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Interaction of Rhodium Trichloride with N-Functionalized Calix[4]resorcinol in Acetone

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Abstract—A supramolecular neutral complex was isolated in the solid state in the reaction of calix[4]-resorcinol having nitrogen-containing substituents [$CH_2N(CH_3)_2$] on the upper rim of the molecule with $RhCl_3 \cdot 3H_2O$ in acetone. The complex, in addition to the calixarene structure and the rhodium-containing fragment, includes the dioxygen molecules bound to the rhodium ion [$Rh^{+3}(O_2^-)$]. The compound was characterized by IR, Raman, ^1H NMR, ESR and electron spectroscopy, and by conductivity. The composition was confirmed by elemental analysis, XRD study and derivatography. The electronic structure of the complex was revealed by analysis of electron spin resonance spectrum and electron absorption spectrum.

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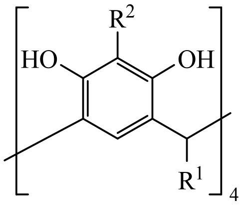
In [1], we have characterized the effect of solvents on the complexation properties of rhodium trichloride with calix[4]resorcinol containing various arylphosphorus fragments on the lower rim of the molecule. It was shown in particular that at the interaction in acetone of rhodium chloride with calix[4]resorcinol functionalized by diphenylphosphinoaryl fragments is formed a complex whose composition includes the dioxygene molecules connected with the rhodium center. Binding and activation of dioxygen is an important fact: it plays a major role in the catalytic oxidation of many biological and industrial processes [2, 3]. For example, in [4, 5] was shown that the porphyrin complexes of rhodium binds dioxygen reversibly. Porphyrin, in turn, is a biologically active substance, which is a part of hemoglobin playing a major role in the processes of respiration (oxidation catalyst) in the form of a heme, that is, the iron–porphyrin coordination complex. The porphyrin molecule composition includes amino group. As known [6], the calix[4]resocynols containing a cavity formed by the aromatic rings and various functional groups on the lower or upper rim are the models of ferments. Of particular interest are the nitrogen-containing, in particular, amine-containing, calix[4]resorcinols. The size and the steric proximity of the functional groups in supramolecular systems define a number of significant features in their chemical behavior.

In this paper, continuing a series of studies of the ions of Group VIII metals interaction with macrocyclic compounds [1, 7], we report on the results of study the feasibility of producing and physicochemical features of supramolecular rhodium(III) dioxygen complex formed in the reaction between $RhCl_3 \cdot 3H_2O$ (**I**) and the calix[4]resorcinol (L) modified by the amine fragments (see the figure) [8]. The compound (L) has *cone* conformation and *ccc*-configuration [8, 9]: the four functional groups [$CH_2N(CH_3)_2$] are above the plane passing through the carbon atoms of the methine groups. The amine groups in the calix[4]resorcinol (L) composition, are tertiary amines [10].

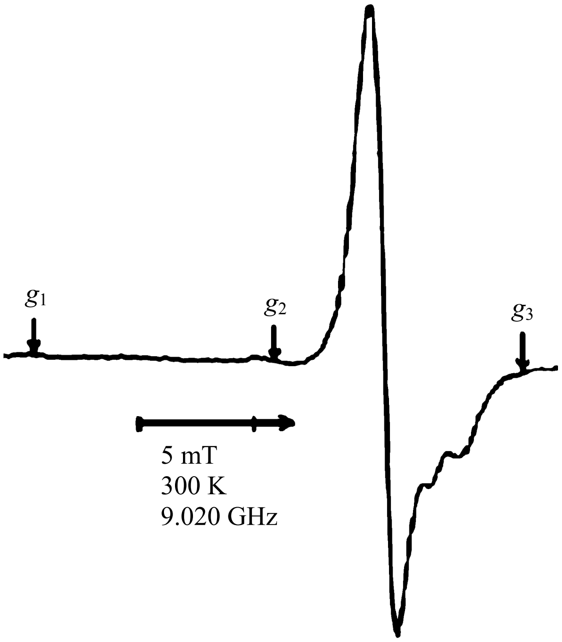


$R^1 = C_6H_4–CH_3$, $R^2 = CH_2N(CH_3)_2$.

The reaction of the compounds **I** and (L) in acetone leads to the formation of a stable in air finely crystalline maroon product **II** with mp 218°C, decomposition occurs at 243°C. Compound **II** is readily soluble in DMSO and methanol, no change in composition occurs at varying the molar ratio of starting materials. The conductometric measuring the electrical conductivity of the solution of the complex **II** in methanol evidenced in favor of neutral type (1.5 μS, 5–8 μS for methanol).

Studies using electron spin resonance (ESR) of the compound **II** (see the figure) showed that there is a signal from a system with $S = 1/2$ indicating by the integral intensity the presence of approximately equal parts of the resorcinol fragment with $g = 2.0038$, and the rhodium complex having a value of g-tensor: $g_1 = 2.103$, $g_2 = 2.034$, $g_3 = 1.970$, $\langle g \rangle = 2.036$. The g-factors approach the pure spin value indicating a partial transfer of electron density from the metal to ligand and the covalent character of the bond [11, 12]. The ESR spectra of this type with rombicity for g_1, $g_2 > 2$, for $g_3 < 2$, are given in a series of papers [4, 5, 13–16] for the complexes of cobalt, rhodium, palladium and ruthenium with the dioxygen. In these complexes the functional groups (amino, phosphinophenyl) of natural and synthetic biologically active supramolecules also act as ligands.

A distinctive feature of the electron absorption spectra (EAS) of such radical systems is the presence of a singlet band of high intensity in the region of 303–400 nm associated with the high-energy σ–σ* transition and a doublet in the region of 500–770 nm associated with charge transfer from the metal to the ligand [5, 13, 17]. In methanol solution of the complex **II** is fixed a σ–σ* transition in the form of high-intensity singlet with λ_{max} ~400 nm. A strong doublet of the metal–ligand charge transfer is observed at λ_{max} ~460, 500 nm. The *d–d* transitions bands, apparently, are overlapped by the σ–σ* bands and the metal–ligand charge transfer bands. In the EAS also are observed changes in the position and intensity of the bands in the region of 200–380 nm related to intra-ligand π→π* transitions in the aromatic fragments of calix[4]rezortsinol structure (λ_{max} ~230, 245, 280 nm) and charge transfer bands (λ_{max} ~310, 360, 380 nm). In the EAS of compound **I** there are the bands with λ_{max} ~510, 470, 440, 410, 375, 250, and 225 nm, indicating the presence of various forms of the rhodium(III) aqua-chloro complexes. This fact seems to be associated with polynuclear structure of compound **I** [18]. In the EAS of free ligand L the bands of π→π* and *n*→σ* transitions in the aryl and auxochome fragments are in the positions with λ_{max} ~220, 245, 290, 300, 320, 350, and 370 nm [19–21]. Thus, the changes in position and intensity ratio of the the absorption band maxima in the UV region, as well as the appearance of new bands in the visible region confirm the complexation.



EPR spectrum of compound **II**.

According to the calculations of the ESR and EAS spectra, the unpaired electron of the dioxygen can be localized either on the central atom at the formation of low-spin complex of rhodium with the electron configuration d^7 [12], or on the $Rh(III)O_2^-$ oxygen [13, 14]. As is known [13], for the Rh(II) complexes $\langle g \rangle = 2.2$. Therefore, formally, the compound **II** structure can be designated as $[Rh^{+3}(O_2^{\bullet-})]$, since the formation of peroxocomplexes is favorable thermodynamically in terms of stabilization of the metal ion coordination sphere [17]. Stretching vibrations of O–O bond in such structures can be manifested in both the IR and Raman spectra. In the Raman spectrum of compound **II** the frequency ν(O–O) is observed as a strong singlet line at 1030 cm^{-1}. In the IR spectrum, to it corresponds a weak band at ~1027 cm^{-1} [4, 13, 14, 22].

Noteworthy that the ESR signal of the radical was fixed also for the tetracarboxylate dirhodium(II) complex with the calix[4]resorcinol modified by four $CH_2N(C_2H_5)_2$ groups on the upper rim of the molecule [7]. The resorcynol oxide ions belong to the class of π-radicals, and their g-factor magnitudes are very sensitive to changes in the structure of phenoxyl radicals ($PhO^{\bullet}$) or resorcynol radicals (O^-–Ar–$O^{\bullet}$) [23]. The ESR signal in the complex **II** is likely due to both the state of the ligand in solution during the synthesis, Parameters of IR spectra (ν, cm^{-1}) of compounds L and **II**

Assignments	L	**II**
ν(O–H)$_{res}$	3250	3428
ν(CH)$_{Ar}$	3050, 3020	3028
ν[CH_3, CH_2, (CH)$_{CH}$]	2928, 2890, 2872	2964
ν(Ar)	1608,1582, 1505	1601, 1551, 1493
[$\delta_{as}(CH_3) + \delta_{as}(CH_2)$]	1464	1471
δ(CH)$_{CH}$	1420	1410
[$\delta_S(CH_3) + \omega(CH_2)$]	1376, 1350	1384, 1338
[$\tau(CH_2) + \delta(CH)_{CH} + \nu(C_{Ar}–O)$]	1300, 1288	1288, 1248
ν(C–N)	1212, 1090	1226, 1090
ν(C_{Ar}–O)	1196	
[ν(Ar), ν(CH), ν(C_{Ar}–O), δ(CH)$_{Ar}$]	1181, 1157, 1143	1186, 1163, 1140
[ν(CCC)$_{Ar}$, ν(C–C), ν(C_{Ar}–O), ν(CH), planar δ(CH)$_{Ar}$]	1110, 1072, 1040, 1016, 1000	1075, 1031, 1016
ν(O–O)		1027
ν(CCO)$_{Ar}$	930	963
δ(CH)$_{Ar}$	900	936
[nonplanar δ(CH)$_{Ar}$, ν(Ar), ν(C–C)}]	846	825
[ρ(CH_3, CH_2) + nonplanar δ(CH)$_{Ar}$]	792, 784, 728, 712, 696	760, 702
[δ(CCC)$_{Ar}$, δ(CCO)$_{Ar}$ + rot(Ar)]	632, 601, 551, 532	553
ν(Rh–N)		425
ν(Rh–Cl$_{term}$)		333

and the general electron distribution in the supramolecular assemble, which makes the latter sustainable and stable. According to [24], the most probable state of aminoresorcynol in solution is the zwitter-ion form, which facilitates the processes of one- and two-electron transfer and stabilization of the electron transfer product.

To determine the nature of coordination of the nitrogen-containing groups and the rhodum-containing fragment, we studied the compounds L and **II** by means of IR spectroscopy in the near and far regions.

The functionally of substituted calix[4]resorcinol is a polyatomic system. Therefore, most of the oscillations is of complex nature and are manifested as broad overlapping bands with asymmetric contour, splittings and shoulders. Moreover, coordination of the rhodum-containing fragment leads to very significant changes in all areas of the IR spectrum and to the emergence of many other bands, whose strict classification is hardly possible and is not necessary. Tentative assignment of the bands observed in the region of 3500–200 cm^{-1} is given in the table.

The main analytical bands of the ligand L in the IR spectrum are the absorption bands associated with the vibrations of the amine and hydroxyl groups and their environment. In the region of 3500–3100 cm^{-1} in the IR spectrum of L there is a broad band ν(OH)$_{res}$ ~3250 cm^{-1} indicating formation of strong intra-molecular and intermolecular hydrogen bonds [9, 20, 25, 26]. In the region of 1230–1000 cm^{-1} together with a series of vibrations of the calixarene structure [9] manifested as the multiple splitting of the bands are seen the bands of skeletal vibrations of the (C–N) bonds: a singlet band at ~1212 cm^{-1} and a high-frequency component at ~1090 cm^{-1} of a multiplet band. The ν(CC)$_{Ar}$ vibrations are observed as a strong singlet at ~1608 cm^{-1} with a weak splitting at ~1582 cm^{-1} and as a high-frequency components of the multiplet band at ~1505 cm^{-1}. In the region of 650–500 cm^{-1} in the IR spectrum of compound L the deformation vibrations at the bond angles [$\delta(\mathrm{CCC})_{\mathrm{Ar}}$, $\delta(\mathrm{CCO})_{\mathrm{Ar}}$+ rot(Ar)] are manifested as a band ~632 cm^{-1} and a broad triplet ~601, 551, 532 cm^{-1} of low intensity [9, 19, 25].

The greatest changes at the complexation exert the frequencies of stretching vibrations of the donor groups involved in coordination. However, the supramolecular complexes are multimolecular systems, held in the complex by the bonds of different types (covalent and noncovalent interactions) [2, 27], so the vibration frequency of a donor group may increase or decrease slightly at the complexation.

In compound **II** the frequency ν(C–N) is shifted to high-frequency region by 14 cm^{-1} and observed at ~1226 cm^{-1}. The second ν(C–N) band does not change its value (~1090 cm^{-1}), but appears as a high-frequency component of a doublet band. The frequency $\nu(\mathrm{OH})_{\mathrm{res}}$ is shifted to the high-frequency region by 178 cm^{-1} and is observed as a broad intense band at ~3428 cm^{-1}.

In the region below 500 cm^{-1}, in the IR spectrum is observed a new broad band at ~333 cm^{-1}, characteristic of terminal $\nu(\mathrm{Rh{-}Cl_{term}})$ bond. This fact indicates the multimuclear composition of the rhodium-containing fragment and evidences the outer-sphere coordination of the latter with the calixresorcynol matrix [22, 28, 29]. Vibrations of the Rh–N bonds are observed in the range of 600–400 cm^{-1} as a weak but broad bands [22, 30]. In the long-wave infrared spectrum is observed a new absorption band ν(Rh–N) at ~425 cm^{-1}, which indicates coordination of Rh(III) to the N(III)-donor center. The ligands containing donor nitrogen atoms can break the halogen bridges [31]. Coordination node in the compound **II** is a mononuclear Rh(III) complex formed as the *trans*-isomer, as follows from the fact that in the IR spectrum is observed only one $\nu(\mathrm{Rh{-}Cl_{term}})$ band [32].

In the region of 500–650 cm^{-1} in the IR spectrum are observed the intraligand vibrations [$\delta(\mathrm{CCC})_{\mathrm{Ar}}$, $\delta(\mathrm{CCO})_{\mathrm{Ar}}$ + rot(Ar)] as a broad band with the main absorption at ~553 cm^{-1}. In the region below 500 cm^{-1} the bands of intraligand vibrations are of low intensity. In the ranges of 1180–1140 cm^{-1} and 870–820 cm^{-1} are manifested the conformation-sensitive vibrations [ν(Ar), ν(CH) of CH, ν(C–O), $\delta(\mathrm{CH})_{\mathrm{Ar}}$] at ~1186, 1163, 1140 cm^{-1}, [$\delta(\mathrm{CH})_{\mathrm{Ar}}$, ν(Ar), ν(C–C)] at ~825 cm^{-1} appearing, respectively, as a triplet and a broad asymmetric band. Since the nature of the bands does not change compared to those of the ligand L, this indicates preservation of the cone conformation and configuration in the *ccc*-isomer [9].

Note that in the ^{1}H NMR spectrum of product **II** the conformation-dependent signals of the protons are retained, and their values are close to those of the compound L [8, 19, 20] in the following intervals, δ (ppm): 5.89–5.92 s (4H, CH), 6.23–6.27 s (4H, *m*-$\mathrm{CH_{arom}}$, $\mathrm{C_6H_2}$), 5.9 s (4H, CH), 6.6–6.7 d (8H, *m*-$\mathrm{CH_{arom}}$, $\mathrm{C_6H_4}$), 6.67–6.72 d (8H, *o*-$\mathrm{CH_{arom}}$, $\mathrm{C_6H_4}$). This indicates retention of the *ccc*-isomer configuretion and *cone* conformation in the complexes. The complex formation leads also to a doubling of the signals of conformation-dependent resorcynol ring protons in the same areas, indicating the complex formation [19, 20].

Thus, the data of physico-chemical investigations and elemental analysis, taking into account the conformation of the ligand, lead to the conclusion that at the complexation of compounds **I** and L in acetone the structural unit is the compound **II** of the composition $\{\mathrm{L{\cdot}4[Rh^{+3}(O_2^{-}){\cdot}2(Cl^{-})]}\}$.

EXPERIMENTAL

We used the compound **I** of analytical grade and compound L obtained by the procedure [8]. Solvents were purified before use and dehydrated by standard methods. Preparatory operations and synthesis were carried out under argon using Schlenk techniques. ^{1}H NMR spectra were recorded on a Bruker MSL–400 instrument (400.13 MHz). The IR spectra in the range of 600–200 cm^{-1} were recorded using a FTIR UFS 113-V spectrometer, in the region of 4000–450 cm^{-1} on a Bruker FTIR Vector 22 device. Crystalline samples were investigated as an emulsion in the dry liquid paraffin. Raman spectra were recorded on a Bruker FT-Raman RAMI spectrometer. The electron absorption spectra were recorded on a SF-16 spectrophotometer in the range of 200–350 nm and on a Specol device in the range of 350–700 nm (cell thickness 1 cm, the solute concentration 1×10^{-3} mol l^{-1}). Crystalline samples were studied as solutions in anhydrous methanol. The ESR spectra were recorded on a SE/X-2544 (Radiopan) spectrometer. Measurement of ionic conductivity of solutions of complexes in methanol at 25°C was carried out on a conductivity meter LM-301 (the standard cell LM-3000).

Determination of carbon, hydrogen and nitrogen was carried out by the microanalytical method on a Carlo Erba analyzer; the rhodium content was determined using X-ray fluorescence analysis on a X-ray spectrometer RMS-02 RENOME F1, the chlorine content was determined according to the procedure [33]. Termogravimetry diagrams of compounds were recorded on a Q-1500D derivatograph of Paulik–Paulik–Erdey system (sample weight 50–60 mg, heating rate 10 deg min^{-1}). The calculation of the starting materials for the synthesis and the yield of the final product correspond to the L:**I** ratio 1:4.

Octachlorotetradioxygen{(4,6,10,12,16,18,22,24-octahydroxy-5,7,17,23-tetrakisdimethylaminomethyl-2,8,14,20-tetra[*p*-tolyl]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)}tetrarhodium(III) (II). Compound **I** (0.098 g, 0.373 mmol) was dissolved in acetone (20 ml) while passing argon through the solution for 30 min (cherry color of the solution). Then, under argon and with stirring, was added a suspension of 0.1 g (0.093 mmol) of ligand L in acetone (20 ml), the color changed to dark-pink. The mixture was stirred for 30 min at a temperature of 50–55°C. The reaction mixture was left for 48 h under argon. The dark-crimson precipitate dropped, the solution above the precipitate was transparent. The obtained product was washed with acetone, ethanol and benzene in an argon atmosphere, and dried under vacuum at 40°C (0.06 Torr) over Al_2O_3 to constant weight. Yield 0.082 g (~46%). Found, %: C 42.98, H 3.98, Cl 14.98, N 3.00, Rh 22.00. $C_{68}H_{76}Cl_8N_4O_{16}Rh_4$. Calculated, %: C 42.95, H 4.00, Cl 14.95, N 2.95, Rh 21.68.

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