ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 3, pp. 478–484. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.V. Guseva, E.M. Kasymova, G.V. Egorov, A.R. Kayupov, A.R. Khamatgalimov, R.A. Khasanshin, A. R. Burilov, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 3, pp. 455–461.

Reaction of Rhodium Trichloride with Oxyethylated Calix[4]resorcinarene

E. V. Guseva[a], E. M. Kasymova[b], G. V. Egorov[a], A. R. Kayupov[b], A. R. Khamatgalimov[b], R. A. Khasanshin[c], and A. R. Burilov[b]

[a] *Kazan State Technological University, ul. K. Marksa 68, Russia, Kazan, 420015 Tatarstan, Russia*
e-mail: leylaha@mail.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*

[c] *Kazanorgsintez Co., ul. Belomorskaya 101, Kazan, 420051 Tatarstan, Russia*

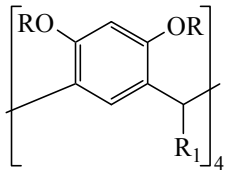
Received May 28, 2009

Abstract—Reaction of rhodium trichloride with a new ligand, oxyethylated calix[4]resorcinarene was examined in an inert atmosphere in different solvents (acetone, acetone + chloroform). The product was characterized by IR, Raman, ^{1}H NMR, ESR, ESCA spectroscopy, conductometry. Its composition was proved by the data of elemental and X-ray fluorescent analyses. The solvent used does not affect the composition of the product but only its yield. The structure of the coordination node and the type of coordination of the rhodium-containing fragment was investigated by calculating the model molecules of the ligand and the complex using the molecular mechanics method (MM+).

DOI: 10.1134/S1070363210030199

INTRODUCTION

An important role in the coordination chemistry of macrocyclic ligands plays the problem of specific solvation of molecules that substantially affects the regularities of both the processes of complex formation and the isolation of stable products [1] and the processes of the thermodynamically controlled self-organisation of closed cyclic structures vs. formation of open linear coordination polymers [2]. Rigid pre-organized macrocycles, calix[4]resorcinarenes, are of interest for catalytic and biological studies. Their modification with various functional groups is interesting by several reasons, the most important being that they can participate in formation of coordination bonds with the transition metal ions and to form new supramolecular structures possessing high catalytic and biological activity [3, 4]. On the other hand, the complexes of platinum metals, in particular, rhodium, with organoelemental compounds are precursors of effective catalysts for various organic reactions [5]. A high biological activity of some drugs based on rhodium complexes is also known [2, 6]. Potentially interesting for design of catalytic systems of this type can be calix[4]resorcinarenes modified by introduction of oxyethyl fragments in their aromatic rings [7].



R = CH_2CH_2OH, $R_1 = C_5H_{11}$.

Such systems, which have the properties of the complex-forming agents and molecular receptors, are capable of self-organisation depending on the nature of the solvent, and show a number of interesting properties [8]. Moreover, in reactions of rhodium halides with ligands having hydroxy or alkoxy groups, substitution of the halide atoms by hydride or carbonyl group may occur [9]. Compounds with the latter groups are known to have often high catalytic activity [10].

Therefore, it seemed interesting to investigate the influence of solvating ability of some solvents on the interaction in the system "rhodium trichloride–oxyethylated calix [4]resorcinarene."

Reaction of $RhCl_3 \cdot 3H_2O$ **I** with oxyethylated calix [4]resorcinarene (L) in the molar ratio **I**:L=8:1, both in acetone and in the mixture of acetone and chloroform, leads to formation of fine-disperse precipitates of dark-pink color **IIa, IIb**. The largest yield was obtained in acetone. With this, in the mixture of acetone with chloroform, from the filtrate, which looks like nontransparent claret-brown solution, after its cooling below zero and crystallization from benzene, a fine-crystalline product of dark-pink color is formed **IIc**. All three products have mp 195°C (decomp. at 236°C), which is indicative of their identical composition. Let us define compounds **IIa–IIc** as product **II**.

To determine the stability in solution and to prove the complex formation we have studied the electron absorption spectra (EAS) of the methanol solutions of the starting compounds **I**, L, and the products in the UV and visible region.

The EAS of compound **I** contains bands at λ_{max} ~ 510, 470, 440, 410, 375, 250, 225 nm, which suggest the presence of different forms of rhodium **III** aquachlorocomplexes, that, apparently, is connected with its polynuclear structure and the effect of the protic solvent [11]. In the region of 200–300 nm in the EAS of L bands with λ_{max} ~ 220, 233, 237, 241, 284, 288 nm are observed, connected with $\pi \rightarrow \pi^*$ transitions with the participation of chromophore fragments of the macromolecule [12, 13].

Investigation of the EAS of compounds **IIa–IIc** has shown that all three products have identical absorption regions, the shape and the maxima of the absorption bands; moreover, their IR spectra also coincide, that allows to regard these three products as one compound **II**.

In the EAS of product **II**, apart from the $\pi \rightarrow \pi^*$ intraligand transitions of the aromatic fragments of the calix[4]resorcinarene structure and the charge transfer bands with λ_{max} ~230–220, 245, 265, 290, 310 nm, intense bands of the *d–d* transitions from the ground state $^1A_{1g}$ to higher states $^1T_{1g}$ and $^1T_{2g}$ are observed at λ_{max} ~410, 460 nm, which point to the low-spin six-coordination configuration of Rh(III) [14].

Conductometric measurements of electroconductivity in methanol solutions of compounds **IIa–IIc** are indicative of their neutral character (20–22 μS; for methanol 5–8 μS); ESR spectra of compounds **IIa–IIc** do not show the presence of paramagnetic products, so, they are diamagnetic. Investigation by the method of the electron spectroscopy for chemical analysis (ESCA) have shown that the value of the bonding energy $3d_{5/2}$ in products **IIa–IIc** equal to 310.7 eV also corresponds to Rh^{+3} complex [15].

To determine the nature of coordination of the rhodium-containing fragment we have investigated the vibration spectra (Table 1) and the ^1H NMR spectra of compounds L, **II**. In compound L the main structural unit of the tetramer is the monomer fragment HO–$(CH_2)_2$–O–Ar–O–$(CH_2)_2$–OH, which can be considered as an analog of the open-chain crown ether, podand, which is an acyclic polydentate ligand. Compounds of this type form coordination nodes of different types: chelates containing O–Me–O bonds; with participation of the terminal OH or OR groups; lone electron pairs of the ether oxygen can be also involved in the formation of bonds [1, 16–18]. It is known [19] that by its properties Rh(III) approaches acceptors of class "a" or hard acids, and forms rather strong complexes with participation of OH ions and, consequently, with fragments like (–ORO–), (–ROH). Then, to determine the nature and the type of coordination in these fragments, it is possible to use the vibration spectroscopy data for podands, crown ethers, calix[4]resorcinarenes, as well as structures with bonds Rh–Cl, Rh–O and the chelate ring structures with bonds (–O–M–O–) [18, 20–30]. It should be mentioned that in such a complex polyatomic system as functionally modified calix[4]-resorcinarene most of vibrations have complex character and appear as overlapping bands with wide asymmetric shapes, splitting and inflections.

In the IR spectrum of L in the range 3750–3100 cm^{-1} a strong wide ν(OH) band is observed with the main absorption at ~3335 cm^{-1} and a weak splitting at ~3552 cm^{-1} suggesting the presence of intramolecular hydrogen bonds and cyclic intermolecular hydrogen bonds in the structure [31–33].

Vibrations $\nu(CH_3,CH_2)$, $\nu(CH)_{CH}$ are observed as a strong complex band with the main absorption at 2923, 2855, 2727 cm^{-1}. It corresponds to the bands at 2920, 2869, 2727 cm^{-1} in the Raman spectrum. $[\delta_{as}(CH_3) + \delta_{as}(CH_2)]$ vibrations are responsible for the band at 1456 cm^{-1} (in the Raman spectrum, 1454 cm^{-1}); $[\delta_s(CH_3) + \omega(CH_2)]$ and $\delta(CH)_{CH}$ are observed, respectively, at 1377 cm^{-1} and 1410 cm^{-1}. For struc-

Table 1. Assignment of the main vibration frequencies (cm^{-1}) in the IR and Raman spectra of compounds L**, II**

Assignment	L		**II**	
	IR	Raman	IR	Raman
ν(O–H)	3335		3471	
	3552			
$\nu(CH)_{Ar}$		3085		3085
$\nu(CH_3, CH_3,), \nu(CH)_{CH}$	2923	2920	2920	2874
	2854	2869	2856	2701
	2727	2727		
ν(Ar)	1609, 1584	1611	1609, 1586	1614
	1503	1587		
$[\delta_{as}(CH_3) + \delta_{as}(CH_2)]$	1456	1454	1456	1458
$[\delta_s(CH_3) + \omega(CH_2)], \delta(CH)_{CH}$	1377, 1410		1400, 1300	1299
$[\tau(CH_2) + \delta(CH)_{CH} + \nu(C_{Ar}–O)] + \nu(Ar– OC)$	1299, 1240	1301, 1231	1286	
	1260			
$\nu(C_{Ar}–O)$	1192	1201	1196	
$[\nu(Ar), \nu(CH)_{CH}, \nu(C_{Ar}–O), \delta(CH)_{Ar}]$	1158	1158	1160	
$\nu_{as}(CCO)_{oxsi}$	1128		1123	
$[\nu(CCC)_{Ar}, \nu(C–C), \nu(C_{Ar}–O), \nu(CH)_{CH}$, planar $\delta(CH)_{Ar}]$	1073	1078	1068	1066
$\nu(CCO)_{Ar}$	983	976	1000	
$\delta(CH)_{Ar}$	914	907	925, 895	
$[\text{nonplanar } (CH)_{Ar}, \nu(Ar), \nu(C–C)]$	818	865	818	
$[\rho(CH_3) + \text{nonplanar } \delta(CH)_{Ar}]$	723	781, 743 654	731	747, 617
		613		
$[\delta(CCC)_{Ar}, \delta(CCO)_{Ar} + \text{rot}(Ar)]$	590, 562, 521	587	590	
[ν(COC), ν(CCC), macrocyclic vibrations]	475, 412, 306	477, 398 270	270, 239	292, 175
	256, 239, 216	194	108	
	197, 166, 146			
	131			
ν(Rh–OH)			555	
ν(Rh–O–Ar)			428	
$\nu(Rh–Cl_{term})$			332	345

tures with Ar–OC– groups, the ν(Ar–OC) vibrations are observed in the range 1260–1220 cm^{-1}; in this range, the $\tau(CH_2)$ and $\nu(C_{Ar}–O)$ are observed. An intense split band with the high-frequency component at ~1299 cm^{-1} and a small shoulder at ~1240 cm^{-1} correspond to the $[\tau(CH_2) + \delta(CH)_{CH} + \nu(C_{Ar}–O)]$ vibrations; a low-frequency component at 1260 cm^{-1} belongs to ν(Ar–OC). In the Raman spectrum, the $[\tau(CH_2) + \delta(CH)_{CH} + \nu(C_{Ar}–O)]$ vibrations are responsible for the lines at 1301, 1231 cm^{-1} [24, 27, 32, 34].

Stretching vibrations of the carbon–carbon double bond appear in specific narrow ranges. In the range 1500–1600 cm^{-1} of the IR spectrum two bands ν(Ar) appear: a symmetric doublet of medium intensity at ~1609, 1584 cm^{-1} and an intense band at 1503 cm^{-1}. These bands correspond to a doublet with intense high-frequency component at 1611 cm^{-1} and weak low-frequency component at 1587 cm^{-1} in the Raman spectrum. $\nu(CH)_{Ar}$ vibrations in the Raman spectrum are observed at 3085 cm^{-1} [27, 32].

In the range 1200–800 cm^{-1} a series of bands of complex overlapping vibrations of the calixresorcinarene structure is observed: $\nu(C_{Ar}–O)$ at ~1192 cm^{-1} as a singlet; $[\nu(CCC)_{Ar}, \nu(C–C), \nu(C_{Ar}–O), \nu(CH)_{CH}$, planar $\delta(CH)_{Ar}]$ as a strong low-frequency component of the doublet band with absorption at ~1073 cm^{-1}. In the region 1000–900 cm^{-1} a weak band $\nu(CCO)_{Ar}$ ~983 cm^{-1} and a wide intense band $\delta(CH)_{Ar}$ with the main absorption at ~914 cm^{-1} are observed. At 800–700 cm^{-1} complex bands $[\rho(CH_3) + \text{nonplanar } \delta(CH)_{Ar}]$ ~723 cm^{-1} appear as a wide asymmetric band. In the

Raman spectrum these bands correspond to intense complex lines at 1201, 1078, 976, 907, 781, 743, 654, 613 cm^{-1}. In the range 1100–1160 cm^{-1}, along with vibrations of the calixresorcinarene structure, the conformationally sensitive vibration bands $\nu_{as}(CCO)_{oxsi}$ of the oxyethylene fragments should be specially mentioned [18, 35]: $\nu_{as}(CCO)_{oxsi}$ at 1120–1130 cm^{-1} belong to vibrations $\nu_{as}(CCO)_{oxsi}$ of the TGG-conformation. A high-frequency component at 1128 cm^{-1} of the intense doublet at 1150–1000 cm^{-1} belongs to $\nu(CCO)_{oxsi}$. In the ranges 1180–1140 cm^{-1} and 870–820 cm^{-1} conformationally sensitive vibrations [ν(Ar), $\nu(CH)_{CH}$, $\nu(C_{Ar}–O)$, $\delta(CH)_{Ar}$] of the calixresorcinarene structure appear as a triplet with the main absorption at ~1158 cm^{-1} and a wide asymmetric band of complex overlapping vibrations [nonplanar $\delta(CH)_{Ar}$, ν(Ar), ν(C–C)] at ~818 cm^{-1}, which is typical for the ccc-isomer. In the Raman spectrum, these vibrations appear, respectively, as a weak band with maximum at ~1158 cm^{-1} and an asymmetric band with the main absorption at 865 cm^{-1}. At the same time, the conformationally sensitive bands of the oxyethylene fragments and the calixresorcinarene structure overlap to give an asymmetric triplet in the IR spectrum. The bands of bending vibrations [$\delta(CCC)_{Ar}$, $\delta(CCO)_{Ar}$ + rot(Ar)] and [ν(COC), ν(CCC), macrocyclic vibrations] appear, respectively, as a wide multiplet at ~590, 562, 521 cm^{-1} and 475, 412, 306, 256, 239, 216, 197, 166, 146, 131 cm^{-1} (in the Raman spectrum at 587, 477, 398, 270, 194 cm^{-1}) [24, 27].

The following changes can be mentioned by comparing the vibration spectra of L and compound **II**. The main absorption ν(OH) is shifted to high-frequencies by 136 cm^{-1} and appears as a wide band at ~3471 cm^{-1} with clear vibronic structure at high frequencies ~3650–4000 cm^{-1}, suggesting formation of intermolecular hydrogen bonds [31, 33] and metal–oxygen bonds [28, 36].

The intensity of vibration bands $\nu(CH_3, CH_2)$, $\nu(CH)_{CH}$ decreases and they appear as a doublet at 2920, 2856 cm^{-1} with a weak low-frequency component. In the Raman spectrum they correspond to strongly polarized lines at 2935, 2874, 2701 cm^{-1}.

The [$\delta_{as}(CH_3)$ + $\delta_{as}(CH_2)$] vibration band is not changed and is observed at 1456 cm^{-1} as a strong singlet (in the Raman spectrum at ~1458 cm^{-1}). However, vibration bands [$\delta_s(CH_3)$ + $\omega(CH_2)$], $\delta(CH)_{CH}$ are shifted and appear as two narrow asymmetric bands with the main absorption at ~1400, 1300 cm^{-1} (in the Raman spectrum at ~1299 cm^{-1}). Vibrations of groups [$\tau(CH_2)$ + $\delta(CH)_{CH}$ + $\nu(C_{Ar}–O)$] and ν(Ar–OC) appear as a combined strong asymmetric band with the main absorption at ~1286 cm^{-1}.

Vibration bands ν(Ar) are observed as a unsymmetrical doublet at ~1609, 1586 cm^{-1}; in the Raman spectrum they correspond to the band at 1614 cm^{-1}. The $\nu(CH)_{Ar}$ vibrations in the Raman spectrum appear at ~3085 cm^{-1}.

A shift and redistribution of vibration bands in the range 1200-800 cm^{-1} is observed: $\nu(C_{Ar}–O)$ at ~1196 cm^{-1} as a singlet; [$\nu(CCC)_{Ar}$, ν(C–C), $\nu(C_{Ar}–O)$, $\nu(CH)_{CH}$, planar $\delta(CH)_{Ar}$] with the main absorption at ~1068 cm^{-1} as a wide intense asymmetric band. In the range 1000–900 cm^{-1} a weak band $\nu(CCO)_{Ar}$ at ~1000 cm^{-1} and an intense doublet band $\delta(CH)_{Ar}$ at ~925, 895 cm^{-1} appear. At 800–700 cm^{-1} complex bands [$\rho(CH_3)$ + nonplanar $\delta(CH)_{Ar}$] at ~731 cm^{-1} are observed as a wide asymmetric band. In the Raman spectrum these vibrations appear as intense lines at 1066, 747, 617 cm^{-1}. A negligible shift of the $\nu_{as}(CCO)_{oxsi}$ at ~1123 cm^{-1} is observed, which is indicative of a predominant ion-dipole character of interaction of the oxyethyl oxygen atom, with retention of the TGG-conformation.

At 500–650 cm^{-1} a wide complex band [$\delta(CCC)_{Ar}$, $\delta(CCO)_{Ar}$+rot(Ar)] is observed with the main absorption at ~590 cm^{-1}. The intraligand vibrations [ν(COC), ν(CCC), macrocyclic vibrations] below 500 cm^{-1} (IR: ~428, 270, 239, 108 cm^{-1}; Raman: 292, 175 cm^{-1}) have low intensity and correspond mainly to skeletal vibrations of the macrocycles. In the long-wave region of the IR spectrum new wide bands at ~555 and 428 cm^{-1} correspond, respectively, to ν(Rh–OH) and ν(Rh–O–Ar); a strong band $\nu(Rh–Cl_{term})$ appears at ~332 cm^{-1}. In the Raman spectrum it corresponds to a highly polarized line at ~345 cm^{-1}. This confirms the interaction of Rh(III) ions with the oxyethyl oxygens and incorporation of the metal into the structure of the supramolecular ensemble. Since the bands of the intraligand vibrations in the far region are much less intensive, and the $\nu(Rh–Cl_{term})$ bands have strong intensity, this suggests an outer-sphere coordination of the Rh(III) complexes with respect to the calixresorcinarene matrix. Therefore, the coordination node represents an octahedral mononuclear Rh(III) complex existing in the form of the trans-isomer since only one band $\nu(Rh–Cl_{term})$ is observed in the vibration spectra [28–30, 36].

The vibration spectroscopy data point to deformation of the calixresorcinarene structure, as well as in the methyl and methylene groups caused by incurporation of the metal ion.

Conformationally-dependent vibrations of the calixresorcinarene structure [ν(Ar), $\nu(CH)_{CH}$, $\nu(C_{Ar}–O)$, $\delta(CH)_{Ar}$] at ~1160 cm^{-1} and [nonplanar $\delta(CH)_{Ar}$, ν(Ar), ν(C–C)] at ~818 cm^{-1} appear, respectively, as a triplet and a wide asymmetric band of complex overlapped vibrations, pointing to the retention of the *ccc*-isomer structure in complex **II** [27].

Analysis of the ^1H NMR spectrum showed the presence in complex **II**, apart from groups CH_3 (δ 0.89 ppm; 12H), CH_2 (δ 1.34 ppm, 24H), $CHCH_2(CH_2)_3$ (δ 1.81–1.82 ppm; 8H), CH (δ 4.66-4.62 ppm; 4H), C_6H_2; (δ 6.72–6.20 ppm; $4H_A$, $4H_B$), the functional group Ar-OCH_2CH_2OH with chemical shifts: Ar–OCH_2 (δ 3.94 ppm; 16H), CH_2O, OH; (δ 3.74–3.80 ppm; 16H, 8H) [13, 32]. The ratio of intensities of the Ar–OCH_2 groups to the CH_2O and OH groups is equal to 2:3, that allows to conclude that compound **II** has eight groups Ar–OCH_2CH_2OH.

The nature of the hydroxy group as a ligand as well as that of the ether oxygen connected to Ar and the CH_2 group in Ar–O–CH_2–CH_2–OH are best of all interpreted in terms of sp^3-hybridization of valence orbitals of the oxygen atom by analogy with crown ethers and podands, since the latter, similar to fragment Ar–O–CH_2–CH_2–OH, are built from 1,4-dioxafragment O–CH_2–CH_2–O [12], whose conformation is determined by the torsional angles denoted as *T* (*trans*), *S* (*skew*), *G* (*gauche*), *C* (*cis*) with approximate values of 180, 120, 60, 0° respectively. The minimum energy conformation is of zig-zag type, since the C–C bonds are in the gauche conformation (torsional angle 60°), and the C–O bonds, in the restricted (trans) conformation. At the same time, deviations from these preferable positions due to the complex formation are also possible. During the latter process, the torsional angles can be more or less distorted in order to make the ether oxygens closer to the cation, since the C–C bonds are practically always in the gauche conformation. Note, that if the C–O bonds go over into the gauche conformation, the torsional angles usually exceed 70° to avoid close contact between the 1,4–CH groups. Therefore, such groups, being conformationally flexible and possessing several donor atoms, which can simultaneously contact with a substrate, easily adjust to specific conditions of complex formation resulting in a huge variety of conformations. The introduction of substituents decreases the flexibility of the molecule, that, in turn, leads to higher rigidity of the macrocycle. In complex **II** the torsional angle formed by the aromatic C=C bond adjacent to the oxygen and the C–O bond connected with the aromatic ring must be close to 0° or 180° (*cis* or *trans* conformation) [37] due to the conjugation of the oxygen lone electron pairs with the aromatic ring. As a results, the rhodium ion can enter into the complexation only with the oxyethylene groups of the neighboring resorcinarene fragments of the tetramer structure.

With the aforesaid in mind, to refine the understanding of the structure of the coordination nodes of compound **II**, we performed calculatons of the model molecules of the ligand and the complex and investigated variations of the dihedral angles –O–C–C–O– in the–Ar–O–CH_2–CH_2–OH fragments at the C–C and C–O in clasters Cl–Rh–Cl. A full optimization of geometry was performed without symmetry restriction using the molecular mechanics method MM+ [38] as implemented in the HyperChem program [39]. The results of calculations given in Table 2 show that upon complexing the values of the dihedral angles –O–C–C–O– at the C–C and C–O bonds in all eight fragments –Ar–O–CH_2–CH_2–OH vary negligibly and remain close to 180°. This confirms the conclusion on coordination of the rhodium ion with the ethyleneoxide groups of the neighboring resorcinarene fragments of the tetramer, and the retention of the conformation.

Therefore, the coordination node represents six-coordinated mononuclear Rh(III) complex in the form of trans isomer, in which the chloride ions and the oxygen atoms of the –Ar–OCH_2CH_2OH fragments of the calixresorcinarene structure act as ligands. The data of spectral studies and elemental analysis, taking into account the ligand conformation and calculation of the structure of the ligand and the complex allow us to conclude that the structural unit of compound **II** is L·4[$RhCl_2$].

EXPERIMENTAL

Compound **I** was of analytically pure grade; ligand L was obtained according to [7]. Compounds **I** and L were dried before use by the Fischer method at appropriate temperatures over P_2O_5. Solvents were purified and dried by standard procedures directly before use. All operations were performed in dry argon. ^1H NMR spectra were registered on a Bruker

MSL-400 (400.13 MHz) instrument. Chemical shifts are given with respect to the residual protons of the solvent. IR spectra were taken on a UFS 113-V (600-200 cm^{-1}) and Vector 22 Bruker (4000-450 cm^{-1}) Fourier spectrometers in dried mineral oil. Raman spectra were registered on a FT-Raman RAMI Bruker spectrometer. Electron absorption spectra were recorded on a SF (200–350 nm) and Specol (350–700 nm) spectrophotometers (cell 1 cm, concentration of solutions in dry methanol 1×10^{-3} M). ESR spectra were registered on a SE/X-2544 Radiopan spectrometer. ESCA spectra were obtained with MgK_α X-ray radiation source at 10^{-2} Pa on a VIEE-15 instrument. Ionic conductivity for solutions of complexes in methanol at 25°C was measured on a LM-301 conductometer (standard cell LM-3000). C, H, N analyses were determined on a Carlo Erba analyzer; metal was determined by X-ray fluorescent analysis on a VRA 20L instrument; chlorine was determined according to [40]. Calculation of the amounts of the reagents for synthesis and the yield of the product are given for L: **I** = 1: 8.

Synthesis of compound II, [L·4[$RhCl_2$]] or octachloro[4,6,10,12,16,18,22,24-octakis(2'-hydroxyethoxy)-2,8,14,20-tetrapentylpentacyclo[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). *a*. *In acetone* (compound **IIa**). 0.19 g (0.72 mmol) of compound **I** was dissolved in 10 ml of acetone while passing argon to get cherry-colored solution, it was stirred for 30 min, the suspension of 0.1 g (0.089 mmol) of L in 10 ml of acetone was added; the solution turned claret-brown. The mixture was stirred at reflux for 90 min (color did not change) and allowed to stay under argon for 60 h. The precipitate formed was washed with acetone and ethanol to get dark-pink product, which was dried in a vacuum (0.06 Torr) at 40°C over Al_2O_3 to constant weight (compound **IIa**), yield 0.063 g (~40%), mp 195°C. Found, %: C 42.51; H 5.43; Cl 15.97; Rh 22.87. $C_{64}H_{96}Cl_8O_{16}Rh_4$. Calculated, %: C 42.30; H 5.29; Cl 15.64; Rh 22.74.

b. *In the mixture of acetone and chloroform* (compounds **IIb, IIc**). The reaction of the acetone solution of **I** and the chloroform solution of L was performed as above. After staying for 60 h the precipitate formed was filtered off to give 0.027 g (~17%) of compound **IIb**. From the nontransparent claret-brown filtrate, after cooling below zero and crystallization from benzene, 0.041 g (~25%) of dark-pink fine-crystalline product was obtained (compound **IIc**). Products **IIb, IIc** have mp 195°C and the same elemental composition as compound **IIa**.

Table 2. Calculated and experimental dihedral angles OCCO in the molecules of compounds L, **II** (φ, deg)

L	**II**
172.9	176.2
171.7	176.7
178.6	177.4
173.8	176.9
176.5	170.1
172.5	169.0
172.9	173.6
176.5	174.6
average 174.4	average 174.3

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 08-03-00512-a) and the Grant of the President of RF (project no. MK-3747.2008.3).

REFERENCES

1. Guseva, E.V., Khasanshin, R.A., Zinkicheva, T.T., Yarkova, E.G., and Polovnyak, V.K., *Russ. J. Gen. Chem.,* 2007, vol. 77, no. 11, p. 1864.
2. Steed, J.W. and Atwood, J.L., *Supramolecular Chemistry*, New York: Wiley, 2000, vol.
3. Karakhanov, E.A., Maksimov, A.L., and Runova, E.A., *Russ. J. Gen. Chem.,* 2005, vol. 74, no. 1, p. 97.
4. Finocchiaro, P., Failla, S., Consiglio, G., *Russ. Chem. Bull. Engl. Transl*., 2005, vol. 54, no. 6, p. 1355.
5. Blum, J., *Russ. Chem. Bull. Engl. Transl*., 1993, vol. 42, no. 10, p. 1619.
6. Afzaletdinova, N.G., Murinov, Yu.I., Mullagaliev, I.R., Zarudii, F.S., Davydova, V.A., and Ismagilova, A.F., *Pharm. Chem. J.,* 2000, vol. 34, no. 5, p. 248.
7. Kasymova, E.M., Kayupov, A.R., Burilov, A.R., Pudovik, M.A., Khabikher, V.D., and Konovalov, A.I., *Russ. J. Gen. Chem.,* 2007, vol. 77, no. 8, p. 1472.
8. Barsukova, T.A., Soden, M.N., Mukmeneva, N.A., Nugumanova, G.N., Bukharov, S.V., Kasymova, E.M., Burilov, A.R., and Pudovik, M.A., *Vest. Kaz. Gos. Tekh. Univ.,* 2007, no. 3-4, p. 50.
9. Candlin, J.P., Taylor, K.A., and Thompson, D.T., *Reactions of Transition-metal Complexes*, New York: Elsevier, 1968. 483 p.
10. Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., *Principles and Applications of Organotransition Metal*

Chemistry, Sausalito: University Science Books, 1987.

11. Buslaeva, T.M. and Simanova, S.A., *Russ. J. Coord. Chem.,* 1999, vol. 25, no. 3, p. 151.
12. Vögtle, F. and Weber, E., *Host–Guest Complex Chemistry*, Berlin: Springer-Verlag, 1985..
13. Ioffe, B.V., Kostikov, R.R., and Razin, V.V., *Fizicheskie metody opredeleniya stroeniya organicheskikh soedinenii* (Phisical Methods of Determination of Structure of Organoc Compounds), Moscow: Vysshaya Shkola, 1984.
14. Lever, A., *Inorganic Electron Spectroscopy*, Amsterdam: Elsevier, 1984.
15. Nefedov, V.I., Salyn', Ya.V., Baranovskii, I.B., and Maiorova, A.G., *Zh. Neorg. Khim.,* 1980, vol. 25, no. 1, p. 216.
16. Bulychev, B.M. and Belsky, V.K., *Zh. Neorg. Khim.,* 1995, vol. 40, no. 11, p. 1834.
17. Belsky, V.K. and Bulychev, B.M., *Russ. J. Gen. Chem.,* 1999, vol. 68, no. 2, p. 119.
18. Minacheva, L.Kh., Ivanova, I.S., Kireeva, I.K., Sakharova, V.G., and Baulin, V.E., *Zh. Neorg. Khim.,* 1994, vol. 39, no. 7, p. 1143.
19. Kukushkin, Yu.N., *Khimiya koordinatsionnykh soedinenii* (Chemistry of Coordination Compounds), Moscow: Vysshaya Shkola, 1985.
20. Matsuura, H. and Miyazawa, T., *Bull. Chem. Soc. Japan,* 1968, vol. 41, no. 8, p. 1798.
21. Foussier, M. and Lassegues, J.C., *J. Chem. Phys*., 1978, vol. 75, no. 9, p. 865.
22. Novikov, V.P. Yarkov, A.V., Solotnov, A.F., and Raevsky, O.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1985, no. 5, p. 1047.
23. Ogava, Y., Ohta, M., Sakakibara, M., Matsuura, H., Harada, I., and Shimanouchi, T., *Bull. Chem. Soc. Japan,* 1977, vol. 50, no. 3, p. 650.
24. Tsivadze, A.Yu., Varnek A.A., and Khutorskii, V.E., *Koordinatsionnye soedineniya metallov s kraun-ligandami* (Coordination Compounds of Metal witj Crown Ligands), Moscow: Nauka, 1991.
25. Kireeva, I.K., Gorbunova, Yu.E., Ivanova, I.S., Baulin, V.E., Tsivadze, A.Yu., and Mikhailov, Yu.N., *Russ. J. Coord. Chem.,* 1997, vol. 23, no. 11, p. 801.
26. Ivanova, I.S., Kireeva, I.K., Baulin, V.E., Brusilovskii, Yu.E., and Tsivadze, A.Yu., *Zh. Neorg. Khim.,* 1995, vol. 40, no. 5, p. 792.
27. Kondyurin, A., Rautenberg, C., Steiner, G., Habicher, W.D., and Salzer, R., *J. Mol. Struct.*, 2001, vols. 563–564, p. 503.
28. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
29. Gillard, R.D. and Heaton, B.T., *J. Chem. Soc., A.,* 1969, p. 451.
30. Konovalov, L.V., *Koord. Khim*., 1984, vol. 10, no. 10, p. 1401.
31. Kovalenko, V.I., Chernova, A.V., Shagidullin, R.R., Doroshkina, G.M., Borisoglebskaya, E.I., Nikishin, V.G., *Struktura i dinamika molekulyarnykh system* (Structure and Dynamics of Molecular Systems), Ioshkar-Ola, 1998.
32. Kazitsyna, L.A. and Kupletskaya, N.B., *Primenenie UV, IR i NMR spektroskopii v organicheskoi khimii* (Application of UF, IR, and NMR Spectroscopy in Organic Chemistry). Moscow: Vysshaya Shkola, 1971.
33. Bellamy, L., *New Data on IR Spectroscopy of Complex Molecules*, Moscow: Mir, 1971.
34. Raevsky, O.A., *Koord. Khim*., 1990, vol. 16, no. 6, p. 723.
35. Raevsky, O.A., Tkachev, V.V., and Atovmyan, L.O., *Koord. Khim*., 1988, vol. 14, no. 2, p. 1697.
36. Venkovskii, N.U., *Candidate Sci. (Chem.) Dissertation*, Moscow, 1980.
37. Potapov, V.M., *Stereokhimiya* (Stereochemistry), Moscow: Khimiya, 1988.
38. Stewart, J.J.P., *J. Comp. Chem*., 1989, vol. 10, p. 209.
39. *HyperChem (Release 7.01 for Windows). Molecular Modeling System*, 2002, Hypercube, Inc.
40. *Metody kolichestvennogo organicheskogo elementnogo mikroanaliza* (Methods of Quantitative Organic Elemental Microanalysis), Gelman, A.I., Ed., Moscow: Khimiya, 1987, pp. 230–231.