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Complexes of Rhodium(III) with N-Functionalized Calix[4]Resorcinolol

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Abstract—Singularities of the rhodium trichloride reaction with calix[4]resorcinol functionalized with $CH_2N\cdot(CH_3)_2$ groups in ethanol on the upper rim of the molecule, and also of calix[4]resorcinol with ethanol solution of rhodium trichloride saturated with nitrogen monoxide were studied. Neutral complex compounds separated in the solid form were characterized by IR spectroscopy, Raman spectroscopy, ^{1}H NMR, ESR, X-ray electron spectroscopy, electronic spectroscopy, and conductometry. Quantum-chemical calculations were performed on the basis of the density functional method in order to determine the geometric structure and energy characteristics of the complex compound and the zwitter-ion form of the ligand.

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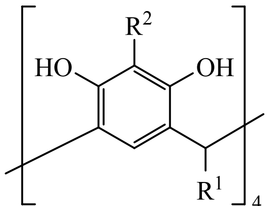
Complex compounds of Rh(III) with nitrogen-containing organic molecules [1–3] attract attention due to their ability to catalyze a number of organic reactions [4] and their significant biological activity [5, 6]. In this context complexes of rhodium with macrocyclic compounds, in particular, with calix[4] resorcinols modified with amino groups, can possess a great potential. The specific feature of calix[4]resorcinols is that they combine properties of complex-forming agents and molecular receptors, which makes it possible to use them in synthesis of new efficient catalytic systems [7, 8]. Amphiphilicity of calix[4]resorcinols allows them to self-arrange into supramolecular aggregates depending on the nature of the solvent. Such properties make it possible to consider calix[4]resorcinols as models of natural metal-protein systems [9].

The present article, which is a continuation of the research on the interaction of macrocyclic compounds with ions of VIII group metals [10, 11], presents the results of physicochemical study of two complex compounds obtained at various conditions from $RhCl_3\cdot3H_2O$ (**I**) and calix[4]resorcinols (L) modified with amino groups [12].

All the reactions were carried out in an inert atmosphere with a variation of the parent substances' molar ratio as follows: L:**I** = (1:2)–(1:4).



L

$R^1 = p\text{-}CH_3C_6H_4$; $R^2 = CH_3N(CH_3)_2$.

Calix[4]resorcinol (L) containing $CH_2N(CH_3)_2$ fragments on the upper rim of the molecule has a *cone* conformation and *ccc*-configuration [13]. The four $CH_2N(CH_3)_2$ functional groups are above the plane passing through carbon atoms of the methine groups.

The reaction between compounds **I** and L in ethanol results in the formation of air-resistant fine-crystalline complex **II**. The reaction between an ethanol solution of $RhCl_3\cdot3H_2O$ (**I**) preliminarily saturated with nitrogen monoxide and an ethanol solution of calixarene L results in the formation of air-resistant fine-crystalline complex **III**. Compounds **II** and **III** are well-soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and methanol; their composition does not change at variation in the parent substances' molar ratio.

Quantum-chemical simulation. In the compound L tertiary amino groups and hydroxy groups of resorcinol fragments are potentially capable of coordination. In amino calixresorcinols strong intramolecular OH···N hydrogen bonds [14] causing the formation of zwitter-ions are formed. For further investigation of the complex formation between compounds **I** and L it seemed reasonable to confirm such a possibility with quantum-chemical calculations. As the structure of the aryl residue on the lower rim of the calixresorcinol matrix has no influence on complex formation, a simulation system, in which there is an unsubstituted aryl residue on the lower rim of the molecule, was used for quantum chemical calculations.

The quantum chemical calculations were performed within the framework of the density functional theory using B3LYP hybrid nonlocal functional with gradient corrections, built into GAUSSIAN-03 software package [15]. The electron shell of the rhodium atom (3*s*3*p*4*d*5*s*5*p*) was described with a double zeta (DZ) basis set; the core-electron effect was taken into account by means of Hay-Wadt relativistic pseudopotential [16]. The standard basis set D95V was applied to describe valence electrons of C, O, N, and H atoms [17]. The geometry of the complexes in question was optimized without symmetry constraints. The presence of an energy minimum (a stationary point) on the potential energy surface was confirmed using the analysis of calculated frequencies of normal vibrations. The effect of the medium (ethanol) was considered within the framework of the Polarizable Continuum Model [15].

An assumption concerning the existence of a part of amino groups in the zwitter-ion form is confirmed by calculations of the ligand in question taking into account ethanol as the solvent. According to the obtained data, the molecule under study exists in an intermediate form, which is close to the zwitter-ion: the proton of phenolic hydroxy group is bound to the nitrogen atom of the amino group (Fig. 1). Average distances between atoms in the selected group are as follows: 1.538 Å for N^1–H^1, 1.060 Å for O^1–H^1, 1.642 Å for O^1–H^2, and 1.008 Å for O^2–H^2 (calculations were performed taking into account the effect of ethanol using the PCM method).

Various coordination alternatives were considered using the quantum-chemical method in order to study

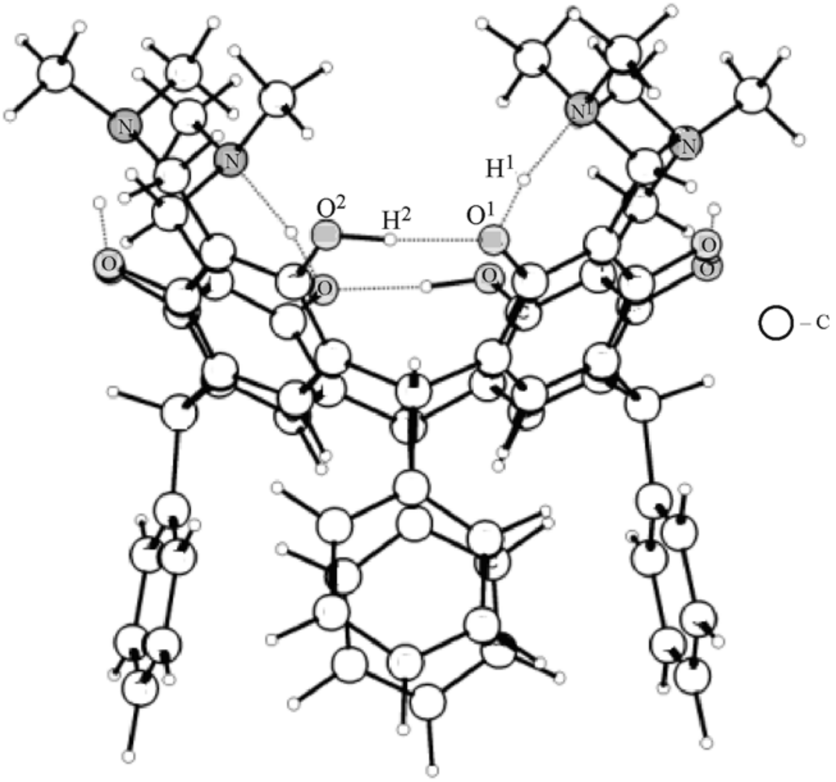


Fig. 1. Optimized structure of calix[4]resorcinol (L). N^1–H^1 1.538 Å, O^1–H^1 1.060 Å, O^1–H^2 1.642 Å, O^2–H^2 1.008 Å. (Calculations were performed on the basis of the PCM method taking into account the influence of ethanol.)

the character of complex formation between the compounds **I** and L in ethanol. According to the elemental analysis, compound **II** has the composition of $\{(L)\cdot[Rh_4Cl_{12}(OH_2)_4]\}$; and the structure shown in Fig. 2 proved to be the most energy advantageous among the investigated alternatives of the unprotonated ligand L coordination in compound **II**.

The energy effect of complex formation in ethanol (ΔH_{solv}) was calculated Eq. (1) in the assumption of dissociation of $RhCl_3\cdot 3H_2O$ salt with a correction for the energy of the crystalline lattice of rhodium trichloride (245 kcal mol^{-1}) [18].

$$\begin{aligned}\Delta H_{solv} = E_{tot}\{(L)\cdot[Rh_4Cl_{12}(OH_2)_4]\} - E_{tot}\{4Rh^{3+}\}\\ - E_{tot}\{12Cl^-\} - \{4H_2O\} - E_{tot}\{L\}.\end{aligned} \tag{1}$$

Here E_{tot} is the total energy of species optimized in view of the effect of the medium (ethanol).

The performed calculations predict the existence of the complex $\{[L]\cdot[Rh_4Cl_{12}]\}$ with double chloride bridges without water molecules, which is by 116 kcal mol^{-1} less stable as compared to the structure given in Fig. 2.

The dependence of the formation energy of zwitterionic forms of $\{(L)\cdot[Rh_4Cl_{12}(OH_2)_4]\}$ complex compound on the number of protonated nitrogen atoms in the ligand L is given in Fig. 3; according to this dependence the most protonated form of the complex compound in ethanol is thermodynamically the most stable.

As the initial rhodium trichloride contains coordination water, we have studied the protonation of nitrogen atoms in complex compound **II** in accordance with Eq. (2).

$$\begin{aligned}\{(L)\cdot[Rh_4Cl_{12}(OH_2)_4]\} + nH_3O^+_{solv}\\ \rightarrow \{(LH)\cdot[Rh_4Cl_{12}(OH_2)_4]\}^+ + nH_2O_{solv},\\ n = 1\text{–}4.\end{aligned} \tag{2}$$

In model calculations the hydrated proton was considered as the hydroxonium ion; it was found that the maximum protonation of nitrogen atoms (as well as

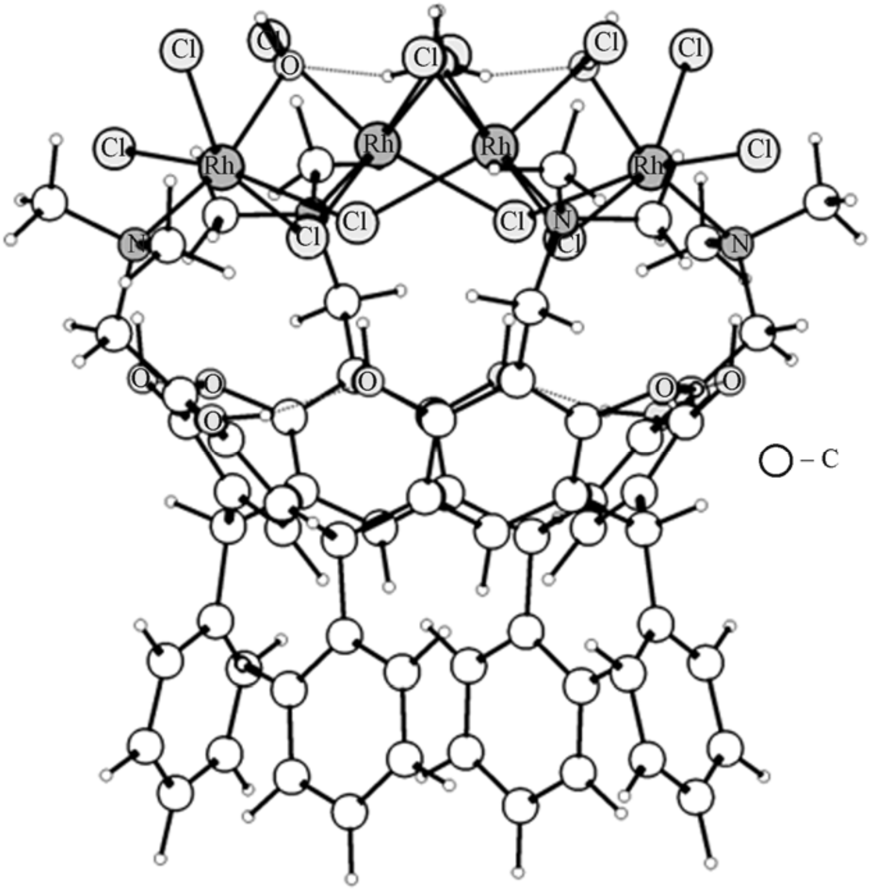


Fig. 2. Version of the optimized structure of complex **II** (unprotonated form).

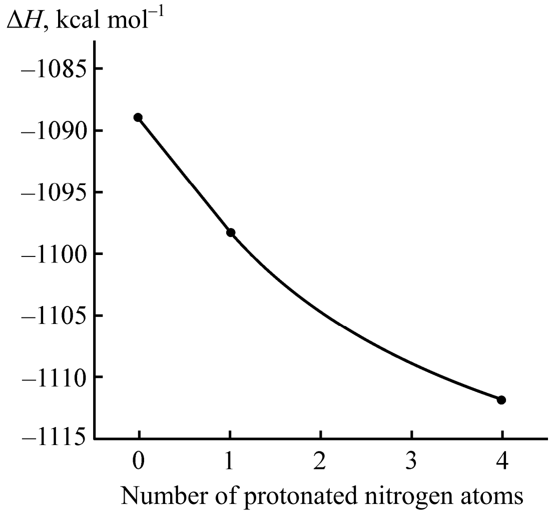


Fig. 3. Dependence of energy of formation of zwitter-ion forms in complex **II** $\{(L)\cdot[Rh_4Cl_{12}(OH_2)_4]\}$ on the number of protonated nitrogen atoms in the ligand (L).

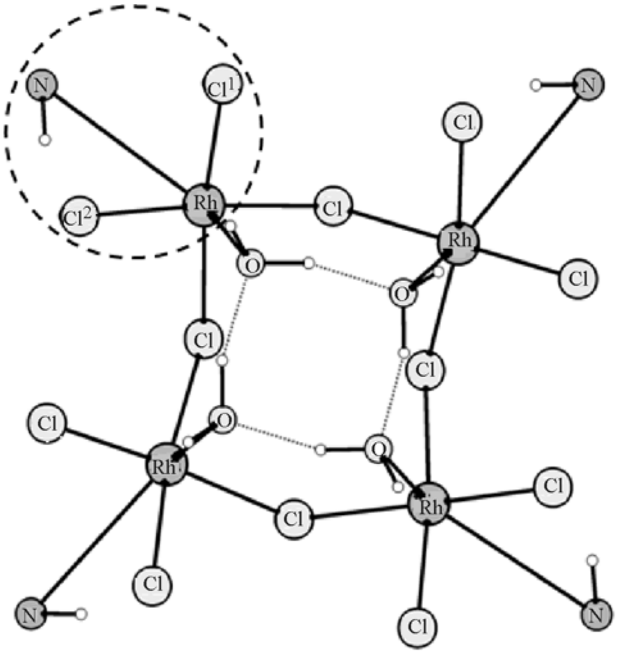


Fig. 4. Selected fragment of optimized exhaustively protonated complex **II**. Rh−N 3.775–3.844 Å, Cl^1−N 3.727–3.769 Å, Cl^2−N 3.041–3.078 Å, Cl^2−H 2.050–2.106 Å; Cl^2HN 153.1°–157.5°.

in case of the zwitter-ionic form) is also energy advantageous. The heat effect of the indicated process amounts to (−54.26) kcal mol^{-1}.

Thus, according to the calculated data, the most energy stable form is the protonated form of the calixresorcinol structure in the complex compound, as well as the poly-nuclear six-coordination structure of the $[Rh_4Cl_{12}(OH_2)_4]$ fragment (Fig. 4). These conclusions agree with the data of electronic and X-ray electron spectroscopy.

The Rh−N and Cl−N distances in the most stable fourfold protonated form of compound **II** are as follows: 3.775−3.844 Å for Rh−N, 3.727−3.769 Å for Cl^1−N, and 3.041−3.078 Å for Cl^2−N. Rhodium and chlorine atoms turn out to be equidistant from the protonated nitrogen atom, which is in agreement with the conclusions presented in [19−22], where it is pointed out that the bonding between chlorine and nitrogen is performed through the hydrogen atom. Our calculations do not contradict this conclusion: Cl^2−H distance amounts to 2.050−2.106 Å and Cl^2HN angle is within a range of 153.1°−157.5° (Fig. 4). Table 1 shows the calculated bond lengths, which are in agreement with the published data on calix[4] resorcinols with a ring of tetrametal complexes with CuCl and AgCl (2.45−2.55 Å for Cu−Cl and 2.69−2.76 Å for Ag−Cl [19]) coordinated on the upper rim and also with experimental crystallographic data for certain anionic chloride complexes of cadmium, zinc, and palladium (2.427 Å for Cd−Cl, 2.267 Å for Zn−Cl, and 2.286−2.298 Å for Pd−Cl [23]). According to Table 1, in the process of protonation Rh−N distances and RhClRh bond angles increase significantly; other bonds change negligibly.

Electronic spectra. Electron absorption spectra (EAS) of methanol solutions of compounds **II** and **III** differ from EAS of compounds **I** and L by the position and ratio of intensities of the maxima of absorption band in the UV region, and also by the appearance of new bands in the visible region, which confirms the complex formation. The bands in the EAS of compound **I** (λ_{max} ~510, 470, 440, 410, 375, 250, and 225 nm) point to the presence of various forms of rhodium(III) aqua chloride complexes, which is apparently related to the polynuclear structure of compound **I** and the effect of the protic solvent [24, 25]. The bands of (π→π*) and (*n*→σ*) transitions in the aryl and auxochrome fragments (λ_{max} ~220, 245, 290, 300, 320, 350, and 370 nm) are observed in EAS of calixarene L [26−28]. In the visible region of the compound **II** EAS there is one band of, apparently, *d*-*d*-transition (λ_{max} ~505 nm), which points to the polynuclear six-coordination structure of rhodium [24, 25] entering into the composition of complex

Table 1. Some bond lengths (Å) and bond angles (deg) of various forms of complex **II**

Bond, angle	Unprotonated form	1 zwitter-ion	4 zwitter-ions	1 nitrogen atom protonated	4 nitrogen atoms protonated
Rh–Cl	2.389–2.433	2.389–2.465	2.406–2.470	2.300–2.448	2.392–2.412
Rh–Cl[a]	2.536–2.725	2.510–2.775	2.425–2.508	2.494–2.801	2.460–2.523
Rh–O	2.110–2.150	2.108–2.262	2.259–2.288	2.111–2.166	2.135–2.205
Rh–N	2.179–2.197	2.177–2.207 (3.660)	3.590–3.619	2.174–2.193 (3.761)[b]	3.775–3.844
∠RhClRh	121.8–125.8	123.3–126.5	129.3–137.4	123.6–126.1	131.8–148.8

[a] Bridging chloride-ion. [b] Protonated nitrogen atoms.

compound **II**. Apart from $\pi\rightarrow\pi^*$ intraligand transitions of the aromatic fragments of the calix[4]resorcinol structure (λ_{max} ~ 230, 245, 260, and 280 nm), intensive charge transfer bands (λ_{max} ~ 310, 340, 360, and 380 nm), pointing at the disturbing effect of the complex-forming metal ion on the conjugation system of calixarene L, can be observed within a range of 200–380 nm in ESA of compound **II**.

The X-ray electron spectroscopy (XRES) study of compound **II** shows that the value of Rh $3d_{5/2}$ bond energy, equal to 310.7 eV, corresponds to a rhodium(III) complex [29].

The electron spin resonance (ESR) study of compound **II** did not detect paramagnetic products, which testifies to the diamagnetic character of this compound.

The ESR study of compound **III** demonstrated (Fig. 5) that a signal from the system with S 1/2 was observed. This signal points to the presence of approximately equal fractions (in terms of integral intensity) of the resorcinol radical ($g = 2.0038$) and of the rhodium complex with the following g-tensor values: $g_1 = 2.102$, $g_2 = 2.023$, $g_3 = 1.974$, and $\langle g\rangle = 2.033$.

Electron paramagnetic resonance spectra of such radical type are observed, for example, for rhodium complexes with porphyrins treated by nitrogen monoxide [30, 31]. Moreover, an ESR signal of the radical type was also observed for dirhodium(II) tetracarboxylate complex with calix[4]resorcinol, modified with four $CH_2N(C_2H_5)_2$ groups on the upper rim of the molecule [32]. Porphyrins are π-cation radical systems. Resorcinol ions also belong to the class of π-radicals; and g-factor values are rather sensitive to modifications in the structure of ($PhO^{\cdot}$) phenoxyl radicals or (O^{-}–Ar–$O^{\cdot}$) resorcinol radicals [33]. It is probable that the ESR signal in compound **III** is caused by both the state of the ligand in the solution during synthesis and the total electron distribution in the complex compound, which makes it strong and stable. According to our quantum-chemical calculations and the data [14], the most probable state of aminoresorcinol in the solution is the zwitter-ion form, facilitating the processes of single and double electron transfer and stabilization of the electron transfer products. It is possible that in the process of synthesis NO accepts electrons from calix-resorcinol π-system; in this connection the coordination number of the rhodium center with 18 valence electrons reaches 6 (d^6). The $Rh^{3+}(NO^{-})$ particle appears as a result of the electron transfer from the porphyrin π-system [31]; therefore, Rh^{+3} is formally observed in the compound **III** as it is known [34] that $\langle g\rangle = 2.2$ for Rh(II) complexes.

Also it should be noted that the rhodium complex in the compound **III** is characterized by rhombic symmetry with: $g_1 > g_2 > g_3$, $\langle g\rangle = 2.033$ [36], which points to nonequivalence of the crystalline field and,

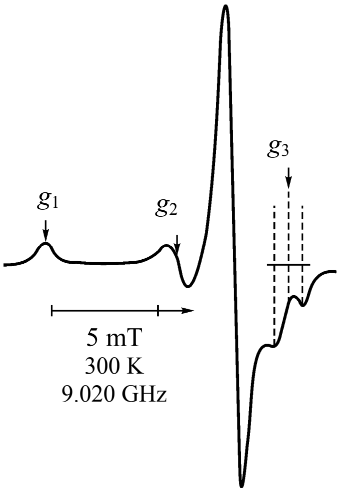


Fig. 5. ESR spectrum of compound **III**.

therefore, nonequivalence of ligands in the complex compound composition.

In the electron absorption spectra of such radical-type compounds it is possible usually to observe a wide intensive doublet band within a range of 400–770 nm, which is related to the charge transfer from a metal to a ligand; within a range of 300–400 nm there is an intensive singlet band, which is connected with a $\sigma-\sigma^*$ high-energy transition [25, 30, 31]. The $\sigma-\sigma^*$ transition for the methanol solution of the compound **III** manifests itself with a high-intensity singlet band (λ_{max} ~400 nm). An intensive doublet band of the charge transfer from the metal to the ligand is observed at λ_{max} ~450 and 480 nm, and it is connected with the electron density transfer from the rhodium(III) ion to NO particles. The bands of *d-d*-transitions are apparently overlapped by $\sigma-\sigma^*$ bands and charge transfer bands. In the electron absorption spectrum of the compound **III** it is also possible to observe wide intensive bands of intraligand transitions (λ_{max} ~235, 240, 280, and 300 nm) and charge transfer bands (λ_{max} ~320, 360, and 380 nm) [25–27].

Electrical conductivity measurements of solutions of compounds **II** and **III** in methanol carried out by the conductometry method demonstrate that they are non-electrolytes: 1.5 (**II**), 2 (**III**), and 5–8 μS (methanol).

IR spectra. Functionally substituted calix[4]-resorcinol (L) is a polyatomic system; therefore, the majority of vibrations have a complex character and manifest themselves in the form of wide overlapping bands with asymmetrical profiles, splitting, and bends. The formation of complexes **II** and **III** results in substantial changes in all regions of IR spectra as compared to compounds **I** and L and in the appearance of many other bands, the precise assignment of which is hardly possible or necessary. Tentative assignment of bands observed within a range of 3500–200 cm^{-1} for compounds L, **II**, and **III** is given in Table 2.

The main analytical bands of ligand L in the IR spectrum are absorption bands connected with the vibrations of amino and hydroxy groups and their environment. In the spectrum of compound L within a range of 3500–3100 cm^{-1} there is a wide ν(OH) band with the main absorption at 3250 cm^{-1}, indicating the formation of a system of strong intramolecular and intermolecular hydrogen bonds. The ν(C–N) frequencies of the amino groups are observed within a range of 1230–1000 cm^{-1} in the form of a singlet band at ~1212 cm^{-1} and a high-frequency component of a multiplet band at ~1090 cm^{-1}. The $\nu(CC)_{Ar}$ frequencies are observed in the form of an intensive singlet band at ~1608 cm^{-1} with weak splitting at ~1582 cm^{-1} and a high-frequency component of a multiplet band at ~1505 cm^{-1}. In the IR spectrum of compound L within a range of 650–500 cm^{-1} it is possible to observe bending vibrations [$\delta(CCC)_{Ar}$, $\delta(CCO)_{Ar}$ + Ar_{rotat}] in the form of a low-intensive band at ~632 cm^{-1} and a wide low-intensive triplet at ~601, 551, and 532 cm^{-1} [13, 26, 27, 36, 37].

As a result of complex formation the greatest changes are experienced by the frequencies of stretching vibrations of the donor groups taking part in the coordination. In the IR spectrum of compound **II** ν(C–N) frequency is shifted by 8 cm^{-1} into a high-frequency spectral region and can be observed at 1220 cm^{-1}. The position of the second ν(C–N) band does not change (~1090 cm^{-1}). A slight shift (8 cm^{-1}) of the ν(C–N) absorption band in complex **II** is due to a low strength of the forming Rh–N bonds, which are, apparently, mainly of the ion-dipole nature with a certain share of a covalent component [19]. According to the quantum-chemical calculations, Rh–N and Cl–N bonds in compound **II** are approximately equivalent (3.775–3.844 Å for Rh–N and 3.727–3.769 Å for Cl–N). The bands of the Rh–N bond appear within the range of 600–400 cm^{-1} [38, 39]; usually these bands are weak and wide. The formation of the bond between rhodium and the nitrogen atoms of the amino groups is confirmed by the appearance of a new wide band of ν (Rh–N) ~418 cm^{-1}. The low intensity and relatively high frequency of this band point to a certain extent of the covalent character of Rh–N bond [40]. Stretching vibrations of the OH groups of resorcinol fragments and stretching vibrations of O–H bonds of water molecules appear together within a range of 3100–3600 cm^{-1} in the form of a wide band with the main absorption at ~ 3290, 3380, 3430, and 3510 cm^{-1} [27, 36, 37]. It is possible to conclude that coordinately bound water is present in the composition of the complex on the basis of the frequency of the δ(H–O–H) bending vibration, which depends only slightly on the metal nature and usually appears within a range of 1580–1650 cm^{-1} [38–41].

In the spectrum of compound **II** δ(HOH) vibrations are recorded at ~1650 cm^{-1}. Apart from δ(HOH) vibrations, $\nu(C\overset{...}{-}C)_{Ar}$ vibrations can be observed within a range of 1700–1500 cm^{-1} at ~1601 and 1520 cm^{-1}. A wide multiplet band with peaks at 632 and 556 cm^{-1} is related to $\delta(CCC)_{Ar}$, $\delta(CCO)_{Ar}$, and

Table 2. Main vibration frequencies (cm^{-1}) of compounds L, **II, III** in IR spectra

Assignment	L	**II**	**III**
ν(O–H)$_{\mathrm{res}}$	3250		3440
ν(O–H)$_{\mathrm{res}}$ + ν(O–H)$_{\mathrm{HOH}}$		3290, 3380, 3430, 3510	
ν(CH$_{\mathrm{Ar}}$)	3050, 3020	3030	
N(CH$_3$, CH$_2$, CH)	2928, 2890, 2872	2921, 2825	2961, 2924, 2825
δ(HOH)		1650	
ν(Ar)	1608,1582, 1505	1601, 1520	1603, 1511
δ_{as}(CH$_3$) + δ_{as}(CH$_2$)	1464	1452	1472
δ(CH)	1420	1410	
δ_{s}(CH$_3$) + ω(CH$_2$)	1376, 1350	1380, 1338	1384
τ(CH$_2$) + δ(CH) + ν(C$_{\mathrm{Ar}}$–O)	1300, 1288	1286, 1250	1284, 1249
ν(C–N)	1212, 1090	1220, 1090	1224, 1087
ν(C$_{\mathrm{Ar}}$–O)	1196		
ν(Ar), ν(CH), ν(C$_{\mathrm{Ar}}$–O), δ(CH)$_{\mathrm{Ar}}$	1181, 1157, 1143	1180, 1163, 1140	1186, 1162, 1138
ν(CCC)$_{\mathrm{Ar}}$, ν(C–C), ν(C$_{\mathrm{Ar}}$–O), ν(CH), planar δ(CH)$_{\mathrm{Ar}}$	1110, 1072, 1040, 1016, 1000	1070,1030, 1016, 1010	1020
ν(CCO)$_{\mathrm{Ar}}$	930	980	963
δ(CH)$_{\mathrm{Ar}}$	900	920	936
Non-planar δ(CH)$_{\mathrm{Ar}}$, ν(Ar), ν(C–C)	846	864	811
ρ(CH$_3$, CH$_2$) + non-planar δ(CH)$_{\mathrm{Ar}}$	792, 784, 728, 712, 696		721
ρ(CH$_3$, CH$_2$) + non-planar δ(CH)$_{\mathrm{Ar}}$ + ρ(H$_2$O)		805, 760, 704	
δ(CCC)$_{\mathrm{Ar}}$, δ(CCO)$_{\mathrm{Ar}}$ + Ar$_{\mathrm{rot}}$	632, 601, 551, 532	632, 560	553, 486
ν(Rh–O$_{\mathrm{coord.\ water}}$)		490, 470	
ν(Rh–N)		418	
ν(Rh–N), ν(Rh–N)$_{\mathrm{NO}}$			430, 412
ν(Rh–Cl$_{\mathrm{term}}$)		340, 332	332
ν(Rh–μ-Cl)		290, 285	

Ar$_{\mathrm{rotat}}$ vibrations; an intensive doublet band related to ν(Rh–O$_{\mathrm{coord.water}}$) vibrations is found within the range of ~ 490 and 470 cm^{-1} [13, 39]. The rhodium fragment in compound (II) has a polynuclear structure; therefore, the IR spectrum contains absorption of ν(Rh–Cl$_{\mathrm{term}}$) at ~340 and 332 cm^{-1}, which is characteristic of terminal bonds, and bands of bridging bonds ν(Rh–μ-Cl), at ~ 290 and 285 cm^{-1} [39, 42, and 43]. The ν(Rh–Cl$_{\mathrm{term}}$) vibrations are observed in the form of a doublet band; the ν(Rh–μ-Cl) vibrations are found in the form of two singlet bands. According to [44], the doublet character of the ν(Rh–Cl$_{\mathrm{term}}$) absorption band points to the *cis*-position of the terminal chloride-ions in relation to each other in the rhodium fragment. This fact is confirmed by the equatorial position of the chloride ions with respect to the rhodium(III) ion. The high intensity of ν(Rh–Cl$_{\mathrm{term}}$) band, as compared to intraligand vibration bands in the far region of the IR spectrum, suggests an outer-sphere character of the rhodium fragment binding with the calixresorcinol structure.

The IR spectral regions at 1180–1140 and 870–820 cm^{-1} are of importance for determination of conformation and configuration of compounds L and **II**. In these regions of the ligand L spectrum conformationally dependent vibrations of the calixresorcinol structure at ~ 1181, 1157, and 1143 cm^{-1} and a wide band of complex overlapping vibrations at ~ 846 cm^{-1} can be observed, which is characteristic for the *ccc*-

isomer. In compound **II** these vibrations are observed in the form of bands, correspondingly, at ~1180, 1163, 1140 cm^{-1} and a wide asymmetrical band at 864 cm^{-1}, which points to the retaining of the *cone* conformation and *ccc*-configuration in compound **II** [13, 26].

Comparative studies of IR spectra of compounds L and **III** also make it possible to record changes pointing to various composition and structure of these compounds. The ν(C−N) frequency in the spectrum of complex **III** increases by 12 cm^{-1} and reaches a value of 1224 cm^{-1}; the second band of skeletal vibrations of C−N bonds is shifted negligibly (up to ~1087 cm^{-1}) and is observed in the form of an intensive singlet band. The ν(OH) frequency (3440 cm^{-1}) in complex **III** increases by 190 cm^{-1}. The frequencies of conformationally sensitive vibrations do not change as compared to the ligand L, which indicates at the retaining of the *cone* conformation and *ccc*-configuration in the calixresorcinol matrix forming a part of the compound **III**. In a range of 500−650 cm^{-1} it is possible to observe an asymmetrical doublet band with an intensive high-frequency component at ~ 553 cm^{-1} and a low-intensity low-frequency component at ~486 cm^{-1} for $\delta(CCC)_{Ar}$, $\delta(CCO)_{Ar}$, and Ar_{rotat} vibrations [13, 26, 37].

A new intensive band at ~1630 cm^{-1} pointing to coordination of the nitrosyl group to the Rh(III) ion [2, 45−47] is detected in the IR spectrum of compound **III** within a range of 1700−1600 cm^{-1}. The ν(M−N) and δ(MNO) vibrations of the coordinated nitrosyl group occur within a range of 500−650 cm^{-1}; they have closely spaced frequencies and, therefore, are mixed [39]. It is also possible to observe a series of vibrations of the calixresorcinol structure within this range [13]; therefore, it is difficult to clearly distinguish ν(M−N) and δ(MNO) vibrations of the nitrosyl group. The coordination of NO to the metal ion results in the formation of complexes either with a linear or an angular M−NO group (linear and bent nitrosyls). Bent nitrosyls have a higher electron density than linear nitrosyls; therefore, in complexes with nonlinear M−NO groups the coordinated nitrosyl interacts with substances of the electrophilic character [2, 46]. Complex **III** was subjected to the action of oxygen, which resulted in the formation of new compound **IVa** without a band in a range of 1700−1600 cm^{-1}, but with new bands at 1222 and 1325 cm^{-1}, which are characteristic for the nitrite ion coordinated to a metal via nitrogen [39].

In a spectral region below 500 cm^{-1} the intraligand vibrations in compound **III** are characterized by a low intensity; however, at 332 cm^{-1} there is a new high-intensity band, which is characteristic of $\nu(Rh{-}Cl_{term})$ of terminal bonds. This band points to the mononuclear composition of the rhodium fragment and testifies to its outer-sphere binding with the calyxresorcinol matrix [39, 42, and 43]. Stretching vibrations of (Rh−N) bonds appear in the IR spectrum as a doublet band with maxima at 430 and 412 cm^{-1}. Apparently, this fact points to the coordination of amino groups to the rhodium ion via the nitrogen atom and to the coordination of the NO particle. Ligands containing donor atoms of nitrogen can cleave halide bridges [39, 47]. The coordination center in compound **III** is a mononuclear complex of Rh(III) formed as the *trans*-isomer, since only one $\nu(Rh{-}Cl_{term})$ band is observed in the IR spectrum [44].

The ^1H NMR study have shown that in compounds **II** and **III** the signals of conformationally dependent protons are retained and have the following values close to those of the signals in the spectrum of the compound (L) [12] (δ, ppm): 5.89−5.92 s (4H, CH), 6.23−6.27 s (4H, H^{μ}_{arom}, C_6H_2), 5.9 s (4H, CH), 6.6−6.7 d (8H, H^{μ}_{arom}, C_6H_4), and 6.67−6.72 d (8H,H^{σ}_{arom}, C_6H_4). This fact points to the retaining of the *cone* conformation and *ccc*-configuration in compounds **II** and **III**. As a result of the complex formation the duplication of signals of conformationally dependent protons of resorcinol rings in the regions specified above is observed, which points to the complex formation [27, 28].

Thus, the data of the physicochemical studies and elemental and X-ray fluorescence analyses with due account of the ligand conformation and quantum-chemical calculations make it possible to conclude that the reaction of compounds **I** and L in ethanol results in the formation of complex **II** with the $\{L\cdot[Rh_4Cl_{12}\cdot(OH_2)_4]\}$ structural unit; the reaction of the ethanol solution of compound L with the ethanol solution of compound (I) previously treated with nitrogen monoxide, results in the formation of complex **III** with the $\{L\cdot4[Rh^{+3}(NO^{-})2(Cl^{-})]\}$ structural unit. The structure of compound **II**, as given by the quantum-chemical calculations, is shown in Figs. 2 and 4.

In order to study antibacterial properties of compounds L, **II**, and **III** they were tested for antimicrobial activity using *Staphylococcus aureus*, *Bacillus cereus* 8035, and *Escherichia coli* F-50 as test objects. The bacteriostatic properties of these compounds were studied by the method of serial dilution in a liquid culture medium. The bacteriostatic effect of the specimens was taken into account with respect to the growth inhibition of test-microorganisms at a concentration of 1 mg ml^{-1} [48]. Comparative analysis of the bacterial properties in relation to the pathogenic cultures showed a high activity of the parent compound L against *Staphylococcus aureus* (0.085 mg ml^{-1}). Compound **III** exhibited a lower activity against *Staphylococcus aureus* (0.2 mg ml^{-1}). As for *Bacillus cereus* 8035 and *Escherichia coli* F-50, compounds L and **III** exhibited a lower activity (0.25 and 0.5 mg ml^{-1}, respectively). Compound **II** shows no antimicrobial activity in relation to the bacteria used in the test. It is probable that the demonstration of antibacterial properties by compound **III**, as compared to compound **II**, is caused by different composition and geometrical structure of these compounds.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker MSL-400 (400.13 MHz) instrument. The δ-values were calculated in relation to signals of the solvent residual protons. The IR spectra were recorded on UFS 113-V and Vector 22 Bruker Fourier spectrometers within ranges of 600−200 cm^{-1} and 4000−450 cm^{-1}, respectively. Crystalline samples were examined in the form of mulls in dried mineral oil. The Raman spectra were recorded on an FT-Raman RAMI Bruker spectrometer. The electron absorption spectra were recorded on SF-16 and Specol spectrophotometers within ranges of 200−350 and 350−700 nm, respectively (l = 1 cm, $c = 1\times10^{-3}$ M). Crystalline samples were studied in the form of solutions in anhydrous methanol. The ESR spectra were recorded on an SE/X-2544 spectrometer (Radiopan.) The X-ray electron spectra were obtained with the help of MgK_α source of X-ray radiation at a pressure 10^{-2} Pa using a VIEE-15 instrument. Ionic conductivity measurements for the solutions of the complexes in methanol at 25°C were performed using an LM-301 conductometer (an LM-3000 standard cell).

Determination of carbon, hydrogen, and nitrogen was performed by the microanalytical method using a Carlo Erba analyzer; rhodium was detected by the X-ray fluorescence analysis using a SUR-02 RENOM F1 X-ray spectrometer; chlorine was detected by the procedure [50].

Compound **I** used in the work was of analytical grade; compound L was obtained as described in [12]. Nitrogen monoxide was obtained by the procedure [49]. The solvents were purified and dehydrated by the standard procedures directly before use. Preparatory operations and syntheses were carried out in dry argon atmosphere using Schlenk technique.

Tetraaquaoctachloro-μ-tetrachloro{[4,6,10,12,16,18,22,24-octahydroxy-5,7,17,23-tetrakis(dimethylaminomethyl)-2,8,14,20-tetra-(4-methylphenyl)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-dodecaen]}tetrarhodium(III), {(L)·[$Rh_4Cl_{12}(OH_2)_4$]} (II). Compound **I** in the amount of 0.098 g (0.373 mmol) was dissolved in ethanol (20 ml) simultaneously flushed with argon within 30 min (the solution color was dark red). Then an orange solution of calixarene L (0.1 g, 0.093 mmol) in ethanol (20 ml) was added with stirring. As a result of stirring at 75°C for 7 h the color became red-brown and a precipitate was formed. The solvent was removed from the reaction mixture in a vacuum; the resulting residue was washed with ethanol and benzene in the argon atmosphere and dried in a vacuum at 40°C (0.06 torr) above Al_2O_3 to a constant weight. Yield 0.092 g (~50%), a brown substance. Found, %: C 41.16; H 4.29; Cl 21.57; N 2.89; Rh 20.83. $C_{68}H_{84}Cl_{12}\cdot O_{12}N_4Rh_4$. Calculated, %: C 41.09; H 4.23; Cl 21.45; N 2.82; and Rh 20.75.

Octachlorotetranitrosyl{[4,6,10,12,16,18,22,24-octahydroxy-5,7,17,23-tetrakis(dimethylaminomethyl)-2,8,14,20-tetra-(4-methylphenyl)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-dodecaen]}tetrarhodium(III), {L·4[$Rh^{+3}(NO^-)2(Cl^-)$]} (III). Compound **I** in the amount of 0.098 g (0.373 mmol) was dissolved in ethanol (20 ml) simultaneously flushed with argon within 15 min (the solution color was dark red). Nitrogen monoxide was passed through the ethanol solution in the argon atmosphere until the color of the solution became orange. Then in the argon atmosphere a solution of calixarene L (0.1 g, 0.093 mmol) in ethanol (20 ml) was added with stirring. The bright red solution was stirred at 75°C for 3 h, while argon was passed through; then the solution was held for 24 h in the argon atmosphere. A bright red precipitate was formed, and the solution above the precipitate was transparent. The solvent was distilled off in a vacuum at 40°C (0.06 torr). The resulting residue was washed with ethanol and benzene in the argon atmosphere and dried in a vacuum at 40°C (0.06 torr) above Al_2O_3 up to a constant weight. Yield 0.094 g (~53%). Found, %: C 43.09; H 4.05; Cl 14.98; N 5.98; Rh 22.00. $C_{68}H_{76}C_{l8}O_{12}N_8Rh_4$. Calculated, %: C 43.13; H 4.02; Cl 15.01; N 5.92; Rh 21.78.

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