Synthesis, Acid–Base Properties, and Deselenation of 5,6,8,9,11,12-Hexakis(4-*tert*-butylphenyl)[1,2,5]selenadiazolo[3,4-*b*]porphyrazine

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Received October 1, 2012

Abstract—Cross cyclotetramerization of bis(4-*tert*-butylphenyl)fumaronitrile with 1,2,5-selenadiazole-3,4-dicarbonitrile in the presence of magnesium butoxide as template afforded a mixture of magnesium(II) porphyrazine complexes, from which magnesium complex of 5,6,8,9,11,12-hexakis(4-*tert*-butylphenyl)[1,2,5]selenadiazolo[3,4-*b*]porphyrazine was isolated by column chromatography and was subjected to demetalation on treatment with trifluoroacetic acid. The free ligand was found to undergo protonation at one *meso*-nitrogen atom in acid medium and deprotonation of one pyrrole ring to form monoanion by the action of bases. Reductive deselenation of the title compound with formation of vicinal diamino porphyrazine was studied by spectral and kinetic methods, and a mechanism involving two hydrosulfide ions was proposed.

DOI: 10.1134/S1070428013060195

Owing to specific electronic structure and unique spectral properties phthalocyanines are widely used as dyes and pigments and basic materials for various electronic, photoelectronic, and optical devices [1, 2] and are promising as materials for nonlinear optics [3]. agents for diagnostics and photodynamic therapy of cancer [4, 5], sensors [6], and catalysts [7]. Low-symmetry porphyrazines that may be regarded as analogs of phthalocyanines exhibit a broad spectrum of properties due to the presence of different substituents in a single molecule [8]. A combination of donor aryl and/or alkyl groups with acceptor electron-deficient aromatic heterocycles, such as pyridine, pyrazine, and 1,2,5-thia- and selenadiazole, seems to be appropriate. Introduction of aryl (alkyl) groups enhances the solubility in organic solvents, whereas fusion of the above listed heterocycles strongly affects physicochemical properties of the porphyrazine macroring [9, 10]. Porphyrazines with fused 1,2,5-chalcogenadiazole rings were recently found to possess valuable properties which make them promising as materials for organic electronics [11, 12] and solar energy converters [13]. In recent years increasing attention is given to the synthesis and properties of low-symmetry porphyrazines containing 1.2.5-selenadiazole fragments [14-18]. Interest in these compounds is determined by the possibility for their transformation into chemically active

vicinal aminoporphyrazines [19] and their derivatives [20, 21], including those having peripheral chelating centers [22, 23], which may be used in the design of complex multimetal molecular systems with unusual magnetic and optical properties. On the other hand, the reductive deselenation reaction itself remains poorly studied, which restricts the scope of its practical applications.

We were the first to synthesize magnesium(II) complex of 5,6,8,9,11,12-hexakis(4-*tert*-butylphenyl)-[1,2,5]selenadiazolo[3,4-*b*]porphyrazine (MgPASe, **IV**) and the corresponding free ligand H₂PASe (**V**) (Scheme 1) and study their spectral properties in different media and reductive deselenation by the action of hydrogen sulfide.

Because of the low reactivity of *tert*-butylphenylsubstituted fumaronitrile I in the Linsted macrocyclization, its direct condensation with 1,2,5-selenadiazole-3,4-dicarbonitrile (III) turned out to be unfeasible. The reactivity of dinitrile I was enhanced via transformation into 2-imino-2*H*-pyrrole-5-amine (II) by treatment with ammonia in the presence of a catalytic amount of sodium alkoxide (Scheme 1). Unlike standard procedure for the synthesis of 3,4-substituted 2-imino-2*H*pyrrol-5-amines [24], the reaction was carried out in butan-1-ol rather than in ethylene glycol. In this case, we were able to avoid intermediate isolation of com-

Scheme 1.



pound II, and the latter was directly brought into template cyclotetramerization with dinitrile III. The condensation of compounds II and III could give rise to both symmetric porphyrazine complexes MgPA and MgPASe₄ and four low-symmetry Mg(II) porphyrazines: MgPASe (3:1), *cis*- and *trans*-MgPASe₂ (2:2),





Fig. 1. MALDI-TOF mass spectrum of magnesium(II) complex **IV**. The insert shows the (a) experimental and (b) theoretical isotope distributions in the molecular ion cluster.

and MgPASe₃ (1:3). In order to increase the relative yield of low-symmetry porphyrazine **IV** (MgPASe), initial compounds **I** and **III** were taken at a ratio of 3:1. Fusion of a heterocycle reduces the solubility of Mg(II) porphyrazines and their chromatographic mobility. Symmetric porphyrazine MgPASe₄ is almost insoluble in methylene chloride. By column chromatography of the methylene chloride extract we isolated symmetric octakis(4-*tert*-butylphenyl)porphyrazine MgPA (in the first fraction) whose spectral parameters coincided with those reported in [25] for the condensation product obtained directly from dinitrile **I** and magnesium. Low-symmetry Mg(II)-porphyrazine MgPASe (3:1) was eluted with methylene chloride containing 0.5% of methanol.

The MALDI-TOF mass spectrum of **IV** contained the strong molecular ion peak with m/z 1235 and isotope distribution typical of the assumed structure (Fig. 1). Demetalation of **IV** with trifluoroacetic acid in methylene chloride gave the corresponding metalfree porphyrazine H₂PASe (**V**). Likewise, H₂PA was synthesized from MgPA [25].

Figure 2 shows the ¹H NMR spectra of porphyrazine V in CDCl₃ and of its Mg(II) complex IV in



Fig. 2. ¹H NMR spectra of (a) porphyrazine V in CDCl₃, (b) magnesium complex IV, and (c) product of deselenation of the latter with hydrogen sulfide in C_5D_5N ; residual proton signals are marked with an asterisk, and signals from associates, with a number sign.

pyridine- d_5 . Complex IV in non-coordinating solvents (chloroform, benzene) at a concentration of higher than 1 mg/ml is strongly associated. The spectra contain signals from three types of *tert*-butylphenyl groups (A-C), which is consistent with the 3:1 structure. Signals from protons in the two A rings nearest to the 1,2,5-selenadiazole ring appear in a stronger field than those in B and C; signals from the latter were essen-

tially overlapped by each other, especially in the aromatic region. The inner NH protons in V resonated in a strong field, at -1.58 ppm (Fig. 2).

The number and structure of heterocyclic fragments, as well as the site of their fusion to porphyrazine macroring, strongly affect the macrocyclic π -chromophore [15, 26]. Therefore, structurally different porphyrazines can be reliably distinguished by



Fig. 3. Electronic absorption spectra of (a) symmetric porphyrazines H_2PA and MgPA and (b) low-symmetry [1,2,5]selenadiazoloporphyrazines H_2PASe (V) and MgPASe (IV) in methylene chloride; the spectra of the free ligands are shown with solid curves, and those of the magnesium complexes, with dashed curves.

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Fig. 4. Spectrophotometric titration of a solution of H_2PASe (**V**) in methylene chloride with CF₃COOH (c = 0-0.3 M).



Fig. 5. Spectrophotometric titration of a solution of H_2PASe (V) in THF with Bu_4NOH (c = 0-0.5 mM).

their electronic absorption spectra, and electronic spectroscopy ensures express monitoring of chromatographic separation of porphyrazine mixtures.

The electronic absorption spectrum of the magnesium(II) complex of symmetric octakis(4-*tert*-butylphenyl)porphyrazine MgPA contains a single narrow Qband in the visible region (λ_{max} 642 nm; Fig. 3a), which is typical of D_{4h} -symmetric porphyrazine complexes. Next eluted low-symmetry complex **IV** displayed a double Q band with its maxima at λ 614 and 681 nm (Fig. 3b) due to lower symmetry ($C_{2\nu}$) of the π -chromophore in which the lower unoccupied molecular orbitals become non-degenerate as a result of sta-

bilization of one of them [16, 17]; splitting of the Q band into Q_x and Q_y components is characterized by $\Delta E(Q) = 15\overline{28} \text{ cm}^{-1}$. Demetalation of the symmetric Mg(II) porphyrazine complex MgPA to H₂PA reduces the molecular symmetry to D_{2h} , and the Q band is also split into two components due to lifting of the LUMO degeneracy [λ_{max} 671 and 605 nm, $\Delta E(Q) = 1626 \text{ cm}^{-1}$; Fig. 3a]. Demetalation of IV (MgPASe) with formation of V (H₂PASe) increases the $\Delta E(Q)$ value to 2896 cm⁻¹ $(\lambda_{max}$ 700 and 582 nm; Fig. 3b). In keeping with the theoretical calculation data for the 1,2,5-thiadiazole analog [15, 17], this may be rationalized by some stabilization of the HOMO and stronger stabilization of the LUMO, the energy of the LUMO+1 changing only slightly. In all cases, the spectra of pure porphyrazines displayed a red shift of the long-wave Q-band component by 20-30 nm as a result of polarization of the π -chromophore arising from the appearance of pyrrole and dihydropyrrole fragments. The *Q* band maxima in the spectra of 4-tert-butylphenyl-substituted porphyrazines, both low-symmetric IV and V and symmetric MgPA and H₂PA, are displaced toward longer wavelengths by 4-10 nm as compared to phenvl-substituted analogs due to electron-donating effect of tert-butyl groups [15, 17].

Porphyrazines act as multicenter ampholytes in acid-base processes, and their electronic absorption spectra in acidic or basic medium essentially differ from those in neutral solvents. Complex IV in acidic medium undergoes fast demetalation, so that its spectrum becomes similar to the spectrum of V, which in turn strongly depends on the acidity.

The acid-base properties of porphyrazine V were estimated by spectrophotometric titration with a solution of trifluoroacetic acid in methylene chloride (Fig. 4). Increase in the acidity was accompanied by increased splitting of the Q band via red shift of its long-wave component Q_x by 838 cm⁻¹, while the position of the Q_v component remained almost unchanged. Analogous spectral variations are typical of protonation of meso-nitrogen atom in the porphyrazine macroring [27, 28]; they were also observed for both symmetric [29, 30] and unsymmetric β-aryl-substituted porphyrazines [31]. The concentration stability constant of the protonated form of H₂PASe (V) ($pK_a 0.82 \pm$ 0.01) is lower than that found for symmetric porphyrazine H_2PA and its β -phenyl-substituted analog H_2PAPh_4 (p $K_a \sim 1.1$ [30]); this indicates reduction of the basicity of the meso-nitrogen atoms upon introduction of a fused 1,2,5-selenadiazole fragment, despite

the presence of electron-donor *tert*-butyl groups in the benzene rings.

Figure 5 illustrates spectrophotometric titration of a solution of H₂PASe in tetrahydrofuran with tetrabutylammonium hydroxide. Addition of base reduces the magnitude of splitting of the Q band, but the spectral pattern differs from that observed for MgPASe which is the Mg(II) complex with macrocyclic dianion (Fig. 3b). Presumably, the titration with base yields not dianion PASe^{2–} but monoanion HPASe[–] where the proton is likely to reside on one of β -*tert*-butyl-substituted pyrrole ring.

Deselenation of 1,2,5-selenadiazoles by the action of various reducing agents (H₂S, Na₂S₂O₄, HI) provides a synthetic route to vicinal diamines, e.g., substituted phenylenediamines [32]. Deselenation of the 1,2,5-selenadiazole fragment fused to porphyrazine macroring smoothly occurred upon treatment with hydrogen sulfide in pyridine and afforded porphyrazinamines [19]. Therefore, [1,2,5]selenadiazoloporphyrazines attract interest as convenient precursors of vicinal porphyrazinediamines which are promising as ligands for the preparation of multimetal complexes [22, 23]. However, the reductive deselenation reaction remains poorly studied, in particular, the role of the nature of the reducing agent and solvent is unclear. With a view to elucidate the mechanism of deselenation, we examined the kinetics of the reaction of H_2PASe (V) and its Mg(II) complex MgPASe (IV) with hydrogen sulfide in pyridine and pyridine-methylene chloride mixtures. Figure 6 shows variations in the electronic absorption spectra in the course of reductive deselenation of compounds IV and V.

It is seen that the reactions are accompanied by considerable changes in the spectral patterns in the visible region: narrow Q_x and Q_y bands typical of the initial compounds disappear, and broadened Q bands appear with their maxima at λ 649 nm for complex IV and λ 576 nm for free ligand V; in both cases, a shoulder at λ 610–620 nm was observed. The distinct isosbestic points indicate participation of two spectrally distinguishable species. The electronic absorption spectra of the resulting porphyrazinediamines H₂PA(NH₂)₂ and MgPA(NH₂)₂ are analogous to those of bis(dimethylamino)-substituted hexapropylporphyrazine H₂PAPr₆(NMe₂)₂ [33].

The product of the reaction of MgPASe (IV) with hydrogen sulfide in pyridine displayed in the ¹H NMR spectrum a new signal at δ 5.67 ppm, which may be



Fig. 6. Spectrophotometric monitoring of the reductive deselenation of (a) MgPASe (**IV**) and (b) H₂PASe (**V**) with hydrogen sulfide ($[H_2S] = 7.62$ and 0.22 mM, respectively) in pyridine.



Fig. 7. Plot of $\ln(c/c_0)$ versus time for the reaction of MgPASe (**IV**) with hydrogen sulfide in pyridine. Hydrogen sulfide concentration: (1) 1.02, (2) 0.762, (3) 0.508, (4) 0.254, (5) 0.152, and (6) 0.044 mM.

[Py], M	[H ₂ S], mM	$k_{\rm obs},{ m s}^{-1}$
12.36 (100%)	0.152	$0.00156 {\pm} 0.00001$
	0.254	0.00459 ± 0.00001
	0.508	$0.01439 {\pm} 0.00003$
	0.762	$0.0254 {\pm} 0.0001$
	1.02	0.0404 ± 0.0003
4.95	2.94	$0.00120 {\pm} 0.00001$
	5.88	0.00399 ± 0.00004
	8.82	$0.00737 \!\pm\! 0.00009$
	11.8	0.0151 ± 0.0003
	14.7	0.0196 ± 0.0005
1.24	8.82	0.000812 ± 0.00001

Table 1. Observed rate constants (k_{obs}) for the reaction of magnesium(II) complex IV with hydrogen sulfide in pyridine–methylene chloride at 20°C

assigned to protons of the amino groups in MgPA(NH₂)₂ (Fig. 2c). Insofar as porphyrazinediamines MgPA(NH₂)₂ and H₂PA(NH₂)₂ are very readily oxidized on exposure to air, we failed to isolate them from solution. Increased sensitivity to photooxidation with atmospheric oxygen was also noted for ZnPAPr₆(NMe₂)₂ [34]; moreover, it was shown that the complex itself acts as sensitizer in the generation of singlet oxygen.

The kinetics of the reductive deselenation of porphyrazines IV and V were studied in pyridine or its mixtures with methylene chloride using 10 to 1000 equiv of hydrogen sulfide, i.e., under pseudofirstorder reaction conditions. The linear plot of $\ln(c_0/c)$ versus time (Fig. 7) indicated the first order of the reaction in porphyrazine (c), so that the observed rate constant k_{obs} was calculated by the formula

$$k_{\rm obs} = (1/\tau) \ln(c_0/c).$$

Table 2. Observed rate constants (k_{obs}) for the reaction of porphyrazine V with hydrogen sulfide in pyridine at 20°C

[H ₂ S], mM	$k_{ m obs},{ m s}^{-1}$
0.56	$0.0384 {\pm} 0.0007$
0.45	$0.0164 {\pm} 0.0001$
0.34	$0.0147 {\pm} 0.0001$
0.22	$0.00764 {\pm} 0.00004$
0.11	0.00191 ± 0.00001
0.056	$0.000287 {\pm} 0.000001$

The ratio c_0/c was determined from the variation of the optical density A_1 at the absorption maximum of the initial porphyrazine. The experimental values of k_{obs} for MgPASe (**IV**) and H₂PASe (**V**) are given in Tables 1 and 2, respectively.

The log dependences of k_{obs} on the concentration of H₂S are linear (Figs. 8a, b), and their slopes correspond to the second order with respect to hydrogen sulfide. We also examined the effect of the concentration of pyridine on the deselenation of magnesium complex **IV** and found the second order with respect to pyridine (Fig. 8c).

Taking into account that the deselenation process requires the presence of a base (pyridine) and that the orders of the reaction with respect to pyridine and hydrogen sulfide are similar, the reactive species is likely to be hydrosulfide ion HS⁻ which is more nucleophilic than H₂S molecule. The kinetic data allowed us to propose a mechanism shown in Scheme 2. In the first reversible step, hydrosulfide ion is coordinated to the selenium atom in a way similar, e.g., to the reaction of dinitrile III with benzenethiolate ion [35], the 1.2.5-selenadiazole aromatic system remaining intact. The second, rate-determining step implies rupture of the aromatic system due to addition of the second hydrosulfide ion, and the subsequent reaction with pyridinium ion as proton donor yields final porphyrazinediamine.

The proposed scheme was qualitatively verified by the following experiment. Complex IV was dissolved in a neutral solvent (THF), and the solution was saturated with hydrogen sulfide. According to the electronic absorption spectrum, no deselenation was observed at this step. A solution of Bu_4NOH was then



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 $\log k_{obs}$

n = 2.00

-1.0

added to the mixture, and its electronic spectrum changed in a way similar to that shown in Fig. 6a. This indicated reductive deselenation by the action of hydrosulfide ion.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi U-2000 spectrophotometer from solutions with a concentration of 10^{-5} to 10^{-6} M using quartz cells with a cell path length of 1 cm. The mass spectra (MALDI-TOF) were recorded on a Bruker Daltonics Ultraflex mass spectrometer. The ¹H NMR spectra were obtained on a Bruker AM-500 instrument. Commercial reagents (Aldrich, Merck, Reakhim) were used for the syntheses and chromatographic separations. Methylene chloride was distilled over K₂CO₃, and butan-1-ol was purified by azeotropic distillation and by treatment with metallic sodium. Dinitriles I [24] and III [19] were synthesized by known methods.

[5,6,8,9,11,12-Hexakis(4-tert-butylphenyl)[1,2,5]selenadiazolo[3,4-b]porphyrazinato]magnesium (MgPASe, IV). Gaseous ammonia was bubbled over a period of 2 h through a boiling suspension of 2.5 g (0.007 mol) of bis(4-tert-butylphenyl)fumaronitrile (I) in 60 ml of anhydrous butan-1-ol containing ~15 mg of sodium to obtain a light green solution of iminopyrrolamine II. Simultaneously, 60 mg of magnesium turnings was dissolved under stirring in 50 ml of thoroughly dried butan-1-ol on heating under reflux. The solution of magnesium butoxide was cooled to room temperature and mixed with the solution of II, 0.67 g (0.003 mol) of 1,2,5-selenadiazole-3,4-dicarbonitrile (III) was added, and the mixture was heated for 6 h under reflux with vigorous stirring. The mixture was cooled and evaporated, the residue was extracted with methylene chloride, and the products were separated by column chromatography on aluminum oxide (gradient elution with methylene chloride-methanol). The first fraction eluted with methylene chloride contained Mg(II) complex of symmetric octakis(4-tertbutylphenyl)porphyrazine (MgPA), and from the second fraction eluted with methylene chloride containing 0.5% of methanol we isolated low-symmetry Mg(II) complex MgPASe (IV). Yield 10% of the overall amount of Mg(II) porphyrazines. ¹H NMR spectrum (pyridine- d_5), δ , ppm: 1.35 s (18H), 1.46 s (18H), 1.51 s (18H), 7.75 d (4H, ${}^{3}J$ = 7.9 Hz), 7.79 d (4H, ${}^{3}J$ = 7.9 Hz), 7.80 d (4H, ${}^{3}J = 7.9$ Hz), 8.69 d (4H, ${}^{3}J =$ 8 Hz), 8.71 d (8H, ${}^{3}J = 8$ Hz). Electronic absorption spectrum (CH₂Cl₂), λ_{max} , nm (log ϵ): 370 (4.44), 615 (4.05), 681 (4.29).

6.0 6.1 6.2 6.3 6.4 6.5 6.6 6.7 log[Py **Fig. 8.** Log dependences of k_{obs} on the concentration of (a, b) hydrogen sulfide and (c) pyridine for the deselenation of (a) porphyrazine **V** and (b, c) its magnesium complex in (a, b) pyridine and (c) pyridine–methylene chloride ([H₂S] = 8.82 mM) at 20°C.



(a)

5,6,8,9,11,12-Hexakis(4-*tert*-butylphenyl)[1,2,5]selenadiazolo[3,4-*b*]porphyrazine (H₂PASe, V). Complex IV, 0.1 g (0.081 mmol), was dissolved in 20 ml of a 10% solution of trifluoroacetic acid in methylene chloride, the solvent was evaporated at room temperature, the dry residue was dissolved in 30 ml of methylene chloride, the solution was filtered, and the solvent was removed. Yield 98%. ¹H NMR spectrum (CDCl₃), δ, ppm: -1.58 (2H), 1.54 s (18H), 1.55 s (36H), 7.63 m (8H), 7.77 d (4H, ³J = 7.9 Hz), 8.26 d (4H, ³J = 7.9 Hz), 8.36 d (8H, ³J = 7.9 Hz). Electronic absorption spectrum (CHCl₃), λ_{max}, nm (log ε): 348 (4.61), 367 (4.60), 582 (4.31), 700 (4.73).

The acid-base properties of porphyrazine V in CH_2Cl_2 -CF₃COOH were studied by spectrophotometric titration [30, 31].

The kinetic measurements were performed under pseudofirst-order reaction conditions using a large excess of hydrogen sulfide relative to porphyrazines IV and V. A solution of hydrogen sulfide was prepared by saturation of cold pyridine with dry H₂S. The amount of absorbed H₂S was determined by the gain in weight, and the solution was then diluted with pyridine and/or methylene chloride to a required concentration and used within 24 h. Solutions of porphyrazines IV and V and hydrogen sulfide were adjusted to 20°C and mixed, and the progress of the deselenation reaction was monitored by spectrophotometry, following the absorbance at λ 700 nm for V and at λ 680 nm for Mg(II) complex IV.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 10-03-01069-a).

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