Synthesis and properties of potassium salts of per-*O*-carboxymethylcalix[4]pyrogallols and their complexes with Cu^{2+}, Fe^{3+}, and La^{3+}

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Synthesis of water-soluble potassium salts of carboxymethyl derivatives of calix[4]pyrogallols and dodeca(carboxylatomethyl)tetramethylcalix[4]pyrogallol (L) complexes with transition metal ions (Cu^{2+}, Fe^{3+}, La^{3+}) is described. Their structures in the solid state and in solution were characterized by NMR spectroscopy, ESR, and IR spectroscopy. Calix[4]pyrogallol dodecacarboxylates exist in the *rccc*-configuration. Calix[4]pyrogallol with methyl substituents at the lower rim in a wide range concentrations exists in water predominantly in the dimeric form. The obtained polynuclear transition metal complexes possess less symmetric structure than potassium salt of calix[4]pyrogallol ($K_{12}L$). All studied complexes contain water molecules bound by rather strong hydrogen bonds. At room temperature the Fe_4L complex is characterized by the environment of the Fe^{3+} ions close to octahedral. The absence of signals in the ESR spectrum of the Cu_6L complex indicates the strong antiferromagnetic interaction Cu^{2+}—Cu^{2+}.

Key words: calix[4]arenes, calix[4]pyrogallols, carboxylic acids, potassium salts, copper complexes, iron complexes, lanthanum complexes, aggregation, complexation.

Carboxylic acids and their complexes are of interest as objects of wide-scope basic research (for example, many publications (see, *e.g.*, Refs 1 and 2) are devoted to studying the properties of one of the simplest carboxylates, namely, Cu^{2+} acetate) and also as compounds promising for practical use.[3—6] Particularly, their use in coordination chemistry is due to the fact that the carboxylate anions are efficient donor groups for binding alkaline and transition metal ions.[7] Several coordination sites are necessary to provide high efficiency and especially selectivity of binding. Therefore, structurally organized polycarboxylic acids serve as a basis for the creation of complexones for a series of metal ions. In addition, they can form various polynuclear complexes including high-spin transition metal atoms.[6] The presence of unpaired electrons results in the appearance of unique magnetic and electrophysical properties, which can be used for the creation of molecular devices.[6,8—12] However, despite achieved success, the synthesis of sterically organized polycarboxylic acids remains urgent.

The development of organic chemistry and especially chemistry of calix[*n*]arenes, which became traditional objects of supramolecular science during the recent decades,[13,14] created exclusive possibilities for the modification of properties of the known ligating groups. Immobilization of several such groups on the calixarene framework allows one to obtain compounds of the new type, which can be named supermolecular ligands. They are characterized by a combination of the properties of chelates, podands, and macrocyclic polydentate compounds. An important feature of these ligands is the manifestation of the cooperative effect of binding groups due to their pre-organization in a molecule.

The immobilization of four acetylhydrazide groups on the calix[4]arene platform produces the efficient and selective extractant of transition metal ions.[15,16] It should be mentioned that these properties were not found for the monomeric analog. The functionalization of calix[4]phenol by carboxy groups[17—19] makes it possible to obtain a more selective ligand for binding lanthanide ions than complexones based on polycarboxylic acids. We have previously[20] found that the introduction of carboxy fragments into the calix[4]resorcinol matrix provided the formation of the efficient ionophore with the pH-controlled selectivity. In the case of calix[4]pyrogallols, the efficiency of complexation with lanthanide and alkaline metal ions was

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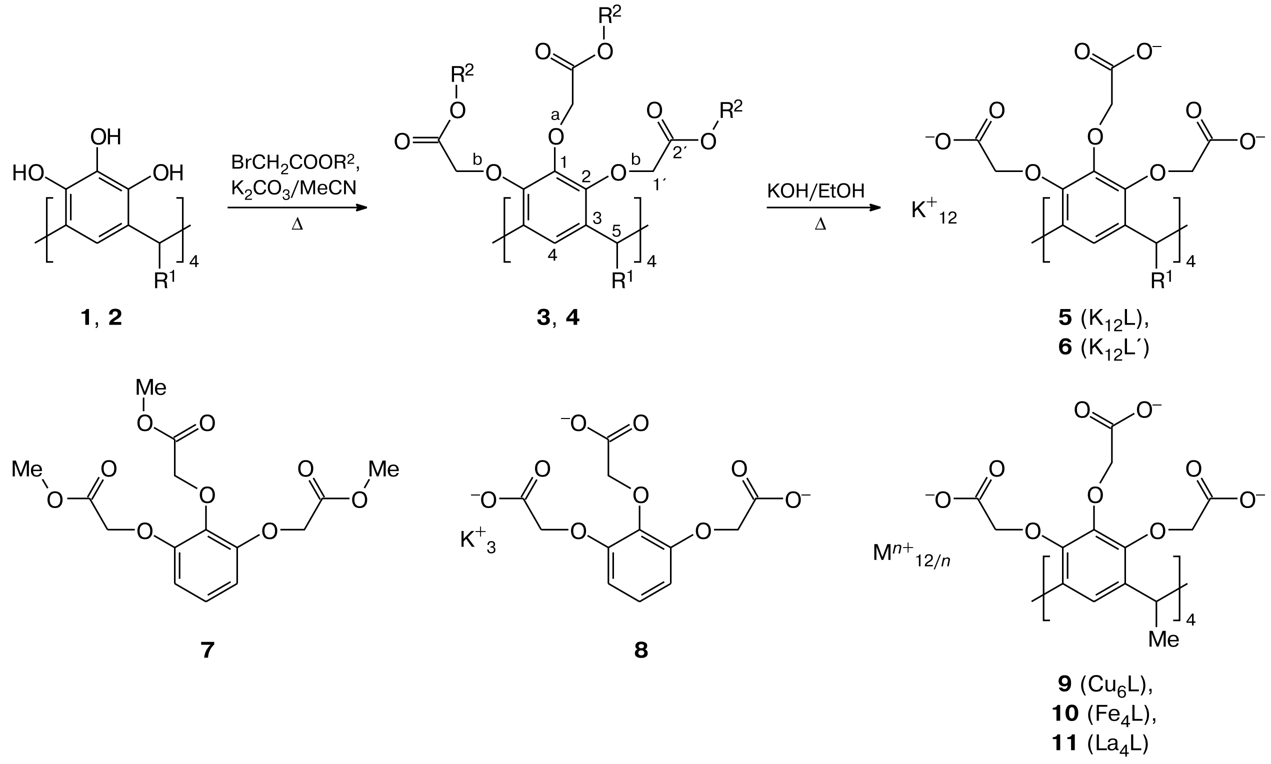
Scheme 1



R^1 = Me (**1**, **5**), C_9H_{19} (**2**, **6**); R^1 = $\overset{6}{\text{Me}}$, R^2 = $\overset{3'}{\text{Me}}$ (**3**); R^1 = $\overset{6}{\text{C}}H_2(\overset{7}{\text{C}}H_2)_7\overset{8}{\text{Me}}$, R^2 = $\overset{3'}{\text{C}}H_2\overset{4'}{\text{Me}}$ (**4**);
M = Cu, *n* = 2 (**9**); M = Fe, *n* = 3 (**10**); M = La, *n* = 3 (**11**)

enhanced compared to their monomeric blocks.[21] It was shown that the efficiency and selectivity of binding are substantially determined by structural features of the synthesized compounds and not only the number (effective concentration) of binding groups in the molecules.

One of the most efficient methods for preparation of transition metal complexes is the exchange reaction of alkaline metal ions in their salts for the corresponding ions. For this purpose, we synthesized potassium salts of calix[4]pyrogallols functionalized at all hydroxy groups by carboxymethyl substituents. Their structural and aggregation properties were studied and compared with the monomeric analog: potassium salt of 1,2,3-tris(carboxymethyl)benzene. New polynuclear Cu^{2+}, Fe^{3+}, and La^{3+} complexes with the 2,8,14,20-tetramethylcalix[4]pyrogallol dodecarboxylate derivative were synthesized. The general route for synthesis of the studied compounds is shown in Scheme 1.

Experimental

The starting unsubstituted calix[4]pyrogallols **1** and **2** were synthesized by known procedures.[22,23] Metal chlorides, nitrates, and hydroxides (analytical purity grade) and distilled water were used. Resorcinol, pyrogallol, methyl and ethyl bromoacetates, $CuCl_2$, $FeCl_3 \cdot 6H_2O$, $CDCl_3$ (99.8%), D_2O (99%), and DMSO-d_6 (99.5%) were purchased from Merck, Acros, or Aldrich and used without additional purification; MeCN and Me_2CO (reagent grade) were dried by distillation over P_2O_5; EtOH (96%) was used as purchased.

The NMR spectra were detected on an AVANCE 600 spectrometer (Bruker) equipped with a gradient block (field gradient to 50 G cm^{-1}); working frequency of the spectrometer being 600.13 (^1H) and 125.86 MHz (^{13}C). A 5-mm inverse sensor with the gradient coil along the *Z* axis was used. The spectra were recorded at 303 K. The chemical shifts are presented relatively to Me_4Si as the internal standard for samples in $CDCl_3$ and residual signals of H_2O for samples in D_2O ($\delta(H_2O)$ 4.72).

In experiments on measuring the self-diffusion coefficient (D_s), the correlation coefficient of the relative decrease in the NMR signal ($\ln I/I_0$) with the pulse gradient of the magnetic field

$$b = \gamma^2\delta^2g^2(\Delta - \delta/3),$$

(γ is the gyromagnetic ratio of protons, *g* is the amplitude of the magnetic field pulse gradient, Δ is the interval between the gradient pulses, and δ is the duration of the gradient pulses) exceeded 0.999 in all presented data. The amplitude of the magnetic gradient was changed linearly from 0 to 32 G cm^{-1} for 16 increments. The duration of the gradient pulses was $\delta = 2.8$ ms, and the interval between the gradient pulses was $\Delta = 50$ ms. The arithmetic mean D_s values are presented for all resolved signals in the NMR spectra. The error of D_s measurement was 5%, and the error of temperature stabilization was 0.1 K. The standard pulse sequences from the spectrometer library were used for all NMR experiments.

The theoretical D_s values were calculated by the HYDRONMR program.[24] The structures of calixarenes used for the calculation of D_s were optimized by the molecular mechanics method using the Chem3D program.[25] The hydrodynamic radius (R_H) was calculated from the self-diffusion coefficients (D_s) by the Stokes—Einstein equation

$$D_s = kT/6\pi\eta R_H,$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

The geometry of the model for the dimeric structure with the K^+ ions was optimized by the semiempirical method (AM1)[26] included into the HyperChem7.03 program package.[27]

The MALDI-TOF mass spectra were measured on a Finnigan MALDI-TOF Dynamo mass spectrometer (1,8,9-trihydroxyanthracene or 4-nitroaniline as the matrix). The IR absorption spectra were recorded for emulsions in Nujol or in KBr pellets on a Vector-22 FT-IR spectrometer (Bruker) with a resolution of 4 cm^{-1} and 16 scan accumulation. In the both cases, the spectra were nearly the same, which excludes the possibility for substances to react with the medium. The ESR spectra were detected on a Radiopan SE/X-2544 spectrometer in the range from 293 to 133 K.

2,8,14,20-Tetramethyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(methoxycarbonylmethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (3). Methyl bromoacetate (15.3 g, 0.1 mol) was added with stirring at ~20 °C to a mixture of calix[4]pyrogallol **1** (3.65 g, 6 mmol) and K_2CO_3 (16.6 g, 0.12 mol) in anhydrous MeCN (100 mL). The reaction mixture was stirred for 3 days with reflux under argon and filtered, and the solvent was distilled off. The oily residue was dissolved in dichloromethane and washed with water several times. The organic layer was separated and dried over $MgSO_4$, and the solvent was distilled off. The solvent residues were removed *in vacuo* at 100 °C. Ester **3** as a white powder was obtained in a yield of 6 g (68%), m.p. 139—141 °C. Found (%): C, 55.44; H, 5.50. $C_{68}H_{80}O_{36}$. Calculated (%): C, 55.43; H, 5.47. MALDI-TOF MS, *m/z*: 1473 $[M + H]^+$, 1497 $[M + Na]^+$, 1512 $[M + K]^+$.

2,8,14,20-Tetranonyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(ethoxycarbonylmethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4). Compound **4** was synthesized similarly to compound **3** from calix[4]pyrogallol **2** (6.3 g, 6 mmol), K_2CO_3 (16.6 g, 0.12 mol), and ethyl bromoacetate (16.7 g, 0.1 mol) in MeCN (100 mL). For spectra studies the product was additionally purified by column chromatography on silica gel using a petroleum ether—AcOEt (20 vol.%) mixture as the eluent. Ester **4** (7.1 g, 57%) was obtained as a viscous light yellow oil. Found (%): C, 63.93; H, 8.37. $C_{112}H_{168}O_{36}$. Calculated (%): C, 64.35; H, 8.10. MALDI-TOF MS, *m/z*: 2116 $[M + Na]^+$, 2132 $[M + K]^+$.

Dodecapotassium salt of 2,8,14,20-tetramethyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(carboxymethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (5), tetrahydrate ($K_{12}L \cdot 4H_2O$). A solution of KOH (1.34 g, 24 mmol) in EtOH (15 mL) was added to crude calix[4]pyrogallol ester **3** (1.47 g, 1 mmol) in boiling EtOH (15 mL). The reaction mixture was stirred for 12 h under reflux. The precipitate that formed was filtered off, washed with hot EtOH, and dried *in vacuo* (0.1 Torr, 2 h) at 110—120 °C. Salt **5** was obtained as a white powder in a yield of 1.68 g (95%), m.p. 320 °C (with decomp.). Found (%): C, 36.45; H, 2.57; K, 25.51. $C_{56}H_{52}K_{12}O_{40}$ (with allowance for four water molecules). Calculated (%): C, 36.67; H, 2.86; K, 25.58.

Dodecapotassium salt of 2,8,14,20-tetranonyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(carboxymethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (6), tetrahydrate ($K_{12}L' \cdot 4H_2O$). Compound **6** was synthesized similarly to compound **5** from calix[4]pyrogallol **4** (2.1 g, 1 mmol) (solution in 20 mL of EtOH) and KOH (1.34 g, 24 mmol) (solution in 15 mL of EtOH). Salt **6** as a white powder was obtained in a yield of 1.5 g (68%), m.p. 305 °C (with decomp.). Found (%): C, 46.34; H, 5.38; K, 20.77. $C_{88}H_{116}K_{12}O_{40}$ (with allowance for four water molecules). Calculated (%): C, 46.30; H, 5.12; K, 20.55.

1,2,3-Tris(methoxycarbonylmethoxy)benzene (7) was synthesized similarly to compound **3** from pyrogallol (12.6 g, 0.1 mol), K_2CO_3 (55 g, 0.4 mol), and methyl bromoacetate (67 g, 0.4 mol) in Me_2CO (200 mL). The reaction mixture was stirred for 24 h with reflux under argon. Ester **7** as a white powder was obtained in a yield of 19.8 g (60%), m.p. 67 °C. Found (%): C, 52.68; H, 5.23. $C_{15}H_{18}O_9$. Calculated (%): C, 52.63; H, 5.30. MALDI-TOF MS, *m/z*: 343 $[M + H]^+$, 366 $[M + Na]^+$, 381 $[M + K]^+$.

Tripotassium salt of 1,2,3-tris(carboxymethoxy)benzene (8), hydrate ($K_3L'' \cdot H_2O$). Compound **8** was synthesized similarly to compound **5** from ester **7** (0.77 g, 2 mmol) (solution in 30 mL of EtOH) and KOH (0.5 g, 9 mmol) (solution in 10 mL of EtOH). Potassium salt **8** as a white powder was obtained in a yield of 0.65 g (80%), m.p. 330 °C (with decomp.). Found (%): C, 33.67; H, 2.87; K, 26.97. $C_{12}H_{11}K_3O_{10}$ (with allowance for one water molecule). Calculated (%): C, 33.32; H, 2.56; K, 27.12.

{2,8,14,20-Tetramethyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(carboxylatomethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene}hexacopper(II) (9), hexahydrate ($Cu_6L \cdot 6H_2O$). A solution of $CuCl_2$ (0.14 g, 1 mmol) in water (5 mL) was poured with vigorous stirring to a solution of potassium salt **5** (0.3 g, 0.17 mmol) in water (5 mL). The reaction mixture was stirred for 1 h at the temperature of the bath 40 °C. The precipitate that formed was filtered off, washed with water and EtOH, and dried *in vacuo* (0.1 Torr, 1 h) at 80 °C. Complex **9** as a light blue powder was obtained in a yield of 0.27 g (90%), m.p. >300 °C. Found (%): C, 37.73; H, 3.34; Cu, 21.73. $C_{56}H_{56}Cu_6O_{42}$ (with allowance for six water molecules). Calculated (%): C, 37.74; H, 3.17; Cu, 21.39.

{2,8,14,20-Tetramethyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(carboxylatomethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene}tetrairon(III) (10), tetrahydrate ($Fe_4L \cdot 4H_2O$). Compound **10** was synthesized analogously to complex **9** from solutions of salt **5** (0.3 g, 0.17 mmol) and $FeCl_3 \cdot 6H_2O$ (0.19 g, 0.7 mmol) in water (5 mL). Complex **10** as a light beige powder was obtained in a yield of 0.26 g (96%), decomp.p. >300 °C. Found (%): C, 42.36; H, 3.11; Fe, 14.56. $C_{56}H_{52}Fe_4O_{40}$ (with allowance for four water molecules). Calculated (%): C, 42.32; H, 3.30; Fe, 14.09.

{2,8,14,20-Tetramethyl-4,5,6,10,11,12,16,17,18,22,23,24-dodeca(carboxylatomethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-

octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene}tetralanthanum(III) (11), hexahydrate ($La_4L \cdot 6H_2O$). Compound **11** was synthesized analogously to complex **9** from solutions of salt **5** (0.3 g, 0.17 mmol) and $La(NO_3)_3 \cdot 6H_2O$ (0.3 g, 0.7 mmol) in water (5 mL). Complex **11** as a white powder was obtained in a yield of 0.32 g (96%), decomp.p. >300 °C. Found (%): C, 34.40; H, 2.97; La, 28.24. $C_{56}H_{56}La_4O_{42}$ (with allowance for six water molecules). Calculated (%): C, 34.38; H, 2.88; La, 28.40.

Results and Discussion

Calix[4]pyrogallols are convenient matrices for the introduction of various functional groups. (Arene-1,2,3-triyl)tris(oxyacetic acid) esters **3**, **4**, and **7** were synthesized by the reactions of methyl or ethyl bromoacetate with calix[4]pyrogallols **1** and **2** and pyrogallol, respectively (see Scheme 1). The hydrolysis of these esters in excess KOH in an EtOH medium produced water-soluble polycarboxylic acids **5**, **6**, and **8**, which required no additional purification. Mixing of potassium salt of calix[4]pyrogallol **5** with equimolar amounts of $CuCl_2$, $FeCl_3$, and $La(NO_3)_3$ in water resulted in the precipitation of complexes **9—11**, which were isolated in high yields.

The compositions and structures of the synthesized macrocyclic compounds were established by the data of elemental analysis, MALDI-TOF mass spectrometry, ^{1}H NMR, and 2D and IR spectroscopies.

Spectral and structural features of potassium salts 5, 6, and 8 according to the IR and NMR spectroscopic data. The IR spectra of potassium salts **5**, **6**, and **8** (Fig. 1)

Table 1. NMR spectra of compounds **3**, **4**, **7** (in $CDCl_3$) and **5**, **6**, **8** (in D_2O) at 303 K

Atom[a] C or H	δ (*J*/Hz)											
	3		**4**		**5**		**6**		**7**		**8**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	—	143.27	—	143.26	—	133.44, 138.72	—	138.70	—	138.33	—	136.12
2	—	147.77	—	148.05	—	147.40[b], 148.15[c]	—	148.39	—	151.87	—	151.93
3	—	135.42	—	134.02	—	133.41, 138.27, 143.94, 144.37	—	144.02	6.58	109.26 (d, ^{1}J = 160)	6.57	107.07 (d, ^{1}J = 162)
4	6.35	121.04 (d, ^{1}J = 156)	6.22, 7.48	121.65	6.22[b], 7.29[c]	120.66[b], 121.66[c]	6.24[b], 6.95[c] (both br)	121.24	6.96	124.17 (d, ^{1}J = 163)	7.04	124.55 (d, ^{1}J = 163)
5	4.72	32.25 (d, ^{1}J = 130)	4.61	37.26	4.77	31.68 (d, ^{1}J = 128)	4.66	36.84	—	—	—	—
6	1.41	20.85	1.83	35.46	1.46	21.99 (q, ^{1}J = 128)	1.77	36.73	—	—	—	—
7	—	—	1.27	22.83, 28.33, 29.51, 29.80, 29.91, 30.18, 32.10	—	—	1.25 (br)	22.97, 28.40, 29.54, 29.72, 30.23, 30.54, 32.33	—	—	—	—
8	—	—	0.88	14.31	—	—	0.77	14.54	—	—	—	—
1´	4.16[d], 4.58[e]	69.82[e], 70.18[d]	4.19, 4.54, 4.65	69.83[e], 70.18[d]	3.24[c,d], 4.24[c,e], 4.37[b,d], 4.54[b,e]	71.44, 71.79, 72.70	3.25 (br), 4.19, 4.21, 4.35	71.77, 72.42	4.72[e], 4.78[d]	66.84[e], 69.92[d]	4.47[d], 4.52[e]	67.50[e] (t, ^{1}J = 148); 71.81[d] (t, ^{1}J = 147)
2´	—	169.29[d], 169.72[e]	—	168.82[d], 169.22[e]	—	176.5, 177.1	—	176.83, 176.41	—	169.44[e], 169.93[d]	—	177.09[e], 177.51[d]
3´	3.65	51.91	4.24	60.83	—	—	—	—	3.80[e], 3.82[d]	52.08[d], 52.31[e]	—	—
4´	—	—	1.26	14.22	—	—	—	—	—	—	—	—

[a] Numbering is given in Scheme 1.

[b] For the fragment pointed outside (see text).

[c] For the fragment pointed inside (see text).

[d] For substituents in position a.

[e] For substituents in position b.

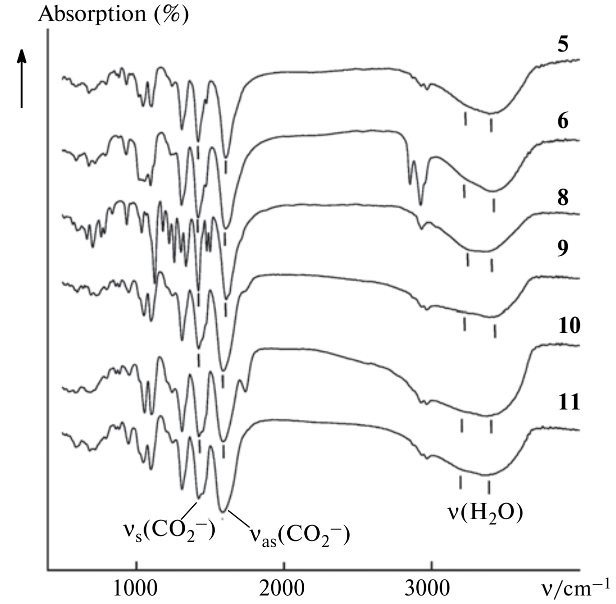


Fig. 1. IR spectra of potassium salts **5**, **6**, and **8** and complexes **9**—**11**.

correspond to the structural formulas ascribed to them, and they are characterized by the following analytical absorption bands known from previous studies[28,29]: ~3390—3250 cm^{-1} (m, vbr, ν(OH)); 3100—2800 cm^{-1} (w, ν(CH)); ~1600 cm^{-1} (vs, $\nu_{as}(CO_2^-)$) and ~1420 cm^{-1} (s, $\nu_s(CO_2^-)$); ~1310 cm^{-1} (s, ν(=C—O) arom.); ~1100—1050 cm^{-1} (m, ν(=C—C), ν(C—O)); ~700 cm^{-1} (m, $\delta(CO_2^-)$). A series low-intensity peaks and inflections are observed at 1600—1400, 1300—1100, 1050—800, and 800—400 cm^{-1} and attributed to stretching and bending vibrations of the C=C, Ph, CH_3, CH_2, and =CH groups.

A characteristic feature of the IR spectra is the pair of intense absorption bands at ~1600 and 1420 cm^{-1} in the spectra of all samples. The presence of these bands related to antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the carboxylate group, respectively,[29,30] confirms the formation of ionized complex structures.

NMR spectroscopy represents very informative methods for the determination of spatial structure of compounds. The signals in the NMR spectra of synthesized compounds **3**—**8** were assigned on the basis of ^{1}H, ^{13}C, HSQC, and HMBC experiments (Table 1).

Several isomeric forms (*rccc*, *rctt*, *rcct*, and *rtct*) are possible for both calix[4]pyrogallols and calix[4]resorcinols.[31] The *rccc*-isomers are usually isolated when basal calix[4]pyrogallols with alkyl substituents at the lower rim are prepared, as in our case.[32] These isomers are characterized by the predomination of the averaged C_{4v} symmetry, which is a result of fast equilibration between two equivalent boat conformations with transition through the cone conformation with the symmetry C_{4v}.[33] The study of calix[4]resorcinols unsubstituted and functionalized at the hydroxy groups of calix[4]resorcinols showed that the *rccc*-isomer does not transform into other isomers even at high temperatures.[33,34]

Other, predominantly *rctt*-isomers are usually formed during the condensation of resorcinols and pyrogallols with more bulky aromatic aldehydes.[21,32] The substitution of protons of the hydroxy groups in calix[4]resorcinols and calix[4]pyrogallols affords more conformationally flexible compounds than the starting calix[4]arenes but with the retention of the isomer type.[31]

With allowance for the aforesaid, to confirm the proposed *rccc*-configuration of calix[4]arenes **1**—**4**, it is enough to determine the spatial structure of their derivatives **5** and **6**. Since the spectra of calix[4]pyrogallols **5** and **6** with methyl and nonyl substituents, in further discussion we will restrict our detailed consideration by the spectra of only compound **5**.

The spectrum of compound **5** contains one signal of the bridging proton H(5) and two signals of aromatic protons H(4) (δ 7.29 and 6.22). This shape of the spectrum is characteristic of calix[4]arene in the boat conformation in which two opposite aromatic rings are nearly parallel to each other along the axial axis and two other rings are turned out and lie in the planes close to the equatorial one. The H(4) protons of the aromatic, turned out rings are between two adjacent aromatic rings and experience the high-field shift due to their circular currents. This made it possible to assign signals of the protons for the both pairs of the fragments using the HMBC experiments in which ^{1}H—^{13}C correlations are manifested through two and three bonds (see Table 1).

The spectra of triester **7** and tripotassium salt **8** exhibit two signals of the OCH_2 groups added to positions a and b (see Scheme 1) with the corresponding intensity ratio. Additional nonequivalence of the chemical shifts of the signals of the OCH_2 groups is observed for ester derivatives **3**, **4** and potassium salts **5**, **6**. The signals of the H(4) aromatic protons in the ^{1}H NMR spectra coalesce with the temperature increase. Magnetic nonequivalence of the protons of the OCH_2 groups is retained (Fig. 2). This can be due to anisotropy of the chemical shift of the carbonyl groups in the substituent itself and from the adjacent groups. In calixarenes, unlike their monomeric analogs, the substituents at the upper rim can experience steric hindrances preventing the averaging in time of their mutual orientations. In addition, the protons in the groups pointed inside the cavity experience an additional upfield shift induced by currents of the aromatic rings.

The presence of many polar groups at the upper rim of calix[4]arenes **5** and **6** can result in the self-association of calix[4]arenes, which also can be a reason for the nonequivalence of the chemical shifts of the protons of the methylcarboxylate groups due to their different participation in hydrogen bonding.

To check the latter assumption, we measured the self-diffusion coefficients by the NMR method with the pulse

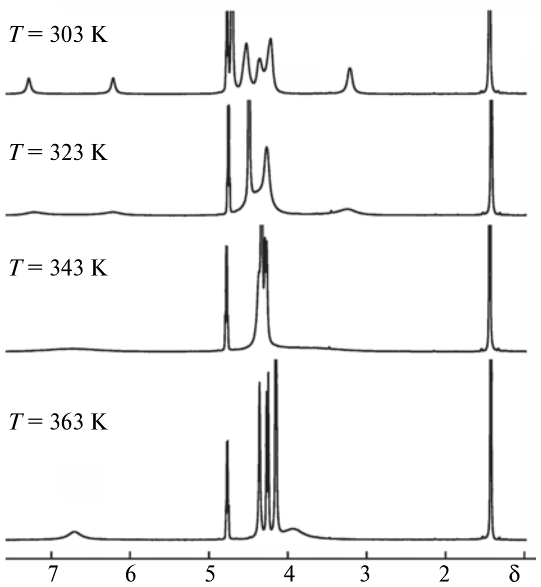


Fig. 2. ^{1}H NMR spectra of potassium salt of calix[4]pyrogallol **5** at different temperatures in D_2O.

magnetic field gradient.[35—37] The obtained D_s value of $2.42 \cdot 10^{-10}$ m^2 s^{-1} (R_H = 11.5 Å) is considerably lower than $D_s = 3.27 \cdot 10^{-10}$ m^2 s^{-1} (R_H = 8.5 Å) theoretically calculated by the HYDRONMR program.[24] This value is also lower than that for calixarenes with close geometric sizes. For example, for the calix[4]resorcinol tetrasulfonate derivative with the methyl substituents at the lower rim[38,39] the experimental values D_s ($3.50 \cdot 10^{-10}$ m^2 s^{-1}) and R_H (7.7 Å) determined for aqueous solutions agree well with the theoretical values: $D_s = 3.73 \cdot 10^{-10}$ m^2 s^{-1} and R_H = 7.4 Å.

According to available data,[40—43] the decrease in D_s of molecules by 25—30% indicates the formation of a dimer. When the concentration of compound **5** decreases from 35 to 0.5 mmol L^{-1}, the D_s value remains unchanged, indicating the stability of the aggregated structures.[44] This does not allow us to determine D_s of the free monomeric form using the standard dilution procedure.

The earlier[21] study of the acidic properties of the *rctt*-isomer of per-*O*-(carboxymethyl)calix[4]pyrogallol (R^1 = 4-$MeOC_6H_4$) showed that the formation of particles was detected only to the decaanion under the pH-metric conditions. This acid dissociates most easily by the first and second steps (pK_1 = 5.05, pK_2 = 4.98), which is due to the formation of an intramolecular hydrogen bond between the adjacent carboxymethylated pyrogallol fragments. Its further dissociation by the third (p$K_{3,4}$ = 12.19), fourth (p$K_{5,6}$ = 13.97), fifth (p$K_{7,8}$ = 15.59), and sixth (p$K_{9,10}$ = 18.15) steps, which proceeds with abstraction of immediately two protons, is substantially impeded with an increase in the total charge of the acid.

A backward process is observed upon the dissolution of potassium salt **5** in aqueous media: protonation of the carboxylate groups determined by the pH value of the medium. Unlike the *rctt*-isomer, in the *rccc*-isomer the functional groups immobilized at different phenyl fragments are spatially approached, which should facilitate their protonation due to the more efficient electrostatic interaction and formation of intramolecular hydrogen bonds. In the studied concentration range, solutions of salt **5** in D_2O were weakly alkaline (pH 7.2—8.7).

Thus, it can be assumed that a part of carboxylate groups is transformed into the carboxy groups upon the dissolution of potassium salt **5**. The fact that calixarene has a boat shape during dimer formation, indicating that only some functional groups are involved in its formation and the baskets in the dimer are shifted relative to each other. For this mutual arrangement different from more symmetric axial arrangement, a greater number of groups

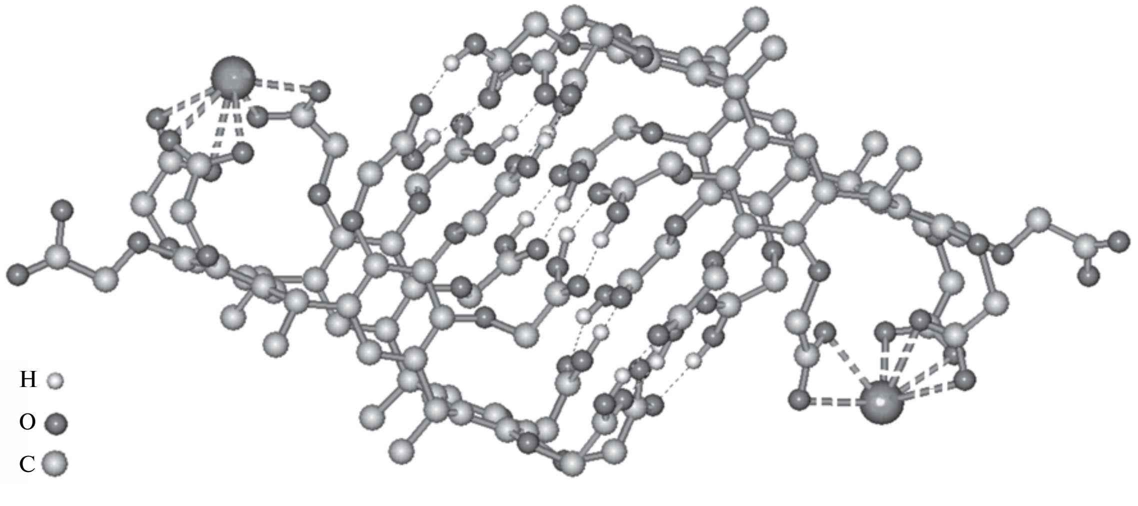


Fig. 3. Optimized by the semiempirical method (AM1) model of the structure of dimer **5** stabilized by two K$^+$ ions. Hydrogen atoms not involving in bonding are omitted.

can participate in binding. In addition, in this case, the destabilizing contribution of the electrostatic repulsion from the charged carboxylate groups, which can be concentrated predominantly on the parts of the baskets that are mostly remote from each other and are not involved in binding. The K^+ ions present in solution can additionally favor the electrostatic stabilization of similar structure due to coordination with the charged parts of the molecules. We have previously[20,21] shown that alkaline metal ion in water—DMSO solutions form mononuclear complexes with per-*O*-(carboxymethyl)calix[4]resorcinols and -pyrrogallols. The formation of binuclear complexes was observed only for the calix[4]resorcinol penta- and hexaanions. The model of the dimeric structure corresponding to the above concepts is shown in Fig. 3.

The addition of 12 equivalents of KOH to an aqueous solution of compound **5** increases D_s to $2.77 \cdot 10^{-10}$ m^2 s^{-1} (R_H = 10.0 Å). When 12 equivalents of HCl are added, a precipitate is formed and dissolved on heating. Therefore, D_s was measured at higher temperature (T = 323 K). Since the viscosity of water decreases on the temperature rise, it is correct to compare only the hydrodynamic radii of R_H. At the same time, the temperature rise should reduce the degree of aggregation. However, in the latter case, R_H increases to 11.9 Å.

Thus, an increase in the basicity of the medium shifts the equilibrium from dimeric to monomeric structures, and an increase in the acidity increases the degree of aggregation. At the same time, not so substantial change in the degree of aggregation of calix[4]pyrogallol **5** with the variation of the concentration and pH of the medium indicates that its dimeric form is stable.

Spectral and structural features of complexes 9—11 according to IR and ESR spectroscopic data. Since the solubility of the complexes is low, the IR and ESR spectra were recorded only for their powders. As should be expected, the IR spectra of complexes **9—11** (taking into account their ionic character) are of the same type and similar to the spectrum of the starting potassium salt **5**. However, more detailed analysis revealed some specific features.

The stretching vibration frequency $\nu_{as}(CO_2^-)$ (1606 cm^{-1}) in the spectrum of complex **5** is higher and the $\nu_s(CO_2^-)$ frequency (1419 cm^{-1}) is lower than the corresponding frequencies in the spectra of complexes **9—11**. In the considered Cu^{2+}, Fe^{3+}, and La^{3+} complexes, the parameters discussed are close, being ~1587 and 1423 cm^{-1}, respectively. This indicates the formation of the bonds with transition metal ions with the same strength but somewhat different compared with those of the univalent K^+ cation.

Proton abstraction from the carboxy group of carboxylic acid results in the situation that the oxygen atoms become equivalent. Monodentate or nonsymmetric bidentate coordination of the metal ion can violate equivalence of bonds. All this reflects the difference in the frequencies $\Delta\nu(CO_2^-) = \nu_{as} - \nu_s$, which reaches the maximum value at monodentate coordination.[30,45] However, the multifactor character and many carboxylate groups, whose absorption is overlapped, in the compounds under study do not allow us to conclude unambiguously about the coordination mode.

The spectrum of the Fe_4L complex contained the absorption of the carboxylate groups and also the high-frequency peak ν(C=O) with the absorption maximum at 1740 cm^{-1}, indicating the presence of nonionized carboxylate groups.[29] This is also confirmed by the difference spectra of compounds **10** and **5** exhibiting broad, typically acidic[46] absorption "hills" with maxima at ~3000 and 2500 cm^{-1} of the Fermi resonance ν_{OH} and overtones.

When $Fe(NO_3)_3$ excess was used instead of the equimolar amount of $FeCl_3$, a complex analogous to complex **10** (according to the elemental analysis and IR spectral data) was isolated. As already mentioned, the dissolution of potassium salt **5** in aqueous media is accompanied by the protonation of the carboxylate groups, and the susceptibility to hydrolysis[47] of the Fe^{3+} salt can favor this process. Taking into account the low relative intensity of the ν(C=O) absorption band of the carboxy groups compared to the $\nu_{as}(CO_2^-)$ band, we can assume that one or two water molecules in the composition of the Fe_4L complex (**10**) are in the hydrolyzed form. The proton of the water molecule is bound to one of the carboxylate groups, and its hydroxy group is coordinated to the Fe^{3+} ion.

The presence of hydroxy groups in the Fe_4L complex (**10**) is confirmed by the broadened IR bands (see Fig. 1) with absorption maxima at ~3390 and 3250 cm^{-1} ($\nu(H_2O)$) and a dome at ~650 cm^{-1} (libration vibrations of bound water) under a series of low-frequency peaks, which is characteristic of water of crystallization.[30,48] Analogous components are observed in the spectra of the Cu_6L (**9**), La_4L (**11**), and $K_{12}L$ (**5**) complexes.

The high-frequency (~3390 cm^{-1}) and low-frequency (~3250 cm^{-1}) absorption $\nu(H_2O)$ in the spectra of the complexes can be due to the Fermi resonance ν(OH) with overtones, manifestation of $\nu_{as}(H_2O)$ and $\nu_s(H_2O)$, and the presence of water molecules coordinated by different modes.[30,46,49—51]

The $\nu(H_2O)$ frequency values in the spectra of compounds **9—11** indicate the involvement of the water molecules in rather strong (up to ~7 kcal per bond) hydrogen bonds.[28,45—48] Evidently, the water molecules are coordinated with the CO_2^- groups ($CO_2^-...H_2O$), forming intra- and intermolecular hydrogen bonds, and also participate in coordination with metal cations.

As a whole, the broadened and smoothened absorption bands in the IR spectra indicate the nonsymmetric and distorted spatial structure of the complexes compared to the ideal C_{4v} symmetry. This is probably due to many polar substituents at the upper rim of calix[4]pyrogallol.

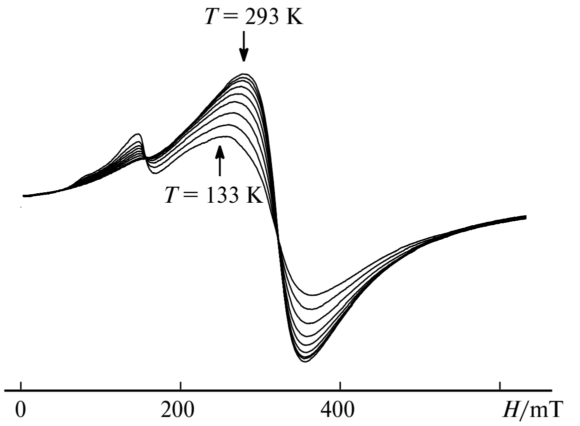


Fig. 4. ESR spectra of solid sample **10** with the temperature decrease from 293 to 133 K ($\Delta T = 20$ K).

The ESR spectrum of the Fe_4L complex (**10**) at room temperature is characterized by the single line with $g = 2.0$ and a width of 73.5 mT (Fig. 4) corresponding[52] to the high-spin configuration $Fe^{3+}(3d^5)$ with the environment of the Fe^{3+} ion close to octahedral. With the temperature decrease, the spectral line with $g = 2.0$ is broadened to 101 mT (at 133 K) with the simultaneous appearance and increase in the line intensity in the halved field. The temperature-dependent exchange elimination in the magnetically condensed state or a symmetry decrease can be assumed. The process is accompanied by an insignificant decrease in the integral intensity of the spectra, which is possibly related to antiferromagnetism of this complex.

No ESR spectra of the Cu_6L complex (**9**) were detected at room temperature or with the temperature decrease down to 133 K. The low-intensity line is observed only at $g = 2.0$. The reduction of Cu^{2+} to Cu^+ during complex formation can result in the absence of signals. However, this assumption is not consistent with the elemental analysis data, because the compensation of charges of the carboxylate groups requires twofold larger metal amount. Were the carboxylate groups transformed into the uncharged carboxy groups, the latter would have been observed in the IR spectrum of the complex. At the same time, it is known[1] that Cu^{2+} carboxylates (for example, Cu^{2+} benzoates and acetates with the lantern shape) are characterized by the direct Cu^{2+}—Cu^{2+} bond with the strong antiferromagnetic interaction. It is most likely that this is a reason for the absence of signals in the ESR spectrum of complex **9** under our conditions.

Thus, the structures of transition metal complexes **9**—**11** are of the same type and differ from ideality: their structures are more distorted than that of potassium salt of calix[4]pyrogallol **5**. The carboxylate groups form approximately equal in strength bonds with transition metal ions that are stronger than the bonds in the case of the univalent K^+ cation. All studied complexes of calix[4]pyrogallols contain water molecules bound by rather strong hydrogen bonds. At room temperature the Fe_4L complex (**10**) is characterized by the environment of the Fe^{3+} ions close to octahedral. The strong antiferromagnetic Cu^{2+}—Cu^{2+} interaction serves as the most probable reason for the absence of signals in the ESR spectrum of the Cu_6L complex (**9**).

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