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Synthesis and Properties of Macroheterocyclic Azomethines Based on 4-Aminobenzo-15-crown-5

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Abstract—A number of new stable azomethine crown ether derivatives have been synthesized by condensation of 4-aminobenzo-15-crown-5 with aromatic aldehydes. Complexation of the products with transition metal cations (Cu^{2+}, Zn^{2+}, Fe^{3+}, Co^{3+}, Ni^{3+}) has been studied by spectrophotometry.

Keywords: crown ethers, Schiff bases, sensors, synthesis, thermal stability, absorption spectra

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An important problem of analytical studies in the field of environmental monitoring is detection of harmful metal cations, such as barium, mercury, thallium, and lead, in wastewaters. Express analysis of metal cations participating in biological processes is equally important. It has been proved that cancer morbidity is related to the concentration of copper and zinc, cobalt and manganese induce myocardial diseases, and nickel is responsible for blood coagulation processes. In some cases, determination of the concentration of these elements in blood allows early disease detection [1].

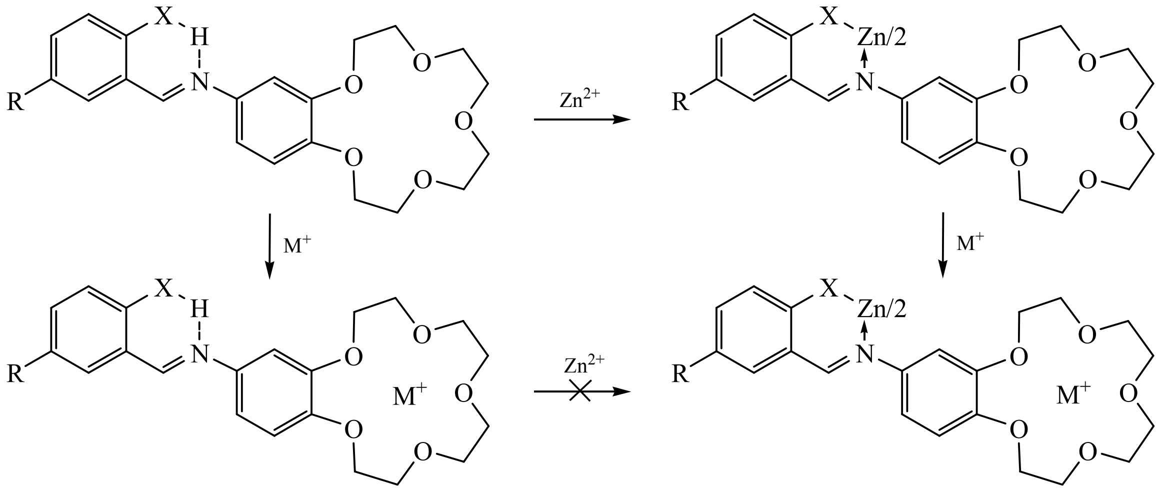
Undoubtedly, a large number of chemosensors for various ions have been developed up to now, but many of them are not free from some disadvantages, including toxicity, low accessibility, and low sensitivity or selectivity. Therefore, search for new efficient compounds capable of precisely, selectively, and rapidly detecting metal ions in solution even at low concentration is very important.

Potential highly sensitive chemosensors for various metal cations in environmental samples and biological liquids are Schiff base derivatives of crown ethers; their complexation with metal ions should be accompanied by change of their spectral parameters.

Schiff bases are commonly synthesized by condensation of aldehydes or ketones with primary amines. The reactions are carried out with simultaneous removal of water by azeotropic distillation or in the presence of drying agents to displace the equilibrium toward the condensation product [2]. Extensive studies on the synthesis, structure, and physicochemical properties of azomethine derivatives of crown ethers, in particular of benzo-15-crown-5, have been performed only in the past decade. A number of procedures for the synthesis of these compounds have been reported. Güler et al. [3] synthesized Schiff bases in high yields (88–92%) from 4-aminobenzo-15-crown-5 and vanillin, *o*-vanillin, 2-hydroxy-4-methoxybenzaldehyde, and 2-hydroxy-5-methoxybenzaldehyde in methanol. Castro-Juiz et al. [4] reacted 4-aminobenzo-15-crown-5 with 2,3,4-trimethoxybenzaldehyde in anhydrous chloroform under reflux using a Dean–Stark trap. Safin et al. [5] studied thermochromic properties of crown ether-based Schiff bases obtained by reaction with substituted salicylaldehydes on heating in ethanol. Various Schiff bases were synthesized from 4-aminobenzo-15-crown-5 and aldehydes following analogous procedures [6–10].

Azomethine derivatives of crown ethers attract interest due to the presence in their molecules of two different coordination centers, imino nitrogen atom and crown ether fragment. Nowadays, researchers' attention is focused on mono- and polynuclear complexes with metal cations. The complexation of a metal cation by the crown ether cavity does not rule out coordination to the imine fragment. In the latter case,

Scheme 1.



R = Br, H; X = O, NTs; M^+ = Li^+, Na^+, K^+.

positive charge on the imine fragment favors intramolecular charge transfer from the crown ether moiety. Study of the complexing properties of Schiff bases derived from crown ethers implies measurement of the absorption spectra of their solutions before and after addition of a metal salt. Burlov et al. [11] studied sensing properties of 4-(5-bromosalicylideneamino)-benzo-15-crown-5 and 4-(2-tosylaminobenzylidene-amino)benzo-15-crown-5 and variation of their electronic absorption spectra upon complexation with zinc, lithium, sodium, and potassium cations (Scheme 1).

The zinc complexes displayed red shifts of the absorption maxima, whereas blue shifts were observed for dinuclear complexes with alkali metal cations.

Klimenko and Mart'yanov [12] studied the properties of new crown-containing derivatives of 9,10-anthraquinone and 1,4-naphthoquinone. Complex formation of these ligands with Li, Na, K, Mg, Ba, Ca, Sr, Cs, Cd, and ammonium cations was accompanied by a blue shift of the long-wave absorption maximum. Analogous variation of spectral parameters was observed for the complexation of pyridine-containing benzo-15-crown-5 with barium cation [8].

As follows from the above stated, search for new chemosensors in the crown ether series is fairly promising. The goal of the present work was to synthesize new crown ether Schiff bases from 4-aminobenzo-15-crown-5 as potential chemosensors for transition metal cations and study their complexing properties and thermal stability.

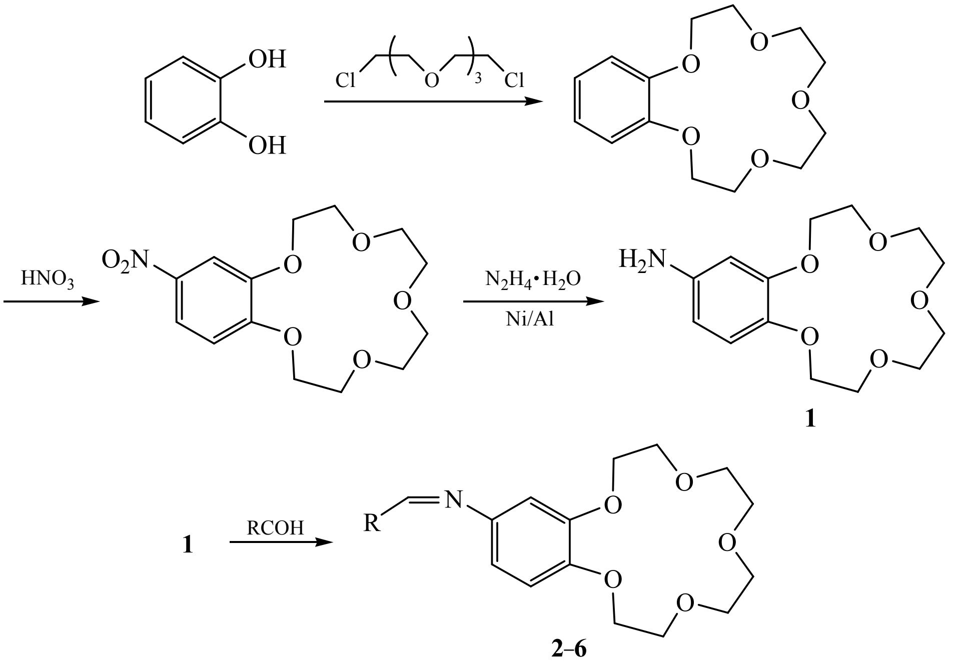
4-Aminobenzo-15-crown-5 (**1**) was prepared as a result of a series of transformations of benzo-15-crown-5 [13] (Scheme 2). The condensation of **1** with aromatic aldehydes in alcohol afforded the corresponding Schiff bases **2**–**6** in 86–94% yield. The structure of **2**–**6** was confirmed by NMR and IR spectra and elemental analyses, and their thermal stability was studied by differential thermal analysis (DTA). Thermal decomposition of **2**–**6** includes two steps, the first of which is removal of outer-sphere and coordinated water molecules. The second step is decomposition of the organic molecule, which starts at 150–250°C.

Removal of outer-sphere water from compound **2** begins at 50°C and is accompanied by melting of the sample. This is reflected by an endothermic peak on the DTA curve in the corresponding temperature range (Fig. 1a). One molecule **2** loses 1.1 equiv of water. Decomposition of **2** starts at 220°C, and it slows down when the temperature reaches 400°C. The weight loss at this step amounts to 75%. Further decomposition leaves almost no incombustible residue.

Compound **3** also contains outer-sphere coordinated water which starts to escape at about 80°C with melting of the sample. The heat flux at that part of the DTA curve is negative. One water molecule per molecule **3** is lost. Complete decomposition of **3** occurs at 150–450°C with a weight loss of 70%.

Unlike compounds **2** and **3**, there is no coordinated water in Schiff base **4**. The DTA curve displays an endothermic peak at 75–80°C without weight loss, which corresponds to melting of the sample. Decom-

Scheme 2.



2, R = Ph; **3**, R = 4-MeOC$_6$H$_4$; **4**, R = pyridin-4-yl; **5**, R = 2-(5-nitrofuran-2-yl)vinyl; **6**, R = biphenyl-4-yl.

position of **4** begins at 200°C and lasts until 400°C (weight loss 61%), and next follows complete oxidation.

Almost no coordinated water is present in a sample of **5**. Melting of the sample gives rise to an endothermic peak without weight loss at about 150°C on the DTA curve (Fig. 1b). Thermal decomposition of **5** begins at ~180°C and shows a more complicated pattern than in the above cases. In the first step, the sample loses 11% of the initial weight. The process then slows down, and two parts can be distinguished on the DTA curve. The first part is characterized by a weight loss of 40%, and the second part corresponds to complete oxidation. Likewise, an endothermic peak without weight loss is observed at ~150°C on the DTA curve of **6** due to melting. The subsequent decomposition begins at 250°C (weight loss 66%) and is followed by complete oxidation.

Thus, thermal decomposition of crown ether Schiff bases **2**–**6** begins at 150–250°C, outer-sphere water (if present) is removed at 50–100°C, and melting of **2**–**6** is clearly observed from the endothermic peaks.

We then proceeded to study the complexing ability of Schiff bases **2**–**6** toward metal ions and their solvatochromic properties. Solutions of **2**–**6** in acetonitrile and methanol are slightly yellowish. An exception is compound **5** whose solutions are bright orange. Solutins of **2** and **6** in chloroform are green, and those of **3** and **4**, orange–yellow. Strong differrences were observed in the electronic absorption spectra of **2**–**6** in nonpolar and polar solvents. Blue shift of the absorption maxima was observed in going from weakly polar chloroform (ε = 4.81) to more polar methanol (ε = 37.92) and acetonitrile (ε = 36.64) (Table 1). 4-(4-Methoxybenzylideneamino)benzo-15-crown-5 (**3**) in chloroform (Fig. 2) displayed an absorption maximum at λ 405 nm, which shifted to 336 and 338 nm in methanol and acetonitrile, respectively.

The reactions of **2**–**6** with metal ions resulted in change of both color and absorption spectra. We examined by spectrophotometry the complexation of **2**–**6** with Cu^{2+}, Zn^{2+}, Fe^{3+}, Co^{3+}, and Ni^{3+} ions. After addition of an aqueous solution of copper(II) chloride (c = 5×10^{-5} M) to solutions of **2**–**4** in methanol (c = 5×10^{-5} M), the color changed to lilac (**2**), violet (**3**), or blue (**4**), and new absorption bands appeared in the electronic absorption spectra at $\lambda_{\max}$ 581, 585, and 592 nm, respectively (Fig. 3, Table 3). No variation of the absorption spectra was observed in the reactions of **5** and **6** with copper(II) salt.

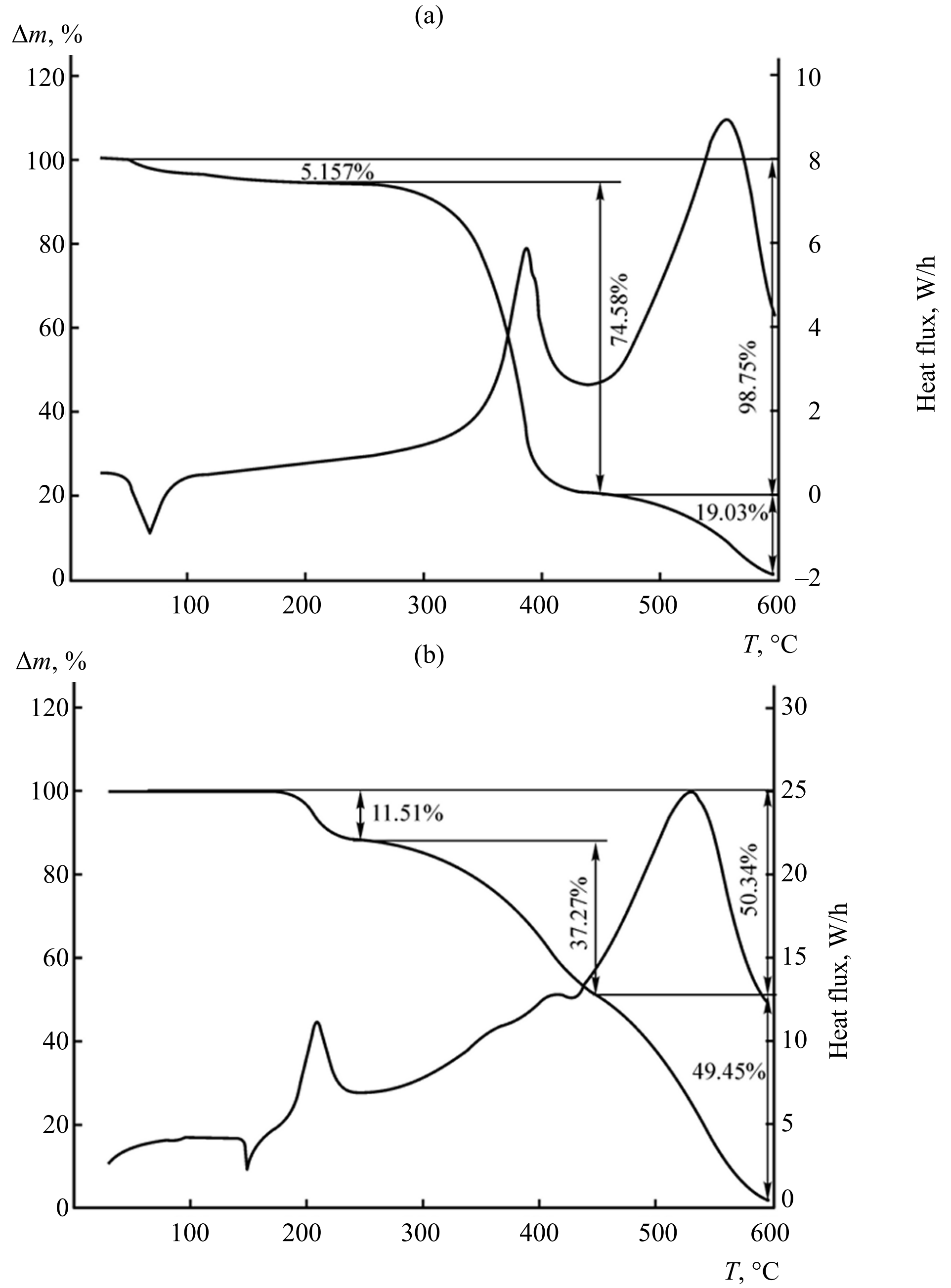


Fig. 1. DTA and TGA curves of compounds (a) **2** and (b) **5**.

Compounds **2–6** reacted with zinc, cobalt, iron, and nickel ions in a different manner. The color did not change after addition of an equimolar amount of zinc, cobalt, iron, or nickel chloride in methanol to methanolic solutions of **2**–**4**. Shifts of the absorption maxima in the electronic spectra were insignificant (Table 3), except for the complexation of **3** with iron(III) chloride where the absorption maximum shifted blue by 16 nm.

In summary, we have synthesized new Schiff base derivatives of benzo-15-crown-5, estimated their thermal stability, and examined their complexation with transition metal cations (Cu^{2+}, Zn^{2+}, Fe^{3+}, Co^{3+}, Ni^{3+}) by spectrophotometry. Visual color change was observed on addition of copper(II) salt to solutions of compounds **2**–**4**. Taking into account the data for other metal cations, it may be presumed that Zn^{2+}, Fe^{3+}, Co^{3+}, and Ni^{3+} ions should not interfere with precise determination of copper(II) ions; therefore, Schiff bases **2**–**4** can be used as selective chemosensors for copper(II) ions.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded at 25°C on a Bruker Avance III NanoBay spectrometer (300.28 and 75.50 MHz, respectively) using DMSO-d_6 as solvent. The IR spectra (400–3800 cm^{-1}) were taken on a Bruker Vertex 70 spectrometer with Fourier transform from samples prepared as KBr discs. The electronic absorption spectra were measured on a Specord 250 PLUS spectrophotometer. The elemental analyses were obtained on a Eurovector EuroEA 3000 CHNS analyzer. Differential thermal analysis was performed on a TA SDT Q-600 instrument. The purity of the synthesized compounds was checked by GLC on a Khromatek-Kristall 5000.2 chromatograph.

Benzo-15-crown-5. A solution of 67.2 g (1.68 mol) of sodium hydroxide in 80 mL of water was added to a solution of 88.0 g (0.80 mol) of catechol in 1200 mL of butan-1-ol heated to 60–65°C. Tetraethylene glycol dichloride, 194.8 g (0.84 mol), was then added dropwise, and the mixture was heated for 5 h and filtered. The filtrate was acidified with 12 mL of concentrated aqueous HCl, and the organic phase was separated, washed with water until neutral reaction, and evaporated to dryness at 48–58°C (30–40). The residue was extracted with hot hexane, the extract was cooled, and the precipitate was filtered off. Yield 47%, colorless transparent crystals, mp 78–79°C, purity 98% (GC/MS). IR spectrum, ν, cm^{-1}: 468 w, 514 w, 538 w, 602 w, 740 s, 779 w, 851 m, 906 w, 938 s, 980 w, 1042 m, 1051 s, 1076 m, 1094 m, 1121 s, 1130 s, 1226 s, 1261 s, 1269 m, 1335 m, 1345 m, 1362 w, 1412 w, 1455 m, 1509 s, 1593 m, 2863 s, 2920 s, 2940 s, 3009 w, 3036 w, 3060 w. ^1H NMR spectrum, δ, ppm: 3.62 br.s (8H), 3.73–3.81 m (4H), 4.00–4.09 m (4H), 6.85–6.99 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 68.42, 68.87, 69.79, 70.42, 113.92, 121.04, 148.63. Found, %: C 62.79; H 7.43. $C_{14}H_{22}O_5$. Calculated, %: C 62.61; H 7.62.

4-Nitrobenzo-15-crown-5. A solution of 26.8 g (0.10 mol) of benzo-15-crown-5 in 14 mL of acetonitrile was heated to 70°C, 12 mL (0.15 mol) of 58% nitric acid was added dropwise, and the mixture was stirred for 20 min, cooled to room temperature, and diluted with 120 mL of cold water. The light yellow crystalline solid was filtered off, recrystallized from propan-2-ol, and dried in air. Yield 72%, mp 95–96°C, purity 97% (GC/MS). IR spectrum, ν, cm^{-1}: 497 w, 538 w, 618 w, 654 m, 723 w, 745 m, 787 w, 806 m, 868 m, 913 w, 934 m, 980 m, 1010 w, 1047 m, 1093 s, 1138 s, 1240 s, 1276 s, 1335 s, 1417 s, 1428 s, 1448 m, 1517 s, 1587 m, 2868 m, 2904 m, 2929 m, 3083 m. ^1H NMR spectrum, δ, ppm: 3.62 br.s (8H), 3.74–3.85 m (4H), 4.13–4.24 m (4H), 7.15 d (1H, J = 8.9), 7.73 d (1H, J = 2.7 Hz), 7.89 d (1H, J = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 70.09, 70.16, 70.30, 100.96, 105.53, 117.49, 139.35, 143.95, 149.92. Found, %: C 54.01; H 6.23 N 4.27. $C_{14}H_{19}NO_7$. Calculated, %: C 53.62; H 6.06; N 4.47.

4-Aminobenzo-15-crown-5 (1). A mixture of 15.65 g (0.05 mol) of 4-nitrobenzo-15-crown-5, 150 mL of methanol, and 10 mL of hydrazine hydrate was heated

Table 1. Absorption maxima (λ, nm) of Schiff bases **2**–**6** in different solvents

Solvent	**2**	**3**	**4**	**5**	**6**
Chloroform	695	405	403	418	693
Methanol	340	336	360	407	348
Acetonitrile	348	338	355	412	381

Table 2. Absorption maxima of Schiff bases **2**–**4** and their complexes with copper(II) ion

Compound no.	λ_{max1}, nm	λ_{max2}, nm
2	257	340
2·Cu^{2+}	272	581
3	283	336
3·Cu^{2+}	275	585
4	287	360
4·Cu^{2+}	270	592

Table 3. Shifts of absorption maxima of Schiff bases **2**–**6** due to complexation with zinc, iron, cobalt, and nickel ions

Comp. no.	λ_{max}, nm	Δλ, nm			
		Zn	Fe	Co	Ni
2	340	1	–5	1	1
3	336	4	–16	1	1
4	360	–4	–5	0	0
5	407	–4	–7	–3	–2
6	348	–3	–2	–1	–3

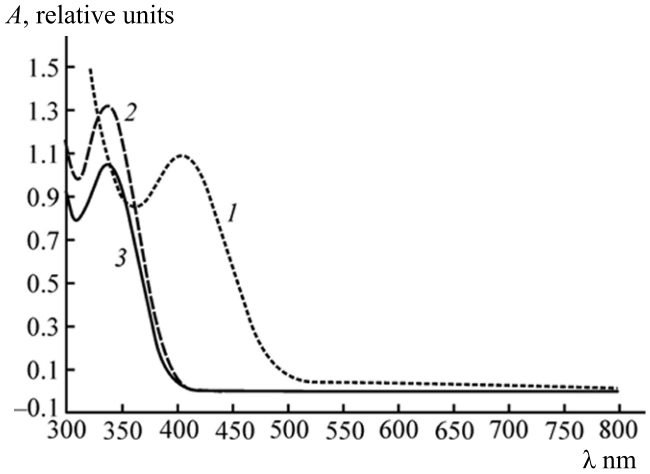


Fig. 2. Electronic absorption spectra of Schiff base **3** in (*1*) chloroform, (*2*) methanol, and (*3*) acetonitrile.

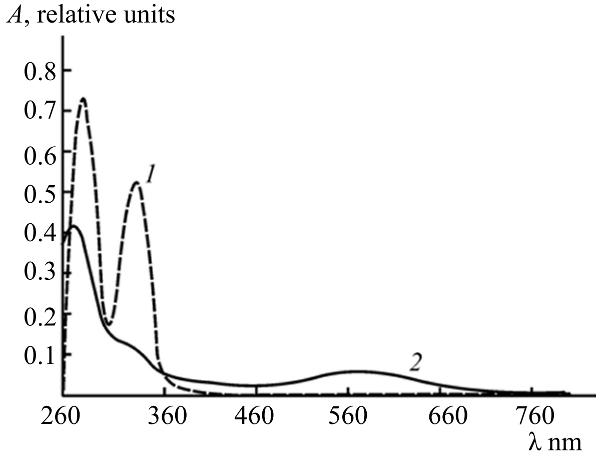


Fig. 3. Electronic absorption spectra of Schiff base **3** (*1*) in the absence and (*2*) in the presence of Cu^{2+} ions.

to 35°C, 3 g of Raney nickel was added, and the mixture was kept for 45 min and was then heated for 1 h under reflux. The mixture was cooled, the catalyst was filtered off, and the filtrate was treated with charcoal on heating under reflux and filtered. After cooling to room temperature, the precipitate was filtered off, recrystallized from 3-methylbutan-1-ol, and dried. Yield 42%, mp 95–96°C, purity 97% (GC/MS). IR spectrum, ν, cm^{-1}: 497 w, 581 w, 631 w, 712 w, 766 w, 793 w, 847 m, 917 w, 940 m, 987 m, 1060 m, 1079 m, 1127 s, 1181 m, 1217 m, 1251 m, 1294 m, 1332 w, 1355 w, 1452 m, 1511 s, 1589 w, 1610 m, 2878 m, 2921 m, 2957 m, 3056, 3346 s, 3396 s. ^1H NMR spectrum, δ, ppm: 3.60 br.s (8H), 3.68–3.77 m (4H), 3.85–3.97 m (4H), 4.67 br.s (2H), 6.05 d.d (1H, *J* = 8.4, 2.5 Hz), 6.22 d (1H, *J* = 2.5 Hz), 6.63 d (1H, *J* = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 67.77, 68.84, 69.27, 69.71, 70.09, 70.16, 70.30, 100.96, 105.53, 117.49, 139.35, 143.95, 149.92. Found, %: C 59.31; H 7.41; N 4.94. $C_{14}H_{21}NO_5$. Calculated, %: C 59.62; H 7.63; N 4.71.

(4-Benzylideneamino)benzo-15-crown-5 (2). Benzaldehyde, 0.5 mL (0.005 mol), was added dropwise to a solution of 1.41 g (0.005 mol) of 4-aminobenzo-15-crown-5 in 20 mL of methanol. The mixture was kept for 2 h at room temperature, and the precipitate was filtered off and dried. Yield 94%, off-white powder, mp 64.5–65.0°C. IR spectrum, ν, cm^{-1}: 500 w, 554 w, 595 w, 697 m, 796 w, 801 w, 847 w, 894 w, 943 w, 986 m, 1053 m, 1107 m, 1131 s, 1234 , 1263 s, 1294 m, 1354 w, 1426 w, 1454 m, 1509 s, 1575 w, 1591 w, 1624 m, 1646 w, 2862 m, 2898 m, 2929 m, 3030 w, 3055 w, 3068 w. ^1H NMR spectrum, δ, ppm: 3.63 br.s (8H), 3.74–3.82 m (4H), 4.03–4.15 m (4H), 6.87 d.d (1H, *J* = 2.3, 8.4 Hz), 6.94–7.02 m (2H), 7.46–7.55 m (3H), 7.87–7.95 m (2H), 8.66 s (1H). Found, %: C 65.12; H 7.21; N 3.48. $C_{21}H_{25}NO_5$. Calculated, %: C 65.32; H 7.43; N 3.71.

4-(4-Methoxybenzylideneamino)benzo-15-crown-5 (3) was synthesized in a similar way from 2.83 g (0.010 mol) of 4-aminobenzo-15-crown-5 and 1.30 mL (0.012 mol) of 4-methoxybenzaldehyde in 17 mL of ethanol; the mixture was kept for 3 h at 42°C. Yield 91%, white powder, mp 99.1–100°C. IR spectrum, ν, cm^{-1}: 526 w, 541 w, 786 w, 808 w, 833 w, 852 w, 943 w, 983 w, 1019 w, 1054 m, 1109 m, 1130 s, 1220 m, 1260 s, 1304 w, 1355 w, 1424 w, 1459 m, 1513 s, 1575 w, 1603 m, 1626 w, 1654 w, 2871 m, 2891 m, 2938 m, 3040 w. ^1H NMR spectrum, δ, ppm: 3.62 br.s (8H), 3.74–3.81 m (4H), 3.83 s (3H), 4.02–4.15 m (4H), 6.81 d.d (1H, *J* = 2.4, 8.4 Hz), 6.91–6.99 m (3H), 7.01–7.09 m (2H), 7.81–7.90 m (2H), 8.56 s (1H). Found, %: C 65.69; H 7.21; N 3.25. $C_{22}H_{27}N_2O_5$. Calculated, %: C 65.32; H 7.33; N 3.49.

4-(4-Pyridin-4-ylmethylideneamino)benzo-15-crown-5 (4) was synthesized in a similar way from 1.41 g (0.005 mol) of 4-aminobenzo-15-crown-5 and 0.535 mL (0.006 mol) of pyridine-4-carbaldehyde in 5 mL of ethanol; the mixture was kept for 3 h at 41°C. Yield 86%, light green powder, mp 75.1–77.0°C. IR spectrum, ν, cm^{-1}: 391 w, 519 w, 548 w, 592 w, 627 w, 761 w, 795 w, 814 w, 851 w, 878 w, 916 w, 934 w, 989 w, 1026 w, 1091 m, 1131 s, 1230 s, 1266 s, 1316 w, 1330 w, 1363 w, 1375 w, 1414 w, 1453 m, 1513 s, 1555 w, 1588 m, 1598 m, 1626 w, 2868 m, 2922 m, 3030 w, 3067 w. ^{1}H NMR spectrum, δ, ppm: 3.63 br. s (8H), 3.72–3.85 m (4H), 4.03–4.17 m (4H), 6.96 d.d (1H, *J* = 2.4, 8.5 Hz), 7.01 d (1H, *J* = 8.5 Hz), 7.08 d (1H, *J* = 2.4 Hz), 7.79–7.84 m (2H), 7.70–7.76 m (3H). ^{13}C NMR spectrum, δ_C, ppm: 68.46, 68.64, 68.76, 68.81, 69.73, 70.48, 106.89, 113.75, 114.73, 121.94, 142.79, 143.49, 148.13, 148.98, 150.39, 156.63. Found, %: C 64.69; H 6.57; N 7.58. $C_{20}H_{24}N_2O_5$. Calculated, %: C 64.50; H 6.53; N 7.52.

4-[3-(5-Nitrofuran-2-yl)prop-2-en-1-ylideneamino]-benzo-15-crown-5 (5) was synthesized in a similar way from 1.41 g (0.005 mol) of 4-aminobenzo-15-crown-5 and 0.535 mL (0.006 mol) of 3-(5-nitrofuran-2-yl)prop-2-enal in 14 mL of methanol; the mixture was kept for 1 h at 35°C. Yield 86%, red powder, mp 148.2–149.9°C. IR spectrum, ν, cm^{-1}: 763 w, 809 w, 858 w, 939 w, 981 w, 1050 m, 1128 s, 1257 s, 1322 w, 1352 s, 1393 w, 1468 s, 1511 s, 1560 w, 1632 s, 2871 m, 2921 m, 3040. ^{1}H NMR spectrum, δ, ppm: 3.62 br.s (8H), 3.73–3.82 m (4H), 4.03–4.14 m (4H), 6.87 d.d (1H, *J* = 2.2, 8.5 Hz), 6.94–7.01 m (2H), 7.14 d.d (1H, *J* = 8.5, 16.0 Hz), 7.21–7.30 m (2H), 7.79 d (1H, *J* = 3.9 Hz), 8.51 d (1H, *J* = 8.5 Hz). Found, %: C 58.33; H 5.76; N 6.54. $C_{21}H_{24}N_2O_8$. Calculated, %: C 58.35; H 5.76; N 6.52

4-(Biphenyl-4-ylmethylideneamino)benzo-15-crown-5 (6) was synthesized in a similar way from 1.41 g (0.005 mol) of 4-aminobenzo-15-crown-5 and 0.95 mL (0.006 mol) of biphenyl-4-carbaldehyde in 10 mL of methanol; the mixture was kept for 1.5 h at 35°C. Yield 89%, light green powder, mp 152.3–153.5°C. IR spectrum, ν, cm^{-1}: 489 w, 567 w, 696 w, 726 w, 768 m, 799 w, 848 w, 875 w, 936 w, 982 m, 1052 m, 1132 s, 1228 m, 1264 s, 1308 w, 1359 w, 1425 w, 1453 m, 1508 s, 1540 w, 1558 w, 1584 w, 1622 s, 2869 m, 2929 m, 3045 w, 3070 w. ^{1}H NMR spectrum, δ, ppm: 3.63 br.s (8H), 3.75–3.84 m (4H), 4.04–4.16 m (4H), 6.90 d.d (1H, *J* = 2.3, 8.5 Hz), 6.95–7.05 m (2H), 7.37–7.45 m (2H), 7.46–7.56 m (2H), 7.72–7.79 m (2H), 7.80–7.87 m (2H), 7.97–8.04 m (2H), 8.71 s (1H). Found, %: C 72.48; H 6.57; N 3.13. $C_{27}H_{29}NO_5$. Calculated, %: C 72.56; H 6.60; N 3.20.

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