

The Synthesis, X-ray Structure and Metal Cation Complexation Properties of Colored Crown with Two Heterocyclic Residues as a Part of Macrocycle

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New azocrown ether with pyrrole and pyridine as parts of macrocycle was synthesized. Metal cation complexation was investigated in acetonitrile and in acetonitrile-water mixture with the use of UV/VIS spectroscopy. Structure of the macrocycle was studied by X-ray diffraction.

Key words: crown, azo compound, heterocycles, synthesis, UV/VIS spectroscopy, metal cation complexation, X-ray structure

Although macrocyclic compounds with oxygen/nitrogen donor atoms are well known for many years, they are still interesting objects to study due to their unique chemical and biochemical properties. Macrocycles possessing heterocyclic subunits are widely investigated group of ligands complexing heavy metal cations [1–3]; on the other hand, *e.g.* calixpyrroles [4] or sapphyrins [5] bind anionic species. The heterocyclic moiety that often extends the macrocycle is pyridine. The first macrocycle bearing pyridine residue was synthesized in 1933 by Ruzicka *et al.* [6] from cyclopentadecanone and 2-aminobenzaldehyde under base-catalyzed condensation. Another well known pyridine macrocycle is "muscopyridine" (Fig. 1a). It was isolated in 1946 by Prelog *et al.* [7] from odoriferous constituents of natural musk from musk deer. Later, this compound was obtained by Büchi [8] from cyclododecanone in a sequence of ten consecutive reactions. Crown ethers with pyridine residue were synthesized by Reinhoudt *et al.* [9] (Fig. 1b). It was found that compounds of this type form in methanol complexes with alkali metal, alkaline earth metal, ammonium and guanidinium cations. Selectivity and values of the respective stability constants are macrocycle size depended. Large group of macrocycles with mixed oxygen/nitrogen donor atoms was investigated by Lindoy *et al.* [10]. For other examples of pyridine containing macrocycles see [11].

Previously we described the synthesis and properties of crown ether analogs with residue of pyrrole or imidazole, and two azo groups comprising parts of macrocycle (Fig. 1c) [12–14]. The pyrrole-containing chromogenic azocrown ethers are lead(II) selective whereas imidazole derivatives do not show such selectivity. In both cases complexes with some metal cations, *e.g.* nickel(II), are formed slowly under measurements conditions. The replacement of oxygen atom in oxyethylene linkage

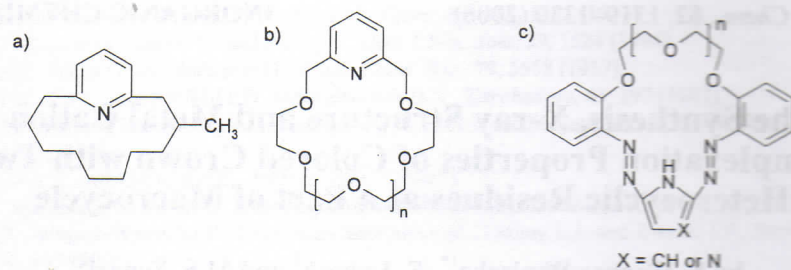


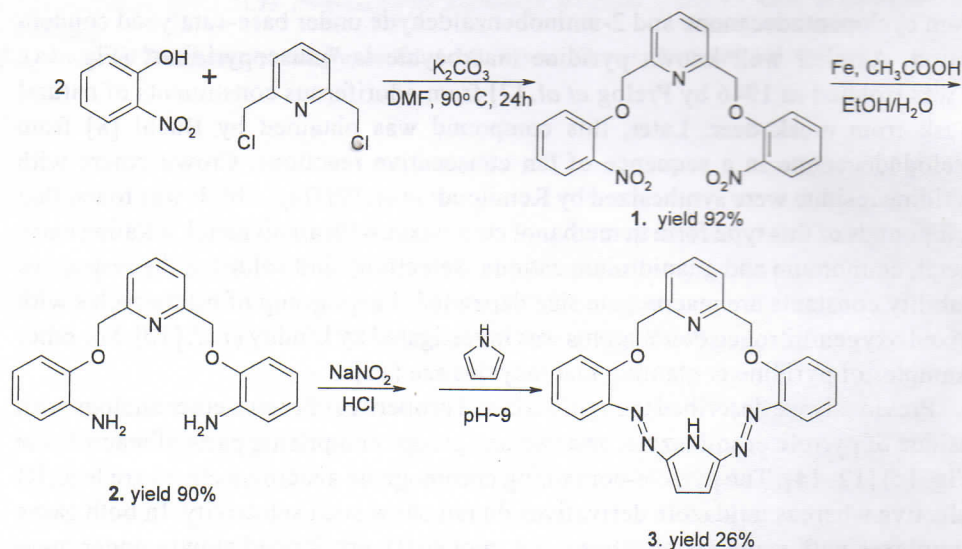
Figure 1. Examples of the macrocycles incorporating heterocyclic residue.

by softer Lewis base (for example by pyridine nitrogen atom) should change the ability of metal cation complexation.

In this paper we present the synthesis and properties of crown ether with pyrrole and pyridine heterocyclic residues and two azo groupings, all constituting parts of the macrocycle. We expected that such modification should change binding ability towards softer and heavier metal compared with 18-membered pyrrole analog with ether fragment (*cf.* Fig. 1c, where $n = 1$ and $X = \text{CH}$) [13].

RESULTS AND DISCUSSION

Synthesis. The crown ether with pyrrole and pyridine heterocyclic subunits was obtained (Scheme 1) in an analogous way to the synthesis of previously described pyrrole azocrown ethers [12,13], under high dilution conditions. For details of the synthesis see Experimental.



Scheme 1. The synthesis of crown with pyridine and pyrrole residues as parts of macrocoring.

X-ray structure. The top and side view of crown **3** with atom numbering scheme is shown in Figure 2.

The details concerning structure solution and refinement are given in Table 1; selected interatomic distances and angles are listed in Table 2. This compound crystallizes in the orthorhombic space group Cmc_21 . The molecule has a mirror symmetry, and the corresponding mirror plane bisects the molecule through the N(1), N(14) and C(16) atoms. The 18-membered skeleton comprises 6 nitrogen, 2 oxygen and 10 carbon atoms with pyridine and pyrrole moieties incorporated in the macrocyclic framework and with two benzene rings attached to it. Eight (N₆O₂) heteroatoms of the macrocycle are coplanar within ± 0.073 Å with the largest deviation of -0.123 Å for N(11) and its symmetry related N(11)ⁱ ($i = -x+1, y, z$) atoms. The cavity is characterized by approximately equidistant arrangement of opposite heteroatoms, N(11)⋯O(4)ⁱ separation being 5.531(1) Å and N(1)⋯N(14) separation being 5.126(2) Å. The rigid moieties (pyrrole and benzene rings) are joined by two azo groups, which adopt *E*-form with *trans*-arrangement of benzene and pyrrole fragments; the torsion angle C(10)–N(11)–N(12)–C(13) adopts the value -174.3° . The molecule has a butterfly shape in the part that incorporates two benzene and one pyrrole rings. In this part the dihedral angle between the benzene [C(5)>C(10)] and pyrrole [N(14), C(13), C(17), C(13)ⁱ, C(17)ⁱ, $i = -x+1, y, z$] planar rings is equal to $22.1(1)^\circ$. The intriguing feature of this molecule is the arrangement of pyridine moiety, which strongly deviates from the mean plane of the remaining aromatic systems; the dihedral angles pyridine/benzene and pyridine/pyrrole rings are equal to $62.9(1)$ and $74.4(1)^\circ$, correspondingly.

The search of Cambridge Structural Database (Version 5.28, updated January, 2007) [15] revealed no crystal structures of 18-membered macrocycles incorporating pyrrole units alongside with the azo-groups. On the other hand, several 18- [16,17], 21- [18–20] and 22-membered [21] cyclophanes as well as open-chain molecules [22] incorporate identical with **3** benzene-pyridine-benzene (or naphthalene-pyridine-naphthalene) fragment with oxymethylene bridges between the aromatic units. The analysis of the mutual arrangement of the neighboring benzene (naphthalene)

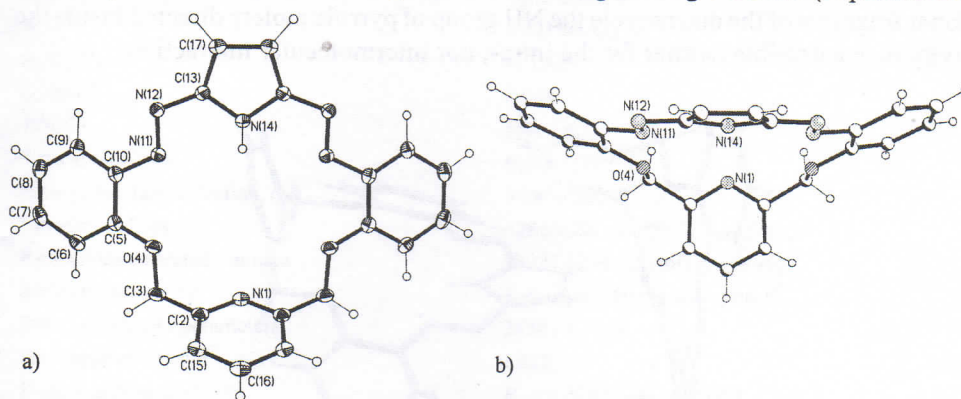


Figure 2. a) ORTEP view of crown **3** with atom numbering scheme in projection on the plane of macrocyclic heteroatoms. Displacement ellipsoids are drawn at 50% probability level; b) Side view of molecule **3** with partial numbering scheme.

and pyridine rings shows that it is very similar to that found in **3**. It is described by the dihedral angle that adopts the values in the interval of 65.9° [17] – 89.6° [18]; in dibenzopyridino-18-crown-6 molecule [16] this angle is 73.8° . Few examples of metal complexes of the relative cyclophanes with the NO_6 or NO_5 set of donor atoms revealed the decreasing of the naphthalene/pyridine dihedral angle up to 65.2° in benzodiphenylpyridino-21-crown-7 in complex with monohydrate of potassium thiocyanate [23] and the benzene/pyridine angle up to 54.1° in dibenzopyridino-18-crown-6 in sodium isothiocyanate complex [16] (for comparison, the same angle in free macrocycle is equal to 73.8°). In the complex of NO_4 -open-chained 2,6-bis((2-hydroxyphenoxy)methyl)pyridine with sodium thiocyanate the ligand is characterized by the perfectly planar skeleton (the dihedral angle between the benzene and pyridine rings is of 4.2°), while in the free ligand the benzene/pyridine angles fall in the range 30.7 – 33.2° [22].

Thus, it might be concluded that the benzene-pyridine-benzene fragment incorporated into molecule **3** has sufficient flexibility to adapt to metal coordination. On the other hand, the planar fragment of **3** that incorporates pyrrole unit alongside with neighboring azo-groups might appear rather rigid and does not possess the necessary flexibility for octahedral coordination. However, the planar arrangement of this fragment and the available N_4O_2 set of donor atoms appear to be rather promising for coordination of Cu(II) exhibiting flexibility towards stereochemical environment or much more rigid Ni(II) preferring regular square-based geometry [10].

The literature search reveals the persistent interest in the metal complexes of N,O-mixed macrocyclic molecules and gives examples of relative 15- [10,24] and 18-membered macrocycles [24] with N_3O_2 and N_4O_2 donor sets and 13- and 19-membered open-chain ligands with N_3O_2 and N_5O_2 donor sets [24,25] capable to effectively bind Cu, Ni, Zn and Cd.

In the crystal of **3** the neighboring molecules, related by the glide plane, joined *via* weak $\text{CH}\cdots\text{O}$ interactions between pyrrole hydrogens and macrocyclic oxygen atoms, $\text{C}(17)\cdots\text{O}4$ ($x, 1-y, -0.5+z$) [$\text{C}\cdots\text{O}$ 3.426(1), $\text{H}\cdots\text{O}$ 2.55(1) Å, angle CHO 146°] are combined into corrugated chains (Fig. 3). The incorporated into the rigid planar fragment of the macrocycle the NH group of pyrrole moiety directed inside the cavity is inaccessible neither for the intra-, nor intermolecular interactions.

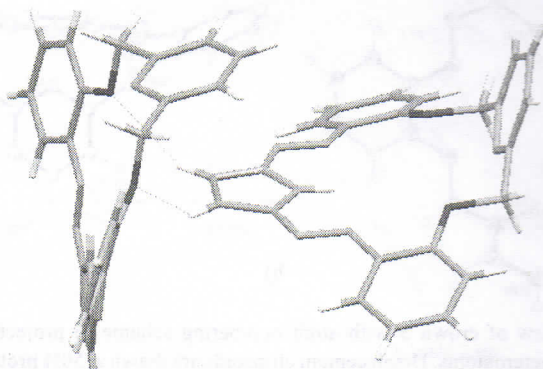


Fig. 3a)

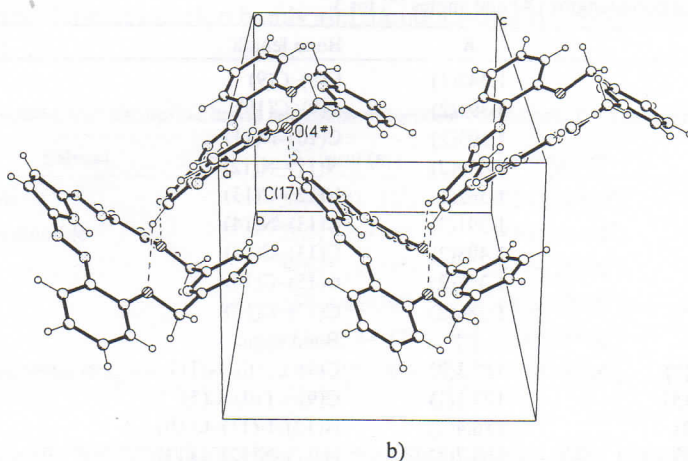


Figure 3. a) Mutual arrangement of the neighboring molecules in the chain. The dihedral angle between pyrrole and pyridine rings is equal to 17.2° , the interatomic intermolecular distances are in the range $3.555\text{--}4.182\text{ \AA}$; b) Fragment of chain in **3**. The $\text{CH}\cdots\text{O}$ interactions are shown by dotted lines.

Table 1. Crystal data and structure refinement details for compound **3**.

Empirical formula	$\text{C}_{23}\text{H}_{18}\text{N}_6\text{O}_2$
Formula weight	410.44
Temperature, K	100(2)
Wavelength, \AA	0.71073
Crystal system, space group	Orthorhombic, $Cmc2_1$
Unit cell dimensions	
a , \AA	21.3474(8)
b , \AA	8.8854(3)
c , \AA	10.2307(4)
V , \AA^3	1940.56(12)
Z , D_x Mg/m^3	4, 1.405
μ , mm^{-1}	0.094
$F(000)$	856
Crystal size, mm	$0.49 \times 0.38 \times 0.33$
θ range for data collection, deg.	3.18 to 28.64
Limiting indices	$-28 \leq h \leq 28$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected / unique	13075 / 2439 [R(int) = 0.0166]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2439 / 1 / 184
Goodness-of-fit on F^2	1.010
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0287$, $wR_2 = 0.0682$
R indices (all data)	$R_1 = 0.0334$, $wR_2 = 0.0691$
Largest diff. peak and hole $e \cdot \text{\AA}^{-3}$	0.207 and -0.207

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] for **3**.

Bond length	\AA	Bond length	\AA
N(1)–C(2)	1.342(1)	C(8)–C(9)	1.383(2)
C(2)–C(15)	1.391(2)	C(9)–C(10)	1.396(2)
C(2)–C(3)	1.503(2)	C(10)–N(11)	1.407(1)
C(3)–O(4)	1.439(2)	N(11)–N(12)	1.281(1)
O(4)–C(5)	1.362(1)	N(12)–C(13)	1.384(1)
C(5)–C(6)	1.391(2)	C(13)–N(14)	1.363(1)
C(5)–C(10)	1.408(2)	C(13)–C(17)	1.397(2)
C(6)–C(7)	1.391(2)	C(15)–C(16)	1.384(2)
C(7)–C(8)	1.386(2)	C(17)–C(17) ⁱ	1.403(2)
Bond angle	$^\circ$	Bond angle	$^\circ$
C(2) ⁱ –N(1)–C(2)	117.3(2)	C(9)–C(10)–N(11)	124.4(1)
N(1)–C(2)–C(15)	123.1(1)	C(9)–C(10)–C(5)	119.7(1)
N(1)–C(2)–C(3)	116.4(1)	N(12)–N(11)–C(10)	115.6(1)
O(4)–C(3)–C(2)	106.7(1)	N(11)–N(12)–C(13)	110.5(1)
C(5)–O(4)–C(3)	117.9(1)	N(14)–C(13)–N(12)	122.7(1)
O(4)–C(5)–C(6)	124.7(1)	N(14)–C(13)–C(17)	108.6(1)
O(4)–C(5)–C(10)	115.8(1)	C(13) ⁱ –N(14)–C(13)	109.0(1)
C(5)–C(6)–C(7)	119.7(1)	C(16)–C(15)–C(2)	119.1(1)
C(8)–C(7)–C(6)	121.1(1)	C(15)–C(16)–C(15) ⁱ	118.4(2)
C(9)–C(8)–C(7)	119.4(1)	C(13)–C(17)–C(17) ⁱ	107.0(1)
C(8)–C(9)–C(10)	120.6(1)		
N(1)–C(2)–C(3)–O(4)	–71.8(1)	C(5)–C(10)–N(11)–N(12)	–170.00(1)
C(2)–C(3)–O(4)–C(5)	–173.9(1)	C(10)–N(11)–N(12)–C(13)	–174.33(1)
C(3)–O(4)–C(5)–C(10)	–172.53(1)	N(11)–N(12)–C(13)–N(14)	6.05(2)
O(4)–C(5)–C(10)–N(11)	6.82(1)	N(12)–C(13)–N(14)–C(13) ⁱ	177.23(1)

Symmetry transformations used to generate equivalent atoms: $i -x+1, y, z$

UV/VIS spectroscopy and metal cation complexation. The general solvatochromic effect for synthesized colored macrocycle **3** was investigated. UV/VIS spectra in acetonitrile, methylene chloride, dimethylformamide, dimethylsulfoxide, methanol and acetonitrile:water (9:1, v/v) mixture are shown in Figure 4.

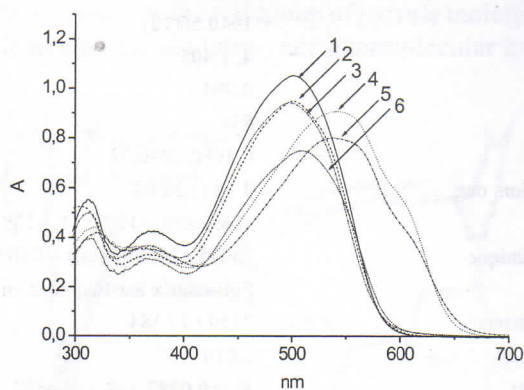


Figure 4. Absorption spectra of crown ether **3** ($c_L = 3.902 \times 10^{-5}$ M) in different solvents: 1 – acetonitrile, 2 – methylene chloride, 3 – methanol, 4 – DMF, 5 – DMSO, 6 – acetonitrile:water (9:1, v/v).

Characteristic absorption bands and molar absorption coefficients are collected in Table 3.

Table 3. Characteristic absorption bands and molar absorption coefficients for **3** in different solvents.

Solvent	λ_1 (nm) (ϵ_1)	λ_2 (nm) (ϵ_2)	λ_3 (nm) (ϵ_3)
Acetonitrile	313 (1.41×10^4)	372 (1.10×10^4)	502 (2.69×10^4)
Methylene chloride	306 (1.35×10^4)	368 (8.43×10^3)	501 (2.43×10^4)
DMF	318 (1.13×10^4)	~364 (9.17×10^3)	543 (2.32×10^4)
DMSO	320 (1.08×10^4)	~369 (9.07×10^3)	543 (2.04×10^4)
Methanol	312 (1.28×10^4)	368 (9.38×10^3)	498 (2.41×10^4)
Acetonitrile:water (9:1, v/v)	315 (1.02×10^4)	367 (8.03×10^3)	510 (1.92×10^4)

Comparing spectrum in acetonitrile with spectra in all other investigated solvents hypochromic effect was observed (the most noticeable for water containing system). Additionally for DMF and DMSO also bathochromic shift of the main band was observed ($\Delta\lambda \sim 40$ nm).

Complexation of metal cations by compound **3** was investigated by UV/VIS spectroscopy in acetonitrile. No changes in absorption spectra were observed in the presence of alkali metal and magnesium cations. In absorption spectra of ligand solution titrated with calcium, strontium and barium salts a new band for complex appears at about 600 nm. It is the best pronounced for calcium and the least for barium complex. Spectral changes upon titration with calcium perchlorate are shown in Figure 5.

In the presence of heavy lead(II) and zinc(II) metal cations the band for complex is more remarkable comparing mentioned above bands for complexes of alkaline earth metal cations; the color of the titrated ligand solution turns from red to violet. Spectral changes upon titration with metal perchlorates are shown in Figure 5. In all spectra an isosbestic point is well pronounced; it might indicate formation of one complex. The stoichiometry of the investigated complexes in all cases was determined as 2:1 (L:M) (from Job's plot and/or molar ratio method).

Stoichiometry of 2:1 (L:M) was also found for other pyridine containing macrocycles, *e.g.* [26], indicating that the pyridine residue is involved in complex formation of this type.

The values of the respective stability constants of complexes were determined with the DynaFit [27] program from titration data. The obtained values are collected in Table 4.

Table 4. Values of stability constants ($\log \beta$) of complexes of compound **3** in acetonitrile at $25 \pm 0.5^\circ\text{C}$.

Ion	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Pb^{2+}
$\log \beta$	9.29 ± 0.09	8.60 ± 0.02	7.10 ± 0.05	9.9 ± 0.8	9.6 ± 0.7

For described earlier pyrrole oxygen analog (Figure 1c, $n = 1$, $X = \text{CH}$) [13] slow complex formation was found for zinc, cobalt and nickel. In the case of pyridine de-

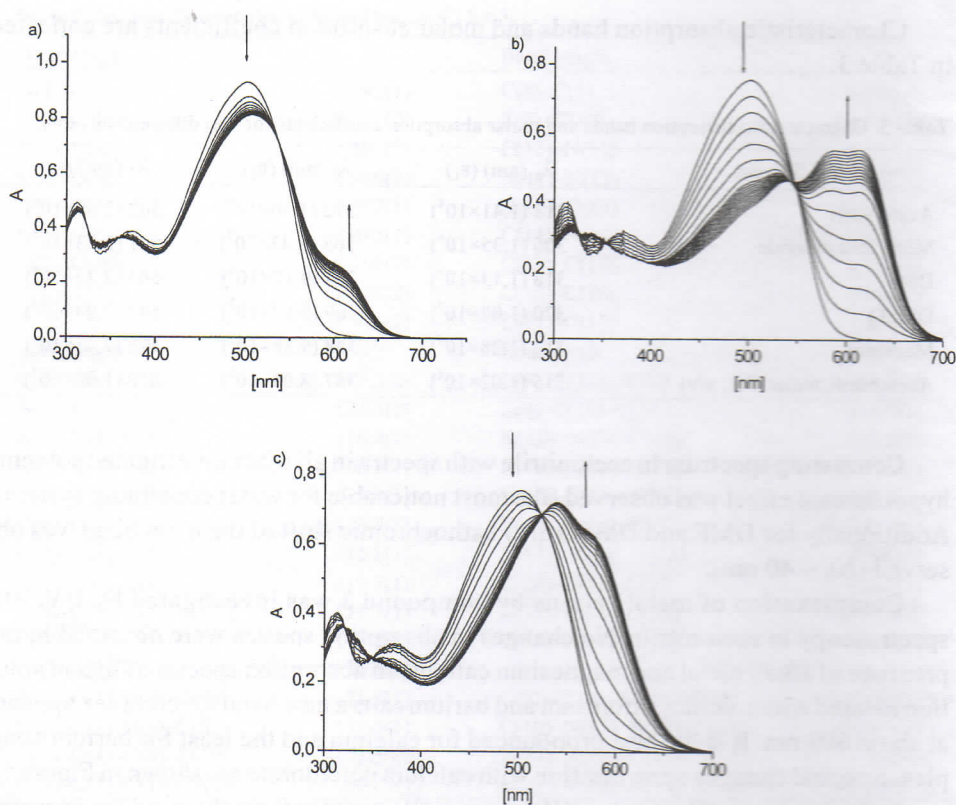
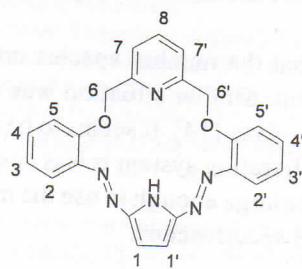


Figure 5. Changes in absorption spectra upon titration of ligand solution with the respective metal perchlorates: a) calcium ($c_L = 4.5 \times 10^{-5}$ M; $c_{Ca} = 3.0 \times 10^{-3}$ M; titration step 0.01 cm^3); b) lead(II) ($c_L = 3.6 \times 10^{-5}$ M; $c_{Pb} = 8.0 \times 10^{-4}$ M; titration step 0.01 cm^3); c) zinc(II) ($c_L = 3.7 \times 10^{-5}$ M; $c_{Zn} = 1.4 \times 10^{-3}$ M; titration step 0.005 cm^3) in acetonitrile. The first spectrum is for free ligand and the last is the limiting spectrum for complex.

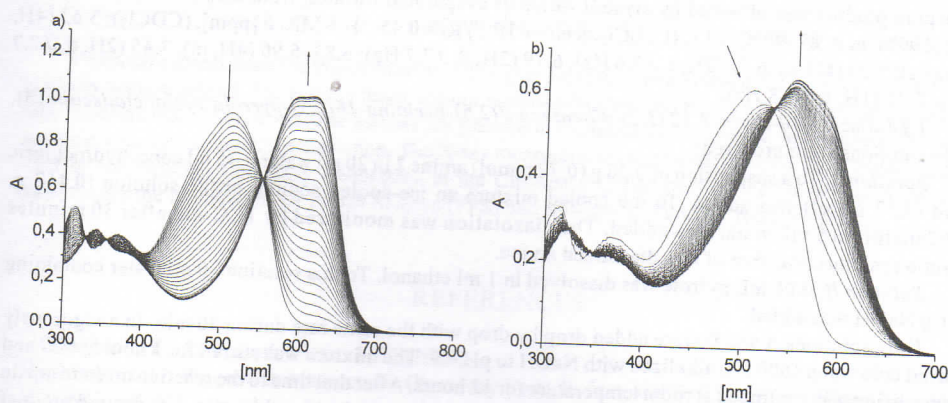
rivative **3** slow kinetics was observed only in the case of nickel(II) and cobalt(II). Slow equilibration is typical rather for N donor macrocycles (e.g. tetra-aza macrocycles) than for mixed O,N donor macrocycles, *cf.* [10].

^1H NMR spectra (in acetonitrile) of **3** recorded in the presence of metal perchlorates indicate that depending on the kind of metal cation different parts of crown are engaged into complex formation. More significant changes in chemical shift of the respective protons were observed for lead(II) complex especially for pyrrole and ether protons. For strontium the largest shift was observed for pyridine proton. Such changes in chemical shifts could suggest that in case of lead(II) complex azogroup(s) participate in higher degree in complex formation than for strontium. The values of the proton shifts differences between metal complexes and the uncomplexed crown are collected in Table 5.

Table 5. Difference of chemical shifts ($\Delta\delta$ [ppm]) in ^1H NMR spectra for **3** and for its strontium or lead(II) complexes (d-acetonitrile). ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$).

	1,1'	2,2'	3,3'	4,4'	5,5'	6,6'	7,7'	8
3·Sr	-0.03	+0.01	+0.03	-0.01	-0.03	+0.10	+0.14	+0.22
3·Pb	+0.18	+0.16	+0.09	+0.05	+0.07	+0.27	+0.12	+0.14

The influence of water addition to acetonitrile on stoichiometry of the formed complexes was also investigated. Due to low solubility of ligand, addition of water was limited to 10% (v/v). No significant changes in absorption spectra for alkaline earth metal cations was found for this solvent system. Noteworthy changes were observed in spectra of **3** in the presence of lead(II) and zinc(II). Changes in absorption spectra upon titration with lead and zinc perchlorates in acetonitrile-water system are shown in Figure 6. It is worth noting that in water containing system only complexes of 1:1 stoichiometry are formed, however the stability constants have lower values. In pure acetonitrile the highest value of stability constant for zinc complex was $\log \beta = 9.9 \pm 0.8$ whereas in mixed solvent it is only 2.70 ± 0.01 . For lead the respective value of stability constant is also lower (6.50 ± 0.02), but the difference is not as dramatically large as for zinc.

**Figure 6.** Changes in absorption spectra upon titration of ligand solution with the respective metal perchlorates in acetonitrile-water (9:1): a) lead(II) ($c_L = 4.2 \times 10^{-5}$ M; $c_{Pb} = 5.2 \times 10^{-3}$ M; titration step 0.01 cm^3); b) zinc(II) ($c_L = 3.2 \times 10^{-5}$ M; $c_{Zn} = 1.5 \times 10^{-1}$ M; titration step 0.01 cm^3). The first spectrum is for ligand and the last is the final limiting spectrum for complex.

Lower stability constant in water containing solvent system is a typical effect of the presence more polar solvent and its competition among ligand and metal molecules.

Water addition effect is that the number species under equilibrium is reduced comparing pure organic solvent. Similar situation was observed in the case of described earlier imidazole derivatives [14]. It seems to be a great advantage from analytical point of view. The equilibrating system is less complicated and the respective values of stability constants are large enough to use the mentioned macrocycles as an analytical reagents in UV/VIS spectroscopy.

EXPERIMENTAL

General. All materials and solvents used were of analytical reagent grade. Aluminum plates covered with Silica gel 60 F₂₅₄ (Merck) were used for TLC chromatography. ¹H NMR spectra were recorded with a Varian instrument at 500 MHz working frequency. Mass spectrum was taken on an AMD-604 spectrometer. IR spectra were registered using a Genesis II (Mattson) instrument. UV/VIS spectra were recorded on a Unicam UV-300 spectrophotometer in acetonitrile (HPLC grade) or its mixture with deionized water.

Synthesis. 2,6-bis-(2-nitro-phenoxy-methyl)-pyridine (1). A mixture of 1 g (5.7 mmol) 2,6-bis-chloromethyl-pyridine, 1.6 g 2-nitrophenol (11.5 mmol), 1.6 g (11.6 mmol) anhydrous potassium carbonate in 10 ml DMF was heated at 90°C for 24 hours. After cooling the product was precipitated with water, filtered off and washed with potassium carbonate solution and water. The product was crystallized from water-ethanol mixture. Yield 92%; m.p. 142–145°C, cf. [28]. TLC (CH₂Cl₂ : acetone 50:1) R_f = 0.48. ¹H NMR: δ [ppm], (CDCl₃): 5.34 (4H, s); 7.09 (2H, t, J 7.8 Hz); 7.17 (2H, d, J 8.3 Hz); 7.55 (2H, t, J 7.8 Hz); 7.64 (2H, d, J 7.3 Hz); 7.85 (1H, t, J 7.8 Hz); 7.91 (2H, t, J 7.8 Hz). IR ν [cm⁻¹], (nujol): 1598, 1514, 1284, 1245, 1155, 1088, 1040, 996, 849, 778, 737.

2,6-bis-(2-amino-phenoxy-methyl)-pyridine (2). Synthesis was carried out analogously to described in [10]: 0.2 g (0.525 mmol) of dinitrocompound 1 and 0.294 g (5.25 mmol) of iron dust was suspended in 11 ml water:ethanol (1:1) mixture. To a boiling reaction mixture 0.16 ml (2.8 mmol) of glacial acetic acid was dropped. Reaction was monitored by TLC in CH₂Cl₂:acetone (10:1). After 17 hours the precipitate was collected and washed with hot mixture of water and methanol (1:1) and next with methylene chloride. The pure product was obtained by crystallization of evaporated filtrates, from methanol-water mixture. Yield 90%, m.p. 87–90°C. TLC (CH₂Cl₂:acetone 10:1) R_f = 0.45. ¹H NMR: δ [ppm], (CDCl₃): 3.63 (4H, broad s); 5.27 (4H, s); 6.72 (2H, t, J 7.6 Hz); 6.79 (2H, d, J 7.7 Hz); 6.83–6.90 (4H, m); 7.45 (2H, d, J 7.7 Hz); 7.75 (1H, t, J 7.8 Hz).

1,14-diazo-5,10-dioxo-3,12(1,2)-dibenzena-7(2,6)-pyridina-16(2,5)-pyrrolo-cyclooctadecane (3). Two solutions were prepared:

Solution A. To a suspension of 0.26 g (0.72 mmol) amine 2 in 20 ml water 0.35 ml conc. hydrochloric acid (3.57 mmol) was added. To the cooled mixture an ice-cooled sodium nitrite solution (0.112 g, 1.62 mmol) in 5 mL water was added. The diazotation was monitored by TLC and after 30 minutes reaction mixture was free of non diazotized amine.

Solution B. 0.06 mL pyrrole was dissolved in 1 ml ethanol. To this solution 20 ml water containing 0.1 g NaOH was added.

Cold solutions A and B were added drop by drop with the same rate during 30 min. to a vigorously stirred cold water (600 ml) alkalized with NaOH to pH ~ 9. The mixture was stirred for 1 hour at 5°C and then stirring was continued at room temperature for 12 hours. After that time to the reaction mixture acetic acid was added (pH ~ 6). The precipitate was collected and washed with cold water. The desired product was isolated with the use of column chromatography. As eluents methylene chloride and mixture of methylene chloride:acetone (30:1 v/v) were used consecutively. The crude product was crystallized from acetone:hexane mixture. Yield of crown ether (golden-brown crystals): 76 mg (26%); m.p. 218–222°C (dec.). TLC (CH₂Cl₂:acetone 50:1) R_f = 0.52. ¹H NMR: δ [ppm], (CDCl₃): 5.46 (4H, s); 7.11 (2H, s); 7.14

(2H, t, J 7.6 Hz); 7.30 (2H, d, J 7.3 Hz); 7.44 (2H, t, J 7.3 Hz); 7.51 (2H, d, J 7.8 Hz); 7.79–7.83 (3H, m); 10.00 (1H, s). IR ν [cm^{-1}], (nujol): 3418; 1582; 1208; 1151; 1030; 981; 783. HRMS (EI): found 410.15043, calculated for $\text{C}_{23}\text{H}_{18}\text{N}_6\text{O}_2$ 410.14912.

^1H NMR spectra in *d*-acetonitrile: Azocrown **3**: δ [ppm]: 5.35 (4H, s); 7.10 (2H, s); 7.15 (2H, t, J 7.8 Hz); 7.44 (2H, d, J 8.3 Hz); 7.55 (2H, t, J 7.3 Hz); 7.58 (2H, d, J 7.8 Hz); 7.77 (2H, dd, J_1 7.8 Hz; J_2 1.8 Hz); 7.91 (1H, t, J 7.8 Hz). Azocrown **3** + $\text{Sr}(\text{ClO}_4)_2$, (1:10 molar ratio), δ [ppm]: 5.45 (4H, s); 7.07 (2H, s); 7.18 (2H, t, J 7.3 Hz); 7.41 (2H, d, J 8.3 Hz); 7.54 (2H, t, J 7.6 Hz); 7.72 (2H, broad); 7.78 (2H, d, J 7.3 Hz); 8.13 (1H, broad). Crown **3** + $\text{Pb}(\text{ClO}_4)_2$, (1:10 molar ratio), δ [ppm]: 5.62 (4H, s); 7.24 (2H, t, J 7.8 Hz); 7.28 (2H, s); 7.51 (2H, d, J 8.3 Hz); 7.60 (2H, t, J 7.8 Hz); 7.70 (2H, broad); 7.93 (2H, s, broad); 8.05 (1H, broad).

X-ray studies. All measurements were performed on a KM4CCD κ -axis diffractometer with graphite-monochromated MoK_α radiation. The crystal was positioned at 62 mm from the CCD camera. 1800 frames were measured at 0.5° intervals with a counting time of 2.5 sec. The data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Oxford Diffraction programs [29]. The structure was solved by direct methods [30] and refined using [31]. The refinement was based on F^2 for all reflections except those with very negative F^2 . Weighted R factors wR and all goodness-of-fit S values are based on F^2 . Conventional R factors are based on F with F set to zero for negative F^2 . The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F . All hydrogen atoms were located geometrically and their position and temperature factors were refined. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 [32]. The structure was refined as an inversion twin with enantiomer ratio 0.3:0.7.

Supplementary data: cif file for compound **3** was deposited with the Cambridge Crystallographic Data Centre as a supplementary publication number CCDC 644844 (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail deposit@ccdc.cam.ac.uk).

UV/VIS spectroscopy and metal cation complexation. The complexation studies were performed using UV/VIS spectroscopy in acetonitrile and acetonitrile-water (9:1, v/v) solvent mixture. In all titration experiments ligand concentration was about 10^{-5} mol dm^{-3} . Starting volume of titrated ligand: 3 cm^3 . All metal perchlorates were used at concentration of about 10^{-2} mol dm^{-3} (stock solution). Titration step: 0.01 cm^3 (if not stated otherwise). The values of appropriate stability constants were calculated using Dynafit program [27]. For systems where complex absorption band do not overlap ligand band the stoichiometry of formed compounds was additionally estimated using molar ratio and/or continuous variation methods.

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