.63 (1H, m, Ar*H*), 1.35 (9H, s, *t*Bu).

2,3-dicyanothianaphthenes [benzo[*b*]thiophene-2,3-dicarbonitriles] (11). $POCl_3$ (2.5 mL, 0.028 mol) was added in portions to a solution of diamide **9a** or **9b** (3.09 mmol) in DMF (10–15 mL) at 0–5 °C. The reaction mixture was stirred further for 2 h, kept overnight and then poured on ice. The precipitate was filtered, washed with water, dried and sublimed. **Dinitrile 11a.** Yield 0.5 g (88%), mp 151–153 °C (lit. 148 °C [15]). Anal. calcd. for $C_{10}H_4N_2S$ (184.21) (%): C, 65.22; H, 2.17; S, 17.39; N, 15.22. Found (%): C, 64.43; H, 2.16; S, 17.03; N, 14.00. IR (KBr): ν, cm^{-1} 2229vs (ν(C≡N)), 1982w, 1940w, 1817w, 1726m, 1589m, 1498s, 1460m, 1423m, 1348m, 1321w, 1267m, 1182m, 1157s, 1134m, 1020w, 993w, 955m, 864m, 764vs, 729s, 661w, 642m, 518m, 488m, 438s, 413m. MS: *m/z* 184 (100%, [M]$^+$). ^{1}H NMR ($CDCl_3$): δ, ppm 7.69 (2H, m, Ar*H*), 7.96 (1H, d, Ar*H*), 8.08 (1H, d, Ar*H*). **Dinitrile 11b.** Yield 0.95 g (84%), mp 96–98 °C. Anal. calcd. for $C_{14}H_{12}SN_2$ (%): C, 69.97; H, 5.03; S, 13.34; N, 11.66. Found (%): C, 68.71; H, 5.01; S, 12.98; N, 10.98. IR (KBr): ν, cm^{-1} 3086m and 3064m (ν(CH)$_{Ar}$), 2964vs, 2837s and 2871s (ν(CH)$_{tBu}$), 2229s (ν(C≡N)), 1934m, 1795vs, 1754m, 1653m, 1544m, 1510s, 1467s, 1440s, 1417s, 1367vs, 1317m, 1297m, 1253s, 1203m, 1159vs, 1105m, 1054m, 1016s, 925m, 916m, 879m, 831s, 777w, 755w, 734m, 690m, 669m, 592m, 517w, 499m, 441m. ^{1}H NMR ($CDCl_3$): δ, ppm 8.02 (1H, m, Ar*H*), 7.91–7.88 (1H, m, Ar*H*), 7.81 (1H, m, Ar*H*), 1.45 (9H, s, *t*Bu).

Preparation of tetra(2,3-thianaphtheno)porphyrazines

Free-bases [H_2SNc] (12a) and [H_2SNc^{t}Bu$_4$] (12b). Dinitrile **11a** (0.5 g, 2.7 mmol) or **11b** (0.5 g, 2.1 mmol) were added to a solution of lithium (0.05 g, 7 mmol) in freshly distilled *n*-amyl alcohol (15 mL), and the reaction mixture was refluxed until dark green color was achieved (4–6 h). The solvent was evaporated, the residue was washed with ethanol, 50% aqueous acetic acid, water, and dried. **[H_2SNc] (12a).** Low solubility prevents further purification. Yield 0.15 g (30%). UV-vis ($CHCl_3$): λ_{max}, nm (A/A_{max}) 325 (2.11), 365sh (1.64), 440sh, 629 (1.01), 642 (0.97), 694 (1). UV-vis (pyridine): λ_{max}, nm (A/A_{max}) 319 (2.87), 370sh (1.73), 631 (1.05), 649 (1.02), 696 (1). **[H_2SNc^{t}Bu$_4$] (12b).** The product was purified by column chromatography on alumina (eluent: $CHCl_3$). Yield 0.26 g (52%). Anal. calcd. for $C_{56}H_{50}SN_8$ (963.30) (%): C, 69.82; H, 5.23; N, 11.63; S, 13.31. Found (%): C, 68.01; H, 5.86; N, 10.98; S, 12.98. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 329 (4.56), 636 (4.22), 653 (4.24), 702 (4.42). UV-vis (pyridine): λ_{max}, nm (log ε) 328 (4.44), 640sh (4.12), 659 (4.28), 705 (4.42). IR (KBr): ν, cm^{-1} 3288w (ν(NH)); 2956s, 2927s and 2858m (ν(CH$_3$)); 1602m, 1571m, 1525m, 1456m, 1417s, 1373s, 1317m, 1297m, 1257m, 1155vs, 1072m, 1016s, 925m, 833m, 809w, 798w, 730w, 690m, 580w, 516w, 487w.

Mg^{II} complex [MgSNc] (13a). To a solution of magnesium chips (15 mg, 0.62 mmol) in dry butanol (15 mL) (dissolution was initiated by iodine crystal) dinitrile **11a** (80 mg, 0.435 mmol) was added and the mixture was refluxed for 20 h. After evaporation of the solvent the residue was stirred with aqueous acetic acid (50% v/v, 30 mL) at room temperature for 30 min. The precipitate was centrifugated and washed thoroughly with water and methanol. After purification by column chromatography (silica, $CHCl_3$) the Mg^{II} complex **13a** was obtained . Yield 34 mg (42%). UV-vis ($CHCl_3$): λ_{max}, nm (A/A_{max}) 337 (1.96), 611 (0.43), 659 (1), 669 (1). UV-vis (pyridine): λ_{max}, nm (A/A_{max}) 326 (1.34), 381 (1.19), 601 (0.34), 658 (0.98), 670 (1). IR (KBr): ν, cm^{-1} 1654s, 1596s, 1523m, 1457s, 1407s, 1317m, 1267m, 1122s, 1095m, 1079m, 1043m, 917w, 858m, 750m, 725m.

Complexes with Al^{III} (14), Ga^{III} (15) and In^{III} (16), [(HO)MSNc] and [(HO)SNc^{t}Bu$_4$]. *General method of preparation.* Mixture of the dinitrile **11a** (0.5 g, 2.7 mmol) or **11b** (0.5 g, 2.1 mmol) with the corresponding metal acetate ([Al(OAc)$_3$] [26]), or hydroxodiacetate ([M(OH)(OAc)$_2$] M = Ga^{III} or In^{III} produced by "Reakhim") in a 2:1 molar ratio was placed in a glass test tube and rapidly heated to 250 ºC in a metallic bath till complete solidification (1–3 min). Unreacted dinitriles were extracted with diethyl ether and the residue purified by column chromatography on Al_2O_3 (eluent: chloroform).

[(HO)AlSNc] (14a). Yield 26%. UV-vis ($CHCl_3$): λ_{max}, nm (A/A_{max}) 331 (1.12), 383 (0.98), 468 (0.37), 611 (0.38) 665 (0.97), 673 (1). UV-vis (pyridine): λ_{max}, nm (A/A_{max}) 387 (0.84), 470 (0.28) 609 (0.33), 670 (1.01), 678 (1). IR (KBr): ν, cm^{-1} 1498m, 1462m, 1417s, 1402m, 1373m, 1319m, 1261m, 1155s, 1107m, 1076m, 1016m, 923m, 762m, 728m, 690w.

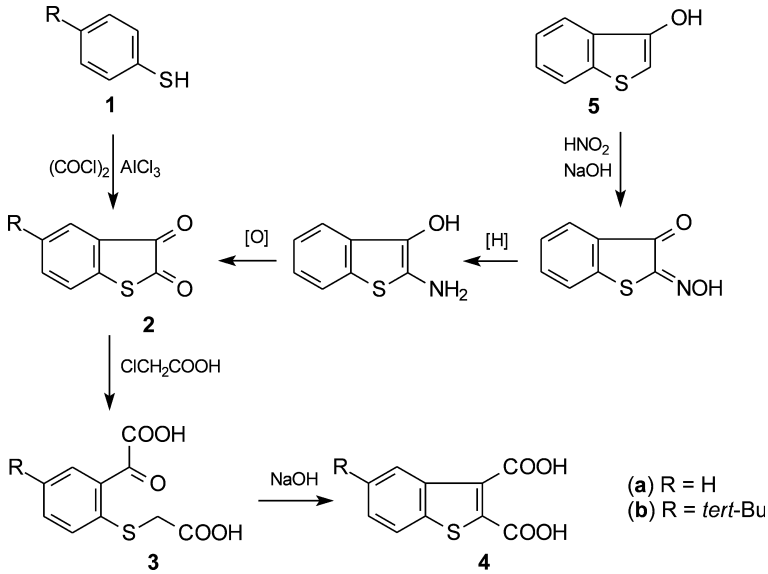
[(HO)AlSNc^{t}Bu$_4$] (14b). Yield 19%. Anal. calcd. for $C_{56}H_{49}S_4N_8OAl + 2H_2O$ (1041.31) (%): C, 64.59; H, 5.13; N, 10.76; S, 12.32. Found (%): C, 65.21; H, 5.04; N, 10.55; S, 12.08. UV-vis ($CHCl_3$): λ_{max}, nm (A/A_{max}) 335 (3.24), 628 (0.56), 684 (1). IR (KBr): ν, cm^{-1} 2958vs and 2863m (ν(CH)$_{tBu}$); 1636m, 1509m, 1463s, 1411s, 1384m, 1360s, 1296s, 1253s, 1222s, 1185s, 1099s, 1015m, 921m, 915s, 883m, 809s, 740s, 701m, 572m, 447m.

[(HO)GaSNc] (15a). Yield 65%. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 334 (3.99), 378sh (3.88), 470sh, 616sh (3.66), 677 (4.08), 684 (4.08). UV-vis (pyridine): λ_{max}, nm (A/A_{max}) 385 (0.73), 469sh, 611 (0.32), 678 (1). IR (KBr): ν, cm^{-1} 3644m ν(OH), 3058m $\nu(CH)_{Ar}$, 1598s, 1498s, 1465s, 1421s, 1400s, 1309s, 1257s, 1228s, 1201s, 1189s, 1157s, 1128s, 1093s, 1060s, 1014s, 921m, 885s, 856m, 819m, 765s, 734s, 686s, 557s. MS (MALDI-TOF): *m/z* 805 $[M - OH]^+$, 822 $[M]^+$, 840 $[M + H_2O]^+$.

[(HO)GaSNc^{t}Bu$_4$] (15b). Yield 58%. Anal. calcd. for $C_{56}H_{49}S_4N_8OGa + 2H_2O$ (1084.04) (%): C, 62.05; H, 4.93; N, 10.34; S, 11.83. Found (%): C, 62.51; H, 4.84; N, 9.68; S, 11.68. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 341 (4.82), 369sh, 433 (4.49), 483 (4.49), 621 (4.27), 688 (4.92). IR (KBr): ν, cm^{-1} 2960vs and 2865m ($\nu(CH)_{tBu}$), 1639s, 1506s, 1463s, 1407s, 1394s, 1361s, 1296s, 1255s, 1222s, 1197vs, 1180vs, 1105s, 1016m, 937m, 916s, 890m, 809s, 757m, 740s, 701m, 632m, 570m, 559m, 457m. ^{1}H NMR (DMSO-d_6): δ, ppm 8.22–8.06 (8H, m, Ar*H*), 7.89–7.75 (4H, m, Ar*H*), 1.39 (36H, s, *t*Bu).

[(HO)InSNc] (16a). Yield 73%. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 333 (4.23), 382 (4.01), 483sh, 618 (3.74), 684 (4.35). UV-vis (pyridine): λ_{max}, nm (A/A_{max}) 330sh, 391(0.68), 616sh (0.22), 683 (1). IR (KBr): ν, cm^{-1} 3616m ν(OH), 3060w and 3023w $\nu(CH)_{Ar}$, 1558m, 1519m, 1492m, 1454m, 1398m, 1309m, 1255m, 1224m, 1195m, 1182m, 1157m, 1124s, 1106s, 1095s, 1064s, 1037m, 914w, 875w, 811vw, 763w, 730w, 698w. MS (MALDI-TOF): *m/z* 851 $[M - OH]^+$, 868 $[M]^+$.

[(HO)InSNc^{t}Bu$_4$] (16b). Yield 61%. Anal. calcd. for $C_{56}H_{49}S_4N_8OIn + 3H_2O$ (1147.16) (%): C, 58.63; H, 4.83; N, 9.77; S, 11.18. Found (%): C, 58.71; H, 5.04; N, 9.38; S, 10.98. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 347 (4.63), 386 (4.51), 420sh, 489 (4.24), 625 (4.26), 693 (4.94). IR (KBr): ν, cm^{-1} 2962s, 2925s and 2867s ($\nu(CH)_{tBu}$); 1633s, 1514s, 1463s, 1415s, 1363s, 1296s, 1257s, 1222s, 1155s, 1088s, 1049s, 1016s, 917s, 885m, 809m, 740m, 701m, 597m, 574m, 435m. ^{1}H NMR ($CDCl_3$): δ, ppm 7.98–7.87 (8H, m, Ar*H*), 7.68 (4H, m, Ar*H*), 1.44 (36H, s, *t*Bu).



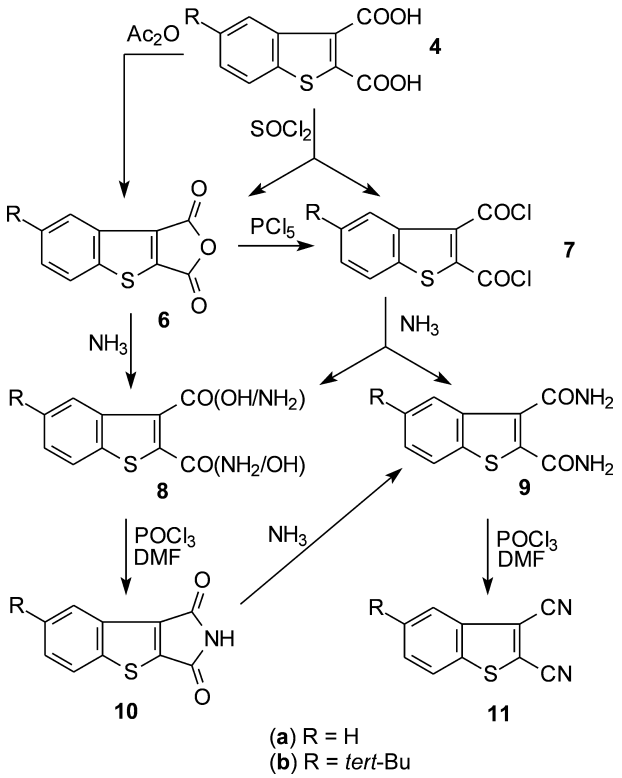
Scheme 1. Synthesis of 2,3-thianaphthendicarboxylic acid **4**

RESULTS AND DISCUSSION

Synthesis of the precursors

Template cyclotetramerization of dinitriles of *ortho*-dicarboxylic acids in the presence of metals or metal salts is the most convenient methodology for the preparation of porphyrazines with various annulated heterocycles [9, 27, 28]. In the original Linstead's work [15] 2,3-thianaphthenedicarboxylic acid **4a**, the key intermediate in the synthesis of the corresponding dinitrile **11a**, was prepared according to Friedlaender [25] from 2,3-thianaphtenequinone **2a** which in turn was synthesised starting from thioindoxyl (benzo[*b*]thiophen-3-ol, **5**) using the 3-stage Mayer's procedure [29] (Scheme 1). In our work we have prepared 2,3-thianaphthenquinone **2a** in one stage from more easily available thiophenol (**1a**) and oxalyl chloride following the approach suggested by Dutta [30] for thiophene-fused phenanthrene. Taking into account the peculiarities of intramolecular acylation processes [31] we have optimized the conditions and carried out the reaction at 0–5 °C under vigorous stirring and short reaction time. As a result, the yield of the quinone **2a** was increased from 13% to 53%.

While the dinitrile **11a** could be easily obtained by dehydration of the diamide **9a** (*e.g.* upon refluxing with acetic anhydride, 80–90% yield [15]), the conversion of the diacid **4a** to its diamide **9a** implicates some difficulties (Scheme 2). According to the procedure used in [15] the diacid **4a** upon treatment with acetic anhydride was dehydrated to the anhydride **6a**, which on heating with PCl_5 was converted to the dichloroanhydride **7a** with high overall yield (*ca*. 90%). However, ammonolysis of the dichloroanhydride **7a** gave after recrystallization from water only 13% of the diamide **9a** along with *ca*. 13% of amidoacids **8a** from the mother liquid. The disadvantage of this synthetic approach and low overall yield of the dinitrile **11a** (*ca*. 9% on the used diacid **4a**), is evidently connected with high sensitivity of the dichloroanhydride **7a** to hydrolysis. This leads to formation of considerable amounts of amidoacids **8a** which were mainly lost during recrystallization. We have elaborated the improved synthetic procedure taken into account that the diamide **9a** can be prepared by ammonolysis of the imide **10a** with almost quantitative yield. According to Linstead's report [15] the imide **10a** is formed upon distillation of amidoacids **8a** with P_2O_5, but the attempts of



Scheme 2. Conversion of 2,3-thianaphthenedicarboxylic acid **4** to dinitrile **11**

its direct preparation from the anhydride **6a** by its melting with urea or ammonium carbonate gave unsatisfactory results. We have synthesized the imide **10a** in two different ways. (*A*) Ammonolysis of the anhydride **6a** with dry NH_3 in chloroform solution leads to precipitation of the mixture of aminoacids **8a**, which upon dehydration with $POCl_3$ in DMF gave the imide **10a** (50% yield after sublimation) along with some amount of mononitrile. (*B*) In another procedure, the imide **10a** was obtained from the diacid **4a** in three stages by consecutive treatment with $SOCl_2$, dry NH_3, $POCl_3$ in DMF and sublimation with 39–40% overall yield. In line with observations made in [15] we have found that treatment of the diacid **4a** with $SOCl_2$ leads to a mixture of the dichloroanhydride **7a** with the anhydride **6a**. It was partly melted at 58–65 °C and completely at 155–165 °C. Melting points for the dichloroanhydride **7a** and the anhydride **6a** reported in [15] are 72 °C and 173 °C, respectively. We could not find conditions for complete conversion of the diacid **4a** to the dichloroanhydride **7a** under action of $SOCl_2$ and separation of the anhydride **6a** and the dichloroanhydride **7a** was a wasteful procedure. Instead we have directly treated their mixture of with dry NH_3 to obtain mixture of amidoacids **8a** and the diamide **9a** which were then dehydrated with $POCl_3$ to the imide **10a** and the dinitrile **11a**. The latter is soluble in $CHCl_3$ and could be isolated with *ca*. 10% yield (on the used diacid **4a**). The reaction of the insoluble imide **10a** with conc. aqueous NH_3 solution yielded the diamide **9a** (84%) which upon treatment with $POCl_3$ in DMF gave the target dinitrile **11a** (88%). So the overall combined yield of the dinitrile **11a** from the diacid **4a** in the "one-pot" procedure (*B*) (*ca*. 45%) was larger than that in the procedure (*A*) (30–35%), and much higher than in the original Linstead's procedure (9–10%).

A similar strategy has being used for the synthesis of the *tert*-butyl substituted dinitrile **11b** from *tert*-butylthophenol **1b** which was prepared by reduction of *tert*-butylbenzenesulfochloride with zinc dust in concentrated sulfuric acid.

Synthesis of porphyrazines

The dinitriles **11** afford tetra(2,3-thianaphtheno)porphyrazines upon cyclotetramerization. Refluxing of the dinitriles **11** in *n*-amyl alcohol in the presence of lithium amylate leads to the dilithium complexes which upon isolation are demetalated to give the corresponding free-base macrocycles [H_2SNc] (**12a**) or [H_2SNc^{t}Bu$_4$] (**12b**). Cyclotetramerization of **11a** in *n*-butanol in the presence of magnesium butylate gives the Mg^{II} complex [MgSNc] (**13a**). Complexes with Ga^{III} (**15a**, **15b**) and In^{III} (**16a**, **16b**) were very easily produced with 65–75% yields by template cyclotetramerization of the dinitriles **11** when melting with the corresponding hydroxydiacetate [M(OH)$(OAc)_2$] in a metallic bath for 3–5 min at 170–250 °C. The Al^{III} complexes (**14a**, **14b**) could be obtained from Al^{III} acetate only with 20–25% yield. Purification were troublesome for the free-base **12a** and Al^{III} complex **14a** due to their extremely low solubility in organic solvents, but complexes of Ga^{III} (**15a**, **15b**) and In^{III} (**15a**, **15b**) as well as *tert*-butyl substituted species **12b**, **14b**–**16b** could be purified by column chromatography. Thianaphthene rings can be 2,3-annulated to four pyrrole rings of the porphyrazine macrocycle in a different manner and we obtained tetra(2,3-thionaphtheno)porphyrazines as a mixture of four randomers having different symmetry (2,3:2,3:2,3:2,3 – C_{4h}, shown in Chart 1; 2,3:2,3:2,3:3,2 – C_s; 2,3:2,3:3,2:3,2 – C_{2v} and 2,3:3,2:2,3:3,2 – D_{2h}, see Chart 2). Unfortunately, our column chromatographic procedure was not effective enough for isolation of the individual randomers. The presence of the mixture of randomers leads to complex multiplets in the aromatic region of the ^{1}H NMR spectra and to broadening or splitting of the Q-band in the UV-vis spectra (see below). Analytical data indicate that metal complexes **14b**–**16b** were obtained as hydrated materials. All new porphyrazines have been characterised by UV-vis and IR spectroscopy, and some of them by MALDI-TOF mass-spectrometry and ^{1}H NMR spectra.

As is usual for Mg^{II} complexes of phthalocyanine [32] and its heterocyclic analogues (see *e.g.* [33]) for the Mg^{II} complex **13a** one water molecule is assumed to be coordinated [(H_2O)MgSNc]. Complexes of Al^{III}, Ga^{III} and In^{III} were obtained as hydroxo complexes [(HO)MSNc] (M = Al^{III}, Ga^{III}, In^{III}). In the MALDI-TOF spectra recorded for **15a** and **16a** the intense peaks of [MSNc$^+$]

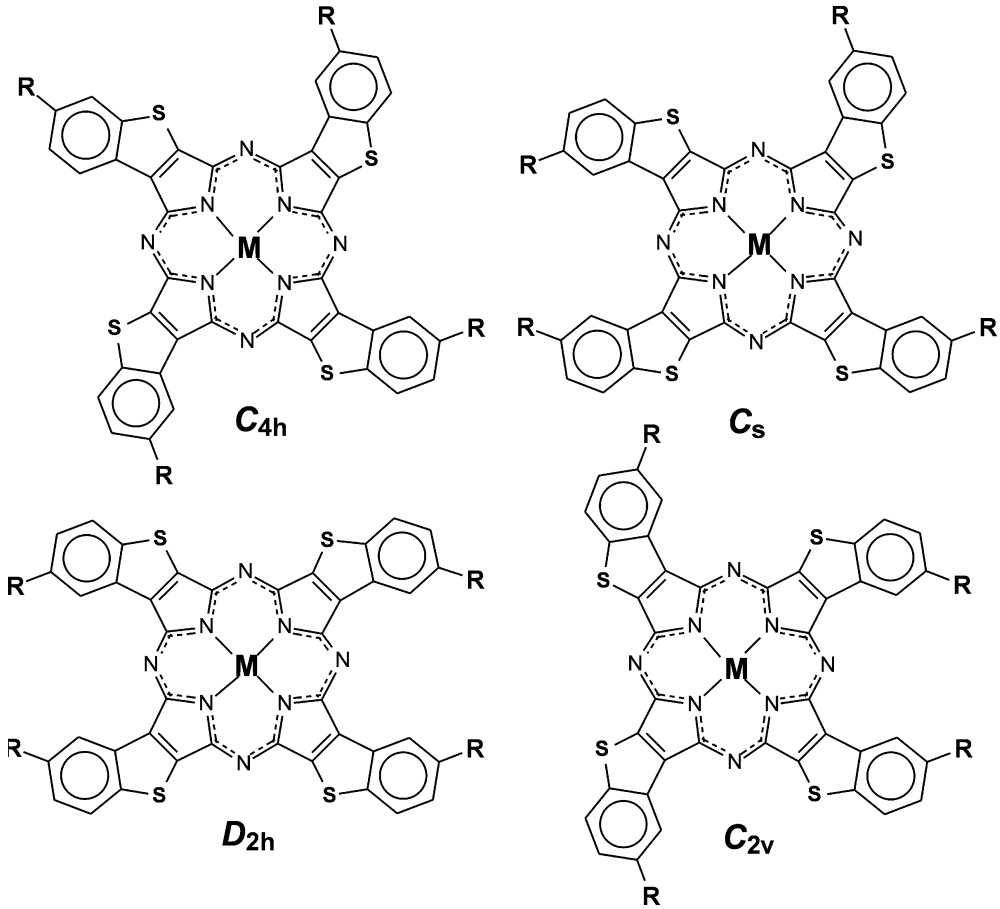


Chart 2. Structural formulae of four possible randomers of tetra(2,3-thianaphtheno)porphyrazines [MSNc] (**12a**–**16a**) and [MSNcBu$_4$] (**12b**,**14b**–**16a**). M = 2H (**12a**,**b**), (H$_2$O)Mg (**13a**), (HO)Al (**14a**,**b**), (HO)Ga (**15a**,**b**), (HO)In (**16a**,**b**). R = H (**a**), R = *tert*-Bu (**b**)

(100%) are accompanied by lower intensity peaks of hydroxocomplexes [(HO)MSNc$^+$] (30% for **15a** and 10% for **16a**), and in the case of the Ga^{III} complex **15a** an additional peak of the aquahydroxo complex [(HO)(H$_2$O)GaSNc$^+$] is also seen in Fig. 1. In the IR spectra, the bands of the stretching OH vibrations ν(OH) can be seen at 3644 cm^{-1} for **15a** and at 3616 cm^{-1} for **16a**. Elemental analysis data obtained for **14b–16b** provide evidence that these species were isolated as hydrated materials.

UV-vis spectra

Due to essentially planar structure of the macrocycle [H$_2$SNc] (**12a**) and its metal complexes [MSNc] **13a**–**16a** have low solubility and exhibit some tendency to aggregate. They are relatively well soluble in pyridine, DMF, α-chloronaphthalene and partly aggregated in CHCl$_3$. The corresponding *tert*-butyl substituted derivatives [H$_2$SNcBu$_4$] (**12b**) and [MSNcBu$_4$] (**14b**–**16b**) have better solubility and are less aggregated. The electronic absorption spectra (UV-vis spectra) recorded for the free-bases **12a**,**b** and for their metal complexes **13**–**16** in CHCl$_3$ and/or in pyridine are shown in Fig. 2. Table 1 compares some spectral characteristics of tetra(thianaphtheno)porphyrazines **12-16** with the data for the related porphyrazines, phthalocyanines and naphthalocyanines taken from the literature.

UV-vis spectra obtained for the metal complexes of the present tetra(thianaphtheno)porphyrazines, [MSNc] and [MSNcBu$_4$] (**13**–**16**) (see Fig. 2), are typical for porphyrazine and phthalocyanine metal complexes (see [9, 34, 35]) and contain the intense absorption bands in the far-red visible and in the UV-region. For the *tert*-butyl substituted species the absorption maxima are shifted slightly to the longer wavelength as compared to the unsubstituted tetra(thianaphtheno)porphyrazines. The low-lying HOMO→LUMO π-π* transitions of the porphyrazine π-chomophore are responsible for the appearance of the intense Q-band absorption at 665–695 nm, which is accompanied by vibronic satellites on the blue side. It should be noted that unlike metal complexes of symmetrically substituted porphyrazines and phthalocyanines which have a strict D_{4h} symmetry of the π-chromophore and hence the degenerated e_g* type LUMO, the present metal complexes of tetra(thionaphtheno)porphyrazines **13**–**16** have lower symmetry due to "angular" 2,3-annulation of

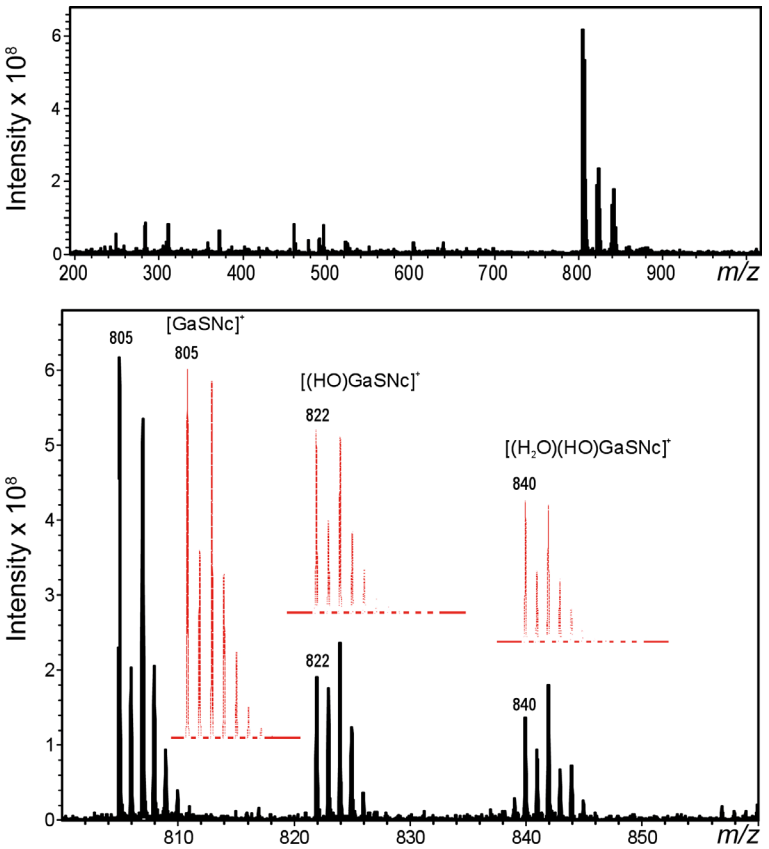


Fig. 1. MALDI-TOF mass-spectrum of the Ga^{III} complex **15a** and comparison of the experimental and calculated isotopic distribution for the molecular ion peaks

thionaphthene moieties. The symmetry of four possible randomers is C_{4h}, C_{2v}, C_s or D_{2h} (see Chart 2) and therefore two LUMO is not degenerated. Indeed, the Q-band for the metal complexes [MSNcBu$_4$] and [MSNcBu$_4$] (**13**–**16**) is broader than for the symmetrical metal porphyrazines [MPA] and phthalocyanines [MPc], and the splitting of the Q-band is definitely seen for the Mg^{II} complex **13a** (658 and 670 nm in pyridine), for the Al^{III} complex **14a** [(HO)AlSNc] (670 and 678 nm in pyridine) and for the Ga^{III} complex **15a** [(HO)GaSNc] (677 and 684 nm in chloroform). A similar situation was observed [36] for the Mg^{II} complex of 1,2-naphthalocyanine [$Mg^{1,2}$Nc] containing "angularly" fused naphthalene units. Four randomers of this latter species were separated chromatographically and distinguished by slight differences in the Q-band maximum position and its splitting (up to 4 nm) taking into account the theoretical prediction of the Q-band splitting values [37]. In our case, although we have observed some spectral differences in the successively eluted fractions of the broad band during column chromatography, the effective separation of the individual randomers was not achieved. The observed splitting of the Q-band for [MSNc] does not exceed 12 nm, indicating that effective symmetry of the π-chromophore in metal complexes is only slightly lower than D_{4h}. This is unlike the free-bases [H_2SNc] (**12a**) and [H_2SNc^{t}Bu$_4$] (**12b**) which, due to the presence of the inequivalent pyrrole and pyrrolenine units, have effective symmetry of the π-chromophore close to D_{2h} and, as can be seen from Fig. 2, exhibit considerable splitting of the Q-band into two components (629 and 694 nm for **12a** and 653 and 702 nm for **12b** in $CHCl_3$).

As can be seen from the data presented in Table 1, the Q-band maxima for the free-bases of the thianaphthene annulated porphyrazines **12a,b** and their metal complexes **13–16** is shifted bathochromically by *ca.* 80 nm as compared to the corresponding β-unsubstituted or *tert*-butyl-substituted of porphyrazines ([MPA] and [MPA^{t}Bu$_4$], M = 2H, Mg^{II}) and by 30–40 nm as compared to the octaphenyl substituted species ([MPAPh$_8$] M = 2H, Mg, ClAl^{III}, ClGa^{III} and ClIn^{III} [38, 39]). Such bathochromic shift is a typical consequence of the extension of π-chromophore by annulation of peripheral aromatic fragments [34]. The bathochromic shift of the Q-band ($\Delta\lambda_Q$) caused by 2,3-fusion of four 10π-electron thianaphthene moieties ($\Delta\lambda_Q$ = 79 nm for [H_2SNc]) is larger than the effect of four 6π-electron thiophene rings ($\Delta\lambda_Q$ = 59 nm for [$H_2^{2,3}$ThPA] [17]), but comparable with annulation of benzene rings in phthalocyanines ($\Delta\lambda_Q$ *ca.* 80 nm for [H_2Pc] [35, 40]. The spectral data available for the Mg^{II} complexes indicate that the bathochromic shift upon 2,3-fusion of four thianaphthene fragments ($\Delta\lambda_Q$ = 86 nm for [MgSNc]) is slightly less that the effect of isoelectronic 1,2-fusion of the naphthalene rings ($\Delta\lambda_Q$ = 96-107 nm for [$Mg^{1,2}$Nc] [36]), but much less that the effect of 2,3-nahthalene annulation ($\Delta\lambda_Q$ = 190 nm for [$Mg^{2,3}$Nc] [41]). These facts show that benzene rings of the thionaphthene units are not effectively involved in conjugation with the central porphyrazine π-chromophore. This is due to the "angular" type of annulation also observed in 1,2-naphthalocyanines. Smaller bathochromic shift for [MSNc] as compared to [$M^{1,2}$Nc] species is consistent with the electron-withdrawing effect of the more electronegative S-atom as compared to the ethylene CH=CH unit.

The maximum of the Q-band for the In^{III} complexes is shifted slightly bathochromically as compared with the Mg^{II}, Al^{III} and Ga^{III} complexes. This is typical for complexes of porphyrazines [MPAPh$_8$] [38, 39] and phthalocyanines [MPc] [35, 42] (see Table 1) and can be explained by larger ionic radius of In^{III} which causes doming of the macrocyclic ligand and destabilization of its HOMO.

The broad absorption band in the UV-region has maximum at 320–340 nm and maximum or shoulder

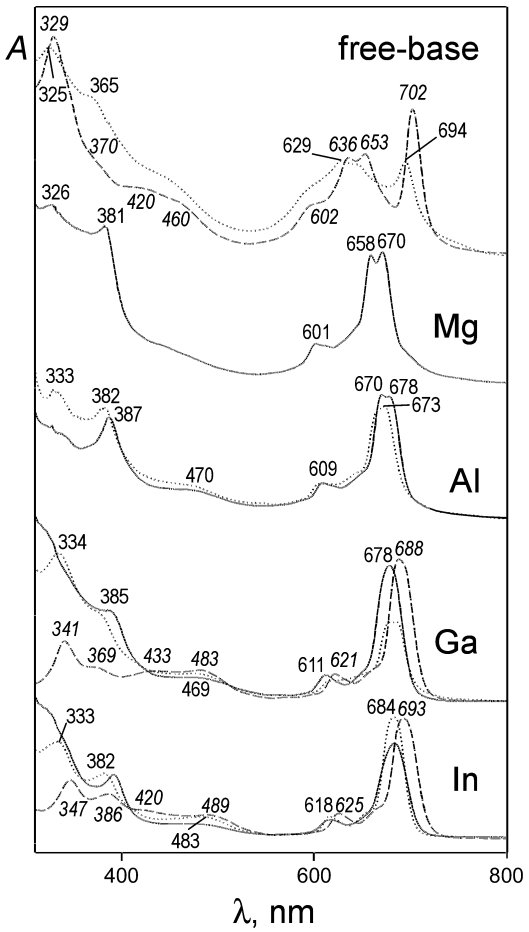


Fig. 2. UV-vis spectra of tetra(2,3-thianaphtheno)porphyrazines **12a**–**16a** (solid and dotted lines) and **12b**, **15b**, **16b** (dashed lines) in pyridine (solid lines) and in chloroform (dotted and dashed lines). Absorption maxima for *tert*-butyl substituted porphyrazines **12b**, **15b**, **16b** are given in italics

at 380–390 nm. The latter can be assigned to the porphyrazine Soret band due to strongly mixed transitions from the lower lying occupied π-MOs to LUMO. Indeed for unsubstituted porphyrazines the Soret band appear near 330 nm (326 nm in [MgPA] [43]), but shifted bathochromically upon introduction of substituents in pyrrole rings (376 nm for [MgPAPh$_8$] [44]) and/or extention of the conjugated π-system by annulation (377–381 nm for [Mg^{1,2}Nc] [36]). In the spectra of metal porphyrazines and phthalocyanines only single maximum is present in the 300–400 nm region. The second UV maximum observed for [MSNc] at 320–340 nm can be therefore assigned to the π-π* transitions localized on the thionaphthene fragments. The broad lower intensity absorption at 450–500 nm can be tentatively assigned to the charge transfer from thionaphthene units to the central porphyrazine macrocycle.

CONCLUSION

We have modified and improved the procedure for the preparation of thianaphthene-2,3-dicarbonitriles — the key intermediates for template synthesis of thianaphthene annulated porphyrazines. This allows us to prepare the symmetrical tetra(2,3-thianaptheno)porphyrazine, its tetra-*tert*-butyl substituted derivative and their complexes with Mg^{II}, Al^{III}, Ga^{III} and In^{III}, which were spectroscopically chasracterized. It is shown that the extension of the porphyrazine π-chromophore by annulation of four thianaphthene fragments have only a moderate effect on its spectral properties which is comparable with fusion of four benzene rings in phthalocyanines. This is due to the angular type of their annulation (similar to that found in 1,2-naphthalocyanines) and negative inductive effect of the sulfur atoms. The effect of thianaphthene annulation on the acid-base properties of porphyrazine macrocycle and on the non-linear spectral properties (optical limiting) is currently under investigation. Our interest on new classes of annulated porphyrazines is also related to possibilities of further structural modification of thianaphthene fragments.

Table 1. Position of the Q-band (λ_{max}, nm) in the UV-vis spectra of tetra(2,3-thianaphtheno)porphyrazines [MSNc] and related porphyrazine, phthalocyanine and naphthalocyanine analogues

Porphyrazine	2H	Mg^{II}	Al^{III}	Ga^{III}	In^{III}	Reference
[MPA]	545, 617[a]	584[b]				[43]
[MPA^{t}Bu$_4$]	547, 620[c]	591[c]				[35]
[MPAPh$_8$]	599, 664[d]	637[d]	636[e]	636[e]	642[e]	[38, 40, 44]
[MPc]	665, 698[a]	675[f]	691[g]	700[g]	690[d]	[35, 40, 42]
[MPc^{t}Bu$_4$]	668, 703[g]	678[h]	683[i]	689[j]	697[d]	[35, 42]
[M^{2,3}Nc]	780[g]	776[g]	815[g]	815[g]	823[d]	[19, 42]
[M^{1,2}Nc]		678, 691[i,k]	694[l]	703[l]		[35, 36]
[MSNc]	629, 642, 694[d]	658, 670[f]	670, 678[f]	678[f]	683[f]	this work
[MSNc^{t}Bu$_4$]	636, 653, 702[d]		684[d]	688[d]	693[d]	this work
[M^{2,3}ThPA]	632, 676[m]					[17]

[a]Chlorobenzene. [b]MeOH. [c]Hexane. [d]$CHCl_3$. [e]CH_2Cl_2. [f]Pyridine. [g]1-Chloronaphthalene. [g]*iso*-AmOH. [i]DMSO. [j]Methyl methacrylate. [k]D_{2h} randomer. [l]o-Dichlorobenzene. [m]Tetrahydrofurane.

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