New polydentate macrocyclic ligands of hybrid amine-imine and amide-imine types as artificial anion receptors. Synthesis and study of anion binding

*E. A. Katayev,[a] G. D. Pantos,[b] V. M. Lynch,[b] J. L. Sessler,[b] M. D. Reshetova,[a] and Yu. A. Ustynyuk[a]**

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation. Fax: +7 (095) 939 2677. E-mail: ustynyuk@ nmr.chem.msu.su*

[b]*Department of Chemistry and Biochemistry and Institute for Cellular and Molecular Biology, University of Texas at Austin, 1 University Station, A5300 Austin, Texas, 78712-0165, USA. Fax: (+1) 51 2471 7550. E-mail: sessler@mail.utexas.edu*

Three new macrocyclic Schiff bases containing an amine or amide structural fragment along with imine groups were synthesized by condensation of 2,6-bis(2-aminophenyliminomethyl)pyridine (**1**) and *N*,*N*′-bis(2-aminophenyl)pyridine-2,6-dicarboxamide (**2**) with 2,5-diformylpyrrole (**3**) and 2,2-bis(5-formylpyrrol-2-yl)propane (**4**). The reaction of compound **1** with **3** proceeds abnormally and is accompanied by redox disproportionation of compound **1** in the first step. The structure of the macrocyclic product of this reaction was established by X-ray diffraction analysis. Spectrophotometric titration showed that hybrid macrocycle **10**, which was prepared by condensation of compound **2** with **4**, possesses the properties of an anion receptor and selectively binds hydrosulfate and dihydrophosphate anions in the presence of bromide and nitrate anions. The structures of **10** and its adduct with the hydrosulfate anion were calculated by density functional theory.

Key words: macrocycles, Schiff bases, X-ray diffraction analysis, spectrophotometry, anion receptors, density functional theory.

Selective binding of cations by polydentate, including macrocyclic, ligands (crown ethers and their heteroanalogs) is a classical problem in coordination chemistry. This is an important and often key step in solving many problems of design of supramolecular systems, catalysis, materials science, and numerous analytical applications.[1] The problem of recognition and selective binding of anions through the formation of "anionic crowns" has been formulated many years ago.[1] However, the significance of this problem has become evident only in the last two decades due primarily to the fact that an exceptionally important role of anion binding and anion transport channels in biological systems has been revealed and also because of broad possibilities of using artificial anion receptors as anion sensors to solve many applied analytical problems.[2—4] The design of such receptors is a complicated problem for several reasons. Being bulkier than isoelectronic cations, anions are characterized by a smaller charge to radius ratio, resulting in a decrease in the contribution of Coulomb interactions to their binding. High ability of anions to form hydrogen bonds with protic solvents increases their solvation energies due to which an anion receptor should possess very high affinity for anions to efficiently compete with solvent molecules in such media. Hence, uncharged (neutral) molecular receptors capable of binding anions only through ion-dipole interactions are inefficient. Their anion affinity can be substantially enhanced by introducing amide and pyrrole fragments, which can form strong NH...X hydrogen bonds with a guest anion. Earlier, the US authors of the present paper have been applied this approach to the design of a series of macrocyclic receptors based on calixpyrroles,[5—8] bipyrrole-containing [2]-catenanes,[9] hybrid *o*-phenylenediamine-dipyrromethane macrocycles, and other structural fragments[10,11] possessing very high affinity for halide ions and a number of other anions. In recent years, the Russian authors of the present paper have developed procedures for the synthesis of a series of new macrocyclic and polydentate ligands and their polynuclear complexes with transition metal ions. Since the resulting compounds also contain structural fragments, which can bind anions,[12—16] we decided to initiate a joint research project with the aim of performing systematic investigation of the influence of the ring size, the number and position of functional groups, and the geometry of macrocyclic ligands on their ability to recognize and selectively bind

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various anions. In the present study, we discuss the results of our research. Some of these results have been reported earlier in the brief communication.[17]

Results and Discussion

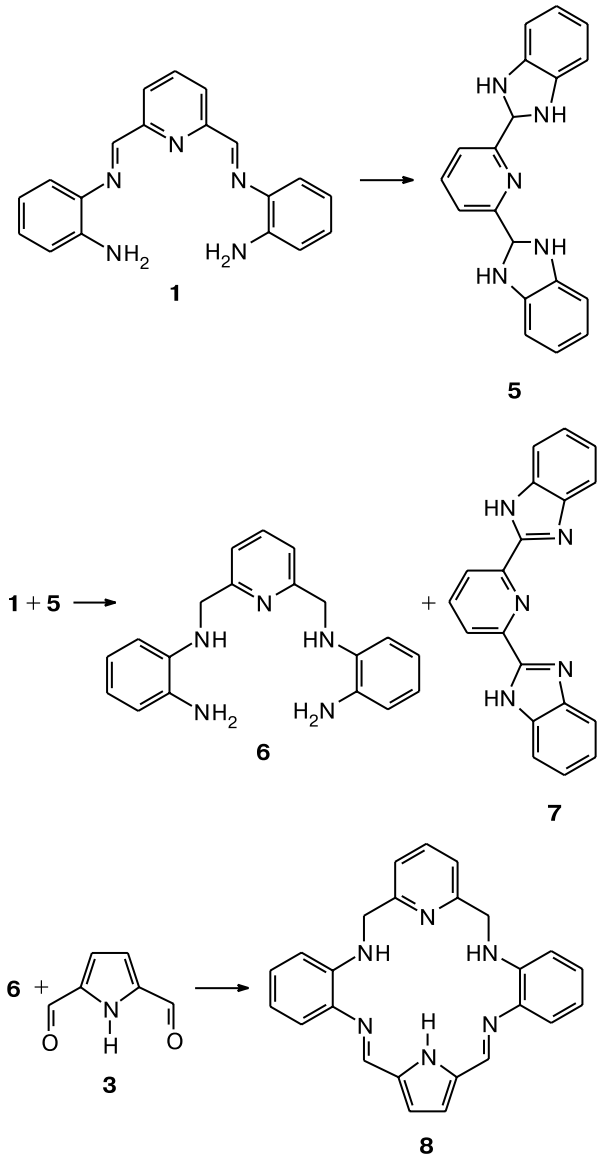
Synthesis of macrocycles

Macrocycles were synthesized by the fragment assembly involving Schiff condensation in the final step. We used 2,6-bis(2-aminophenyliminomethyl)pyridine[15] (**1**), which we have synthesized recently, and *N*,*N*′-bis(2-aminophenyl)pyridine-2,6-dicarboxamide[18] (**2**) as diamine components of building blocks (precursors). The pyridine-2,5-dicarboxamide fragment capable of forming hydrogen bonds with oxygen-containing anions has been used earlier in other anion receptors.[19,20] Diamine **1** contains two imine fragments, which can coordinate hydrosulfate, hydrophosphate, and dihydrophosphate ions through hydrogen bonds and also coordinate most of other anions upon protonation of the imine nitrogen atoms.

We used 2,5-diformylpyrrole (**3**) and 2,2-bis(5-formylpyrrol-2-yl)propane[21] (**4**), which is the main structural fragment of calixpyrroles,[5–8] as dicarbonyl components. Hybrid macrocycles containing these precursors as structural fragments have considerable promise as efficient anion receptors primarily for oxygen-containing tetrahedral anions.

Attempts to perform condensation of diamine **1** with 2,5-diformylpyrrole (**3**) in the presence of protic acids led only to oxidation of **1** (Scheme 1) giving rise to 2,6-bis(benzimidazolyl)pyridine (**7**). However, refluxing of **3** with diamine **1** in toluene in the absence of a catalyst afforded, along with **7**, partially reduced macrocycle **8** in 20% yield. Earlier, we have observed analogous partial reduction upon condensation of 4-alkyl-2,6-diformylphenols with *o*-phenylenediamine.[12,14] The formation of bis-benzimidazolyl derivatives has been described earlier for condensation products of *o*-phenylenediamines with diformyl derivatives of phenols and pyridines.[12,14,15,22,23] Under the reaction conditions, compound **1** is not involved in condensation with **3** but can rather readily undergo cyclization to 2,6-bis(benzimidazolinyl)pyridine (**5**). The latter is a strong reducing agent. It can reduce both azomethine bonds in **1** giving rise to compound **6**, which is accompanied by oxidation of compound **5** to **7**. Apparently, redox disproportionation is very typical of diamine **1**. More stable disproportionation product **7** is isolated in many reactions, whereas the second product, *viz.*, extremely reactive tetramine **6**, is involved, in the presence of dialdehyde **3**, in a conventional Schiff condensation to form macrocycle **8** (Scheme 1). It should be noted that condensation of **1** with 2,6-diformylpyridine under the same conditions produces a mixture of oligomeric condensation products, as evident from the mass-spectrometric data. This suggests that an ease of proton abstraction from 2,5-diformylpyrrole can facilitate cyclization followed by disproportionation.

Scheme 1



Attempts to perform condensation of bis-azomethine **1** with dialdehyde **4** in various protic (MeOH) and aprotic (CH_2Cl_2, $CHCl_3$, THF) solvents under various conditions, including the use of molecular sieves to remove water, failed.

Compound **8** is unstable in most polar solvents and is readily hydrolyzed even in the presence of traces of water. Compound **8** forms a red-orange crystal solvate with chloroform. The crystal structure of the latter was established by X-ray diffraction analysis (Fig. 1). Selected bond lengths, bond angles, and dihedral angles are given in Table 1.

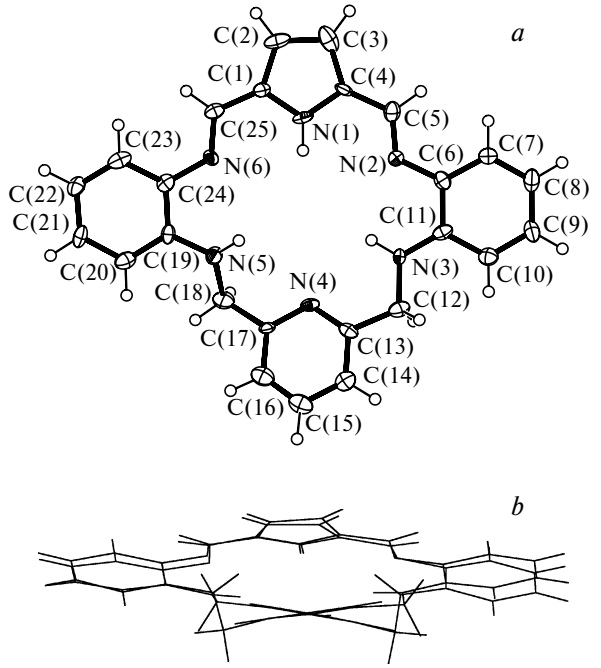


Fig. 1. *a*. Molecular structure of compound **8** determined by X-ray diffraction. The atoms are represented by anisotropic displacement ellipsoids at the 50% probability level. *b*. A projection of a superposition of two molecules in the unit cell.

X-ray diffraction study demonstrated that molecule **8** is nonplanar. The unit cell contains two molecules in different conformations, which are not linked to each other by hydrogen bonds. These molecules can be considered as an image and a mirror image (see Fig. 1, *b*). In each molecule, the plane of the pyridine moiety forms an angle of 24° with the mean plane passing through the pyrrole and phenyl rings. For the molecules of two types,

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **8**

Bond	*d*/Å	Angle	ω/deg
N(1)—C(4)	1.356(7)	N(1)—C(4)—C(3)	107.4(6)
C1)—C(25)	1.419(9)	N(1)—C(4)—C(5)	121.2(6)
C(2)—C(3)	1.406(9)	N(6)—C(25)—C(1)	117.9(7)
N(1)—C(1)	1.359(8)	C(4)—N(1)—C(1)	111.8(6)
N(6)—C(25)	1.287(7)	C(19)—C(24)—N(6)	116.7(6)
N(6)—C(24)	1.415(8)	N(5)—C(18)—C(17)	112.8(6)
N(5)—C(19)	1.387(8)	N(5)—C(19)—C(24)	117.7(6)
N(5)—C(18)	1.432(8)	N(4)—C(17)—C(16)	122.8(7)
N(4)—C(13)	1.313(8)	N(4)—C(17)—C(18)	116.7(6)
N(4)—C(17)	1.337(7)	C(6)—N(2)—C(5)—C(4)	−178.5(6)
C(12)—C(13)	1.514(8)	C(12)—N(3)—C(11)—C(6)	−171.1(6)
C(13)—C(14)	1.408(8)	N(3)—C(12)—C(13)—N(4)	18.5(10)
C(14)—C(15)	1.363(9)	N(4)—C(17)—C(18)—N(5)	−59.7(9)
C(15)—C(16)	1.323(9)	N(5)—C(19)—C(24)—N(6)	3.9(9)
C(16)—C(17)	1.355(8)	C(5)—N(2)—C(6)—C(11)	178.8(6)
C(17)—C(18)	1.531(9)	C(25)—N(6)—C(24)—C(19)	167.2(6)

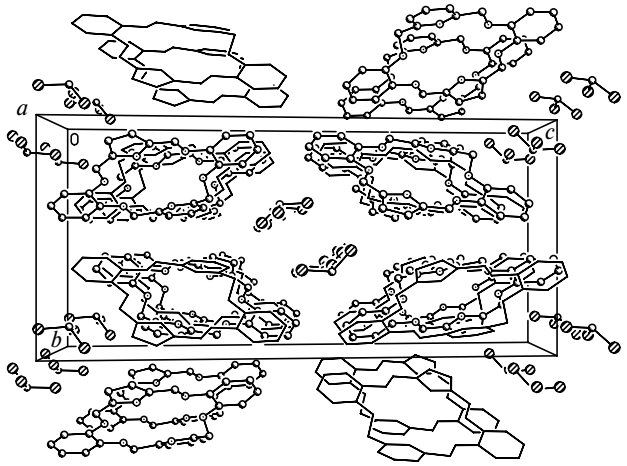
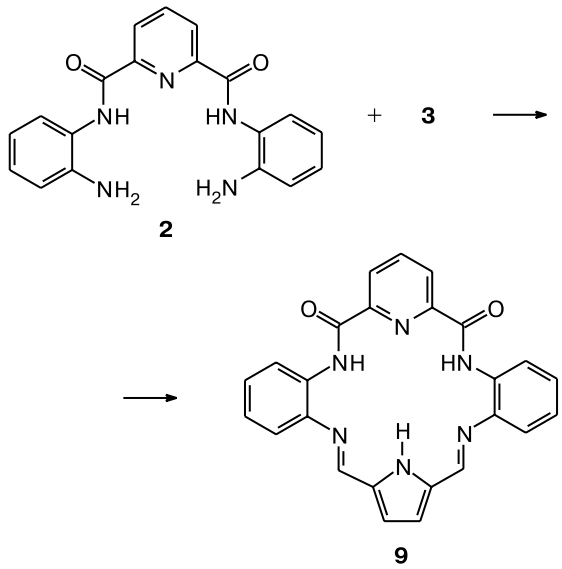


Fig. 2. Molecular packing of **8**. The crystallographic *a* axis is directed inward. The chloroform solvate molecules are disordered and occupy channels running parallel to the *a* axis. The molecules of one type are shown as ball-and-stick models, and the molecules of another type are represented as frames.

the sizes of the inner cavity of the ligand are 5.1 and 5.7 Å. Molecules **8** are asymmetric with respect to the axis passing through the N(1)—N(4) atoms. The $C_{pyrid}—CH_2—NH—C_{arom}$ dihedral angles are strongly different (N(3)—C(12)—C(13)—N(4), 18.5(10)°; N(4)—C(17)—C(18)—N(5), −59.7(9)°). The disordered chloroform solvate molecules are located in channels running parallel to the *a* axis. The molecular packing of **8** is shown in Fig. 2.

Diamide **2** is much more readily involved in Schiff condensation than compound **1**. For example, the reac-

Scheme 2

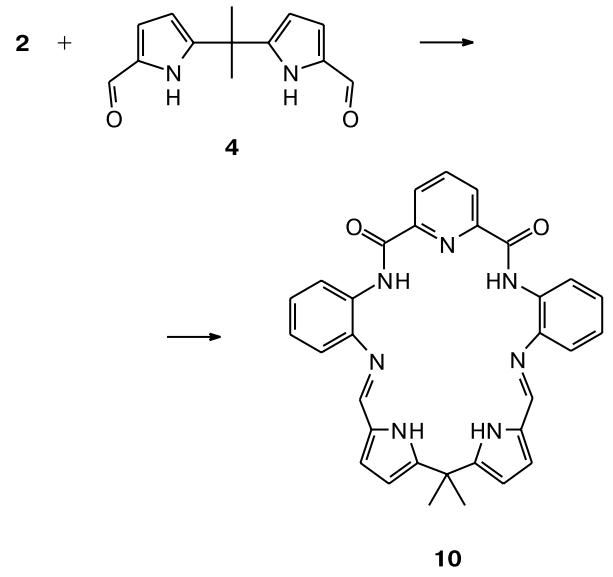


Reagents and conditions: 1) 2 CF_3COOH, MeOH, 20 °C, 24 h; 2) $NaHCO_3$.

tion of 2,5-diformylpyrrole (**3**) with **2** in methanol in the presence of two equivalents of trifluoroacetic acid at room temperature afforded hybrid macrocycle **9** in 64% yield (Scheme 2). After treatment with an aqueous solution of sodium hydrocarbonate, the latter precipitated as pale-yellow crystals.

Under similar conditions, the reaction of **2** with **4** produced hybrid amido-imine macrocycle **10** containing two pyrrole fragments (Scheme 3).

Scheme 3



Reagents and conditions: 1) 2.5 CF_3COOH, MeOH, 64 °C, 15 min; 2) Et_3N.

The highest yield (~90%) was obtained with the use of 2.5 equiv. of trifluoroacetic acid in methanol followed by treatment with triethylamine. The reactions using other acids (HCl, CF_3COOH, HNO_3, H_2SO_4, or H_3PO_4) afforded a precipitate of salt **10** contaminated with various oligomeric products, which hinders isolation and purification of the reaction product.

Determination of stability constants of macrocycle—anion complexes

We studied the reactions of macrocycles **8**, **9**, and **10** with anions by spectrophotometric titration of their solutions in acetonitrile with the corresponding tetrabutylammonium salts according to a standard procedure.[24—26a] The stoichiometry of the resulting ligand—anion complexes was determined from the molar host—guest ratio curves.[26b]

Compounds **8** and **9** do not exhibit affinity for the overall series of anions. The addition of the corresponding salts does not lead to noticeable changes in the UV spectra. Only macrocycle **10** possessing the largest cavity exhibits a noticeable affinity for a series of anions (Table 2). The UV spectral pattern of **10** observed upon titration with tetrabutylammonium hydrosulfate ($TBAHSO_4$) is shown in Fig. 3.

Table 2. Binding constants of anions by macrocycle **10** determined by spectrophotometric titration in acetonitrile

Anion	K_a/mol L^{-1}
Br^-	*
NO_3^-	*
Cl^-	2000±23
CN^-	12000±2500
CH_3COO^-	38000±3000
HSO_4^-	64000±2600
$H_2PO_4^-$	342000±25000; 26000±2500**

* The addition of the corresponding salt of the anion did not lead to a noticeable change in the UV spectrum.

** Successive 2 : 1 (anion—ligand) binding was observed; the binding constants are given for the first and second anion molecules, respectively.

A characteristic feature is that the tetrahedral hydrosulfate and dihydrophosphate anions bind to the macrocycles with the largest stability constants. This selectivity is associated with the ligand geometry providing good binding of these anions. Thus, the ligands have two pairs of NH protons, which can form strong hydrogen bonds with negatively charged oxygen atoms, and two imine fragments capable of coordinating protons of anions. It appeared that the dihydrophosphate anion forms also a 2 : 1 complex. It should be emphasized that compound **10** does not have affinity for the trigonal nitrate anion. The design of artificial anion receptors for binding sulfate in the presence of nitrate is an important problem.[27—37] The necessity of preparing such compounds is associated, in particular, with an important role, which these compounds can play in solving the problem of safe disposal of radioactive wastes. One of the most efficient technologies for disposal of solid low-level radioactive wastes, which are obtained upon evaporation of acidic sulfate nitrate solutions arising from processing of spent fuel elements, involves vitrification by fusion with special composites. However, the presence of sulfates sharply decreases stability of the resulting blocks.[38—41] The necessary separation of sulfates is achieved by precipitation or ion chromatography. After publication of our preliminary results,[17] researchers expected that the use of artificial receptors of type **10** would open up new possibilities in this field.[42]

We confirmed the successive binding of two dihydrophosphate ions by macrocycle **10** in experiments on titration of the latter in the simultaneous presence of hydro-

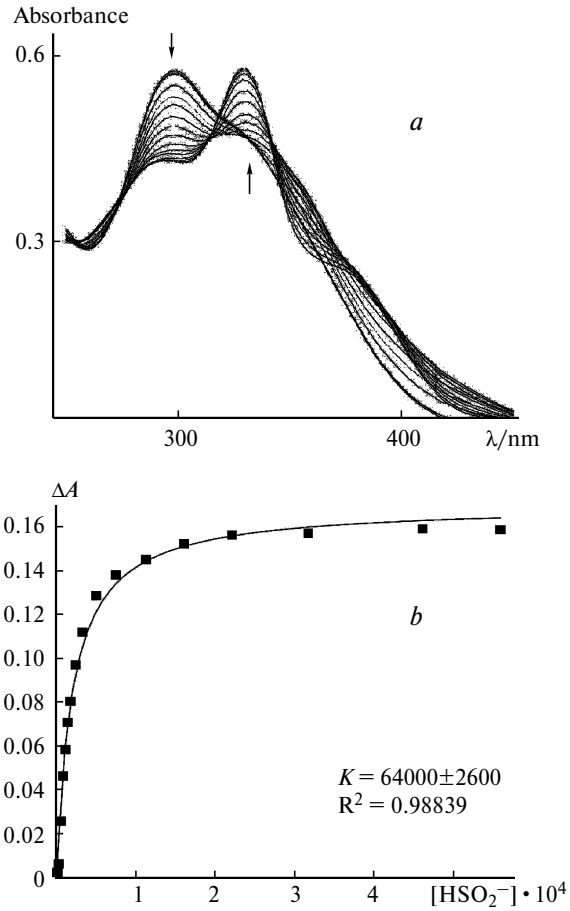


Fig. 3. *a*. Spectrophotometric titration curves of compound **10** with $TBAHSO_4$. *b*. The absorbance change ΔA at λ = 331 nm (dotted line) and the theoretical curve obtained by approximation using the Origin 7.0 program (see the Experimental section).

sulfate and dihydrophosphate ions. Standard titration of compound **10** in an acetonitrile solution with a salt of the dihydrophosphate ion in the presence of 10 equiv. of tetrabutylammonium hydrosulfate did not give rise to a 2 : 1 complex, and the stability constant of the 1 : 1 complex was 15000 mol L^{-1}. Analogous titration of macrocycle **10** with hydrosulfate ions in the presence of 10 equiv. of tetrabutylammonium dihydrophosphate gave the complex with a stability constant of 204 mol L^{-1}. These results suggest that there are two anion-binding centers on the opposite sides of the macrocycle plane.

We failed to grow crystals of complex **10** with the hydrosulfate ion suitable for X-ray diffraction study. In this connection, the character of binding of this anion was studied using quantum-chemical simulation by density functional theory (the nonempirical PBE gradient-corrected functional, the TZ2p extended basis set). The structure of free macrocycle **10** and the principal geometric parameters of the molecule are presented in Fig. 4.

Two projections of the calculated structure of the complex **10** · HSO_4 are shown in Fig. 5.

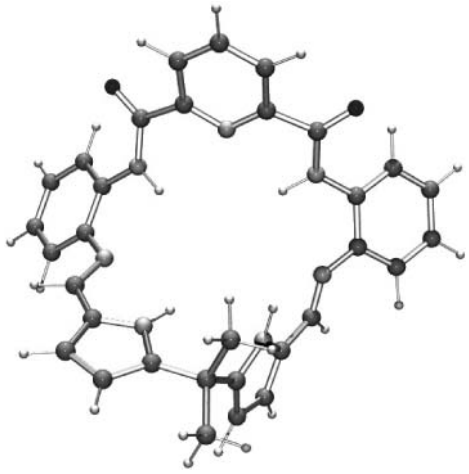


Fig. 4. Structure of free macrocycle **10** calculated by the density functional theory.

Bond	*d*/Å
$N_{pyrrole}$—H	1.020; 1.02
N_{amide}—H	1.01; 1.01
C=N	1.30; 1.30
C=O	1.23; 1.23
$H_{pyrrole}$—H_{amide}	3.67; 4.65; 3.54; 4.83

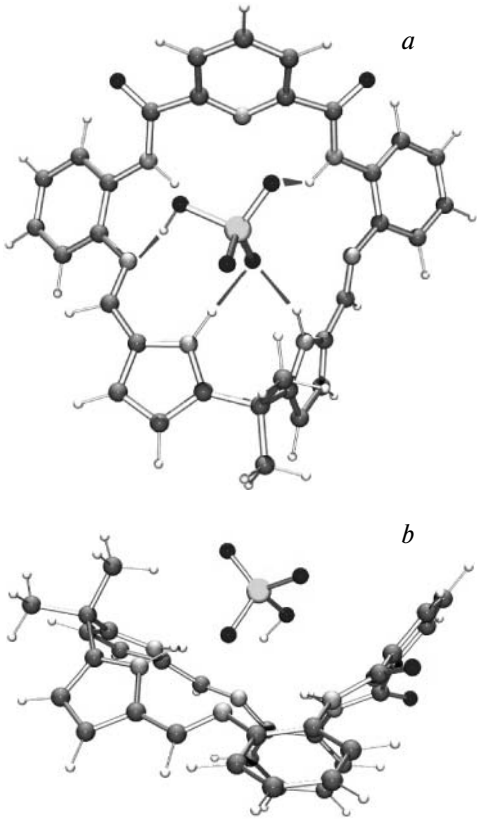


Fig. 5. Structure of the complex **10** · HSO_4 calculated by density functional theory: *a*, a top view; *b*, a side view.

In the complex with the hydrosulfate ion, the macrocycle adopts a more symmetrical conformation. Only three

hydrogen atoms of the ligand are involved in binding. These atoms form hydrogen bonds with three oxygen atoms of the sulfate ion ($d(NH_{pyrrole}...O)$ = 1.74, 1.84 Å; $d(NH_{amide}...O)$ = 2.30 Å). Evidently, the hydrogen bond between the imine nitrogen atom and the hydrogen atom of the hydrosulfate ion ($d(N...H)$ = 2.06 Å) plays an important role in binding. It should also be noted that there is an unusually short contact ($d(O—H_{Me})$ = 2.35 Å) between the hydrogen atom of one methyl group in the *meso* position and the oxygen atom of the sulfate ion.

* * *

To summarize, three new Schiff bases containing simultaneously the imine groups and the amine or amide structural fragment were prepared by condensation of 2,6-bis(2-aminophenyliminomethyl)pyridine (**1**) and *N*,*N*′-bis(2-aminophenyl)pyridine-2,6-dicarboxamide (**2**) with 2,5-diformylpyrrole (**3**) and 2,2-bis(5-formylpyrrol-2-yl)propane (**4**). It was demonstrated that the reaction of **1** with **3** proceeds unusually and is accompanied by redox disproportionation of **1** in the first step. The structure of macrocycle **8** prepared by this reaction was established by X-ray diffraction. Spectrophotometric titration showed that hybrid macrocycle **10** produced by condensation of **2** with **4** possesses properties of an anion receptor and selectively binds the hydrosulfate and dihydrophosphate anions in the presence of bromide and nitrate anions. The structures of macrocycle **10** and its complex with the hydrosulfate anion were studied by density functional theory. High selectivity of **10** with respect to sulfate in the presence of nitrate opens up possibilities of using this type of artificial macrocyclic receptors in technologies for disposal of solid low-level radioactive wastes resulting from processing of spent fuel elements.

Experimental

The UV-Vis spectra were recorded on a Beckmann DU 40 spectrophotometer in a range of 200—900 nm. High-resolution mass spectra (HRMS) were measured on a VG ZAB-3E instrument using chemical ionization. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury instrument (400 MHz) with Me_4Si as the internal standard. The starting compounds, *viz.*, 2,5-diformylpyrrole (**3**),[43] 2,2-bis(5-formylpyrrol-2-yl)propane (**4**)[21], 2,6-bis[(2-aminophenyl)iminomethyl]pyridine (**1**),[15] and *N*,*N*′-bis(2-aminophenyl)pyridine-2,6-diaminedicarboxamide (**2**),[18] were prepared according to procedures described earlier.

2,10,17,24,30,31-Hexaazapentacyclo[23,4,$1^{4,8}$,$1^{19,22}$,$0^{11,16}$,$0^{1,25}$]untriaconta-4,6,8,(30),11,13,15,17,19,21,25,27,29-tridecaene (8). Diamine **1** (200 mg, 0.635 mmol) and 2,5-diformylpyrrole (78 mg, 0.635 mmol) were dissolved in toluene (50 mL). The reaction mixture was refluxed for 30 min using a Dean—Stark trap. The solution was concentrated and the product was isolated by column chromatography on SiO_2 (CH_2Cl_2—MeOH, 95 : 5). Ligand **8** was obtained in a yield of 51 mg (20%) as orange-red crystals, t.decomp. higher than 150 °C. Found (%): C, 73.81; H, 5.53; N, 20.67. $C_{25}H_{22}N_6$. Calculated (%): C, 73.87; H, 5.46; N, 20.68. ^{1}H NMR ($CDCl_3$), δ: 4.46 (s, 4 H); 5.90 (s, 2 H); 6.60 (d, 2 H, J = 2.4 Hz); 6.74 (t, 2 H, J = 7.6 Hz); 6.89 (d, 2 H, J = 7.6 Hz); 7.21 (m, 4 H); 7.32 (d, 2 H, J = 7.6 Hz); 7.71 (t, 1 H, J = 7.6 Hz); 8.43 (s, 2 H); 10.54 (s, 1 H). ^{13}C NMR ($CDCl_3$), δ: 50.14, 111.41, 114.96, 115.41, 117.17, 122.81, 128.21, 134.64, 134.11, 137.25, 142.87, 144.39, 158.19. MS (70 eV), m/z (I_{rel} (%)): 407 [M^+ + H] (100), 408 [M^+ + H + 1] (5).

3,9-Dioxo-2,10,17,24,30,31-hexaazapentacyclo[23,4,$1^{4,8}$,$1^{19,22}$,$0^{11,16}$,$0^{1,25}$]untriaconta-4,6,8,(30),11,13,15,17,19,21,25,27,29-tridecaene (9). Diamine **2** (100 mg, 0.29 mmol) and 2,5-diformylpyrrole (35.44 mg, 0.29 mmol) were dissolved in methanol (25 mL). Then trifluoroacetic acid (42 μL, 0.58 mmol) was added and the solution was stirred at room temperature for ~8 h. The precipitate that formed was filtered off, washed with methanol, dried, dissolved in dichloromethane, and washed with a saturated sodium carbonate solution. The organic layer was separated, dried over sodium sulfate, and concentrated. Ligand **9** was obtained in a yield of 80 mg (64%), t.decomp. higher than 300 °C. Found (%): C, 68.95; H, 4.28; N, 19.40. $C_{25}H_{18}N_6O_2$. Calculated (%): C, 69.11; H, 4.18; N, 19.34. UV (CH_2Cl_2), λ_{max}/nm (logε): 315 (12000), 423 (7700). ^{1}H NMR (DMSO-d_6), δ: 6.80 (d, 2 H, J = 2.1 Hz); 7.28 (m, 4 H); 7.52 (d, 2 H, J = 7.8 Hz); 8.14 (d, 2 H, J = 7.8 Hz); 8.24 (t, 1 H, J = 7.2 Hz); 8.43 (d, 2 H, J = 8.1 Hz); 11.01 (s, 2 H); 11.82 (s, 1 H). MS (70 eV), m/z (I_{rel} (%)): 371 (20), 435 [M^+ + H] (100), 436 (24), 437 (3).

23,23-Dimethyl-3,9-dioxo-2,10,17,29,35,36,37-heptaazahexacyclo[28,4,$1^{4,8}$,$1^{19,22}$,$1^{24,27}$,$0^{11,16}$,$0^{1,30}$]heptatriaconta-4,6,8(35),11(16),12,14,17,19,21,24,26,28,30,32,34-pentadecaene (10). A solution of *N*,*N*′-bis(2-aminophenyl)pyridine-2,6-dicarboxamide (**2**) (100 mg, 0.288 mmol), 2,2-bis(5-formylpyrrol-2-yl)propane (**4**) (66.4 mg, 0.288 mmol), and trifluoroacetic acid (82 mg, 0.72 mmol) in MeOH (50 mL) was refluxed under argon for 15 min. Then Et_3N (2 mL) was added and the mixture was cooled. The solvent was removed on a rotary evaporator at 40°C and the residue was dissolved in ethyl acetate. The solution was passed through a small layer of alumina (to remove the salt TFA·Et_3N) and concentrated. The residue was dissolved in $CHCl_3$ (9 mL), Et_2O (3 mL) was added, and the mixture was kept in a refrigerator for 16 h. The precipitate of oligomeric condensation products that formed was filtered off, the mother liquor was concentrated, and ligand **10** was obtained in a yield of 140 mg (90%), m.p. 185 °C (with decomp.). Found (%): C, 68.32; H, 5.16; N, 17.25. $C_{32}H_{27}N_7O_2 \cdot H_2O$. Calculated (%): C, 68.68; H, 5.22; N, 17.52. ^{1}H NMR ($CDCl_3$), δ: 1.69 (s, 6 H, Me); 6.16 (d, 2 H, $NH_{pyrrole}$, J = 4 Hz); 6.62 (d, 2 H, $NH_{pyrrole}$, J = 4 Hz); 7.08 (m, 2 H, CH_{Ph}); 7.23 (m, 4 H, CH_{Ph}); 7.67 (m, 2 H, CH_{Ph}, J = 8 Hz); 8.06 (t, 1 H, CH_{Py}); 8.19 (s, 2 H, N=CH); 8.40 (d, 2 H, CH_{Py}, J = 8 Hz); 9.77 (br.s, 2 H, $NH_{pyrrole}$). ^{13}C NMR ($CDCl_3$), δ: 30.89, 35.77, 106.82, 118.79, 119.42, 125.76, 126.09, 127.00, 127.24, 129.64, 130.44, 138.81, 144.86, 145.43, 149.69, 151.10, 163.71. High-resolution mass spectrum (CI+): found: m/z 542.2299 [M + H]$^+$. $C_{32}H_{28}N_7O_2$. Calculated: 542.2304.

Determination of the stability constants of complexes of macrocyclic ligands 8, 9, and 10 with anions. Working solutions of ligands **8**, **9**, and **10** in acetonitrile (at concentrations of

$1.750 \cdot 10^{-5}$—$2.215 \cdot 10^{-5}$ mol L^{-1}) were prepared by dissolving the corresponding ligand (1.2 mg) in acetonitrile (10 mL) followed by dilution of the resulting solution with acetonitrile by a factor of 10 (working solution I). The second working solution (II) was prepared by dissolving 10—100 equiv. of the tetrabutylammonium salt of the corresponding anion in solution I (10 mL). Titration was carried out by successive addition of aliquots (1—500 μL) of solution II to solution I (2 mL), which was placed in an UV cell with septa using a Hamilton® syringe.

The binding constants were calculated by the Connors 4.5 equation:[26a]

$$\Delta A/b = (S_t K_{11} \Delta\varepsilon_{11}[L])/(1 + K_{11}[L]),$$

where ΔA is the absorbance change after the addition of a portion of solution II, [L] is the concentration of the anion, b is the cell path length, K_{11} and $\Delta\varepsilon_{11}$ are the constants.

The experimental dependence of the absorbance increment on the concentration of the titrant (see Fig. 2, *b*) was approximated by the equation $y = BK_a x/(1 + K_a x)$ (x = L, $y = \Delta A$, K_a is the equilibrium binding constant) using the Origin 7.0 program. Measurements for each macrocycle were carried out at a wavelength λ at which ΔA had the maximum value. The stoichiometry of the ligand—anion interaction was determined from the molar host—guest ratio curves.[26b]

X-ray diffraction study of 8 ($C_{25}H_{22}N_6 \cdot CHCl_3$). Crystals suitable for X-ray diffraction study were grown as red parallelepipeds of dimensions ~0.44×0.12×0.08 mm by rapid evaporation from a chloroform solution.

Crystals of **8** ($C_{25}H_{22}N_6 \cdot CHCl_3$, M = 525.85) are monoclinic, space group $P2_1/n$; at T = 158 K a = 11.9520(3), b = 13.7752(3), c = 30.0259(8) Å, β = 97.589(2)°, V = 4900.2(2) $Å^3$, Z = 8, d_c = 1.426 g cm^{-3}, $F(000)$ = 2176, μ = 0.402 mm^{-1}. The unit cell parameters and the intensities of 14175 reflections (8540 independent reflections, R_{int} = 0.0662) were measured on an automated Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream cooler (153 K, graphite monochromator, Mo-Kα radiation (λ = 0.71073 Å), ω scanning technique with a scan step of 0.5°; the exposure time was 80 s per frame, a total of 593 frames were measured, θ_{max} = 25°). The X-ray data were processed using the DENZO-SMN program.[44] The structure was solved by direct methods using the SIR97 program[45] and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the SHELXL-97 program package.[46] The asymmetric unit of the crystal structure contains two chloroform solvate molecules, which are disordered as evident from the high isotropic displacement parameters U_{eq} of these molecules. However, we failed to reveal alternative positions of these molecules, due to which the final R factors were rather high. The positions of the hydrogen atoms were calculated geometrically and refined isotropically with fixed positional (a riding model) and thermal parameters ($U_{iso} = 1.5U_{eq}$(C) for CH_3 groups and $U_{iso} = 1.2U_{eq}$(C) for other hydrogen atoms). The final reliability factors were R_1 (against F) = 0.1235 for reflections with $I > 2\sigma(I)$ and wR_2 (against F^2) = 0.2307 for all independent reflections. The atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic displacement parameters were deposited with the Cambridge Structural Database.

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References

1. J.-M. Lehn, *Supramolecular Chemistry. Concept and Perspectives*, VCH, Weinheim, 1995.
2. A. Bianchi, K. Bowman-James, and E. Garcia-Espaca, *Supramolecular Chemistry of Anions*, Wiley—VCH, New York, 1997.
3. P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 486.
4. R. Martinez-Macez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419.
5. P. A. Gale, J. L. Sessler, V. Kral, and V. Lynch, *J. Am. Chem. Soc.,* 1996, **118**, 5140.
6. J. L. Sessler, P. J. Anzenbacher, Jr., J. A. Shriver, K. Jursikova, V. M. Lynch, and M. Marquez, *J. Am. Chem. Soc.,* 2000, **122**, 12061.
7. M. Van Kuijck, H. Miyaji, and J. L. Sessler, *Supramolecular Chemistry*, 2002, **13**, 661.
8. W. Sato, H. Miyaji, and J. L. Sessler, *Tetrahedron Lett.*, 2000, **41**, 6731.
9. A. Andrievsky, F. Ahuis, J. L. Sessler, F. Voegtle, D. Gudat, and M. Moini, *J. Am. Chem. Soc.,* 1998, **120**, 9712.
10. J. L. Sessler, W.-S. Cho, S. P. Dudek, L. Hicks, V. M. Lynch, and M. T. Huggins, *J. Porphyrins Phthalocyanines*, 2003, **7**, 97.
11. C.-H. Lee, H.-K. Na, D.-W. Yoon, D.-H. Won, W.-S. Cho, V. M. Lynch, S. V. Shevchuk, and J. L. Sessler, *J. Am. Chem. Soc.*, 2003, **125**, 7301.
12. Yu. A. Ustynyuk, N. E. Borisova, V. M. Nosova, M. D. Reshetova, S. S. Talismanov, S. E. Nefedov, G. G. Aleksandrov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 454 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 488].
13. N. E. Borisova, Yu. A. Ustynyuk, M. D. Reshetova, G. G. Aleksandrov, I. L. Eremenko, and I. I. Moiseev, *Mendeleev Commun.*, 2003, 2002.
14. N. E. Borisova, M. D. Reshetova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 174 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 181].
15. E. A. Katayev, M. D. Reshetova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 322 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 335].
16. N. E. Borisova, Yu. A. Ustynyuk, M. D. Reshetova, G. G. Aleksandrov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 326 [*Russ. Chem. Bull.*, 2004, *Int. Ed.*, **53**, 340].
17. J. L. Sessler, E. Katayev, G. D. Pantos, and Yu. A. Ustynyuk, *Chem.Commun.*, 2004, 1276.
18. C. Picard, N. Arnaud, and P. Tisnès, *Synthesis*, 2001, 1471.
19. K. Kavallieratos, C. M. Bertao, and R. H. Crabtree, *J. Org. Chem.*, 1999, **64**, 1675.

20. K. Niikura, A. P. Bisson, and E. V. Anslyn, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1111.
21. J. B. Love, A. J. Blake, C. Wilson, S. D. Reid, A. Novak, and P. B. Hitchcock, *Chem. Commun*., 2003, 1682.
22. K. Brychcy, K. Draeger, K.-J. Jens, M. Tilset, and U. Behrens, *Chem. Ber.*, 1994, **127**, 465.
23. F. Benetollo, G. Bombieri, K. K. Fonda, A. Polo, J. R. Quagliano, and L. M. Vallarino, *Inorg. Chem*., 1991, **30**, 1345.
24. G. J. Kirkovits, R. S. Zimmerman, M. T. Huggins, V. M. Lynch, and J. L. Sessler, *Eur. J. Org. Chem.*, 2002, 3768.
25. J. L. Sessler, G. D. Pantos, E. Katayev, and V. M. Lynch, *Org. Lett.*, 2003, **5**, 4141.
26. K. A. Connors, *Binding Constants*; John Wiley & Sons, New York, 1987, (a) p. 148; (b) p. 24.
27. P. D. Beer, D. Hesek, and K. C. Nam, *Organometallics*, 1999, **18**, 3933.
28. K. Choi and A. D. Hamilton, *J. Am. Chem. Soc.,* 2001, **123**, 2456.
29. S. Kubik, R. Kirchner, D. Nolting, and J. Seidel, *J. Am. Chem. Soc.,* 2002, **124**, 12752.
30. H. Ihm, S. Yun, H. G. Kim, J. K. Kim, and K. S. Kim, *Org. Lett.*, 2002, **4**, 2897.
31. R. Herges, A. Dikmans, U. Jana, F. Köhler, P. G. Jones, I. Dix, T. Fricke, and B. König, *Eur. J. Org. Chem.*, 2002, 3004.
32. D. H. Lee, H. Y. Lee, and J.-I. Hong, *Tetrahedron Lett.*, 2002, **43**, 7273.
33. S. O. Kang, J. M. Oh, Y. S. Yang, J. C. Chun, S. Jeon, and K. C. Nam, *Bull. Korean Chem. Soc.*, 2002, **23**, 145.
34. S. J. Coles, G. Denuault, P. A. Gale, P. N. Horton, M. B. Hursthouse, M. E. Light, and C. N. Warriner, *Polyhedron*, 2003, **22**, 699.
35. S. O. Kang, J. M. Llinares, D. Powell, D. Vander Velde, and K. Bowman-James, *J. Am. Chem. Soc.*, 2003, **125**, 10152.
36. S. L. Tobey and E. V. Anslyn, *J. Am. Chem. Soc.*, 2003, **125**, 14807.
37. Y. S. Yang, S. W. Ko, I. H. Song, B. J. Ryu, and K. C. Nam, *Bull. Korean Chem. Soc.*, 2003, **24**, 681.
38. J. D. Vienna, M. J. Schweiger, D. E. Smith, H. D. Smith, J. V. Crum, D. K. Peeler, I. A. Reamer, C. A. Musick, and R. D. Tillotson, *Report PNNL-12234*, Pacific Northwest National Laboratory, Richland, Washington, July 1999.
39. C. I. Crawford, D. M. Ferrara, R. F. Schumacher, and N. E. Bibler, *Report WSRC-MS-2002-00449*, Westinghouse Savannah River Company, Aiken, South Carolina, Apr. 2002.
40. D. E. Kurath, J. R. Bontha, D. L. Blanchard, S. K. Fiskum, and B. M. Rapko, *Report PNWD-3053, BNFL-RPT-036*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington, USA, August 2000.
41. B. A. Moyer, L. H. Delmau, C. J. Fowler, A. Ruas, D. A. Bostick, J. L. Sessler, J. M. Llinares, A. Hossain, S. O. Kang, and K. Bowman-James, *Supramolecular Chemistry of Environmentally Relevant Anions*, ACS Symp. Ser., American Chemical Society, Washington, D. C., 2005—2006.
42. M. Freemantle, *Chem. Eng. News,* 2004, **82**, No. 23, 8.
43. R. Miller and K. Olsson, *Acta Chem. Scand. Ser. B,* 1981, **35**, 303.
44. Z. Otwinowski and W. Minor, in *Methods in Enzymology,* **276***: Macromolecular Crystallography, Part A*, Eds C. W. Carter, Jr., and R. M. Sweets, Academic Press, New York, 1997, p. 307.
45. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. J. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
46. G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen Germany, 1994.

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