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Reaction of Rhodium Trichloride and Dirhodium(II) Acetate with *trans*-4,4'-Bis(diethoxyphosphoryl)biphenyl-18-crown-6

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Abstract—The complexation of $RhCl_3·3H_2O$ and $[RH_2(CH_3COO)_4·2H_2O]$ with *trans*-4,4'-bis (diethoxyphosphoryl)biphenyl-18-crown-6 in various media was studied. In the synthesized compounds the rhodium(III) or dirodium(II) ions form supramolecular ensembles with ligand environment. The compounds were characterized by NMR, IR, Raman, ESR, X-ray electron spectroscopy, conductivity, and the data of elemental and X-ray fluorescence analyses. The predominant role of diethoxyphosphoryl groups at the macrocycle in binding rhodium(III) and dirhodium(II) ions was demonstrated.

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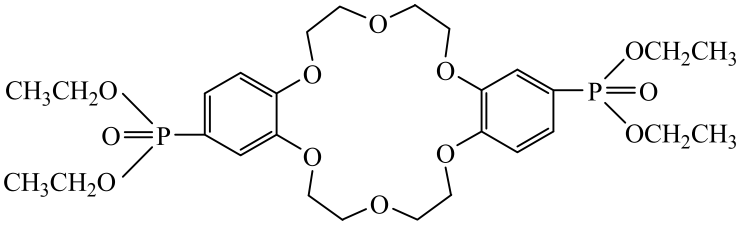
There is a great interest nowadays in a modified type of macrocyclic polyethers containing a variety of additional groups that supply the polyester cycle with a number of useful properties, such as changing the hydrophilic and surfactant properties of polyesters [1], improve the complexing properties towards transition metal cations [2].

In this work, continuing a series of research on the interaction of transition elements with macrocyclic compounds, we studied the complexing ability of $RhCl_3·3H_2O$ (**I**) and $[RH_2(CH_3COO)_4·2H_2O]$ (**II**) with a derivative of dibenzo-18-crown-6 (DB-18-CR-6) containing two diethoxyphosphoryl groups as substituents in the benzene rings in the *trans* position, the *trans*-4,4'-bis(diethoxyphosphoryl)biphenyl-18-crown-6 (L) [3–5].

The main characteristics of the non-coordinated ligand have been described in [5]. In a number of works [6, 7] the reactivity has been studied of certain types of crown ethers with compounds of platinum group metals, however, in the literature we have not found any information on the conditions of complexation of the ligand L with the compounds of rhodium(III) or dirodium(II).

To select the optimal conditions for the synthesis of these complexes we varied solvents and the ratio of the reactants. These parameters play a decisive role in the synthesis. The interaction of compounds **I** and L in a molar ratio of **I**:L = 2:1 in a mixture of ethanol and chloroform produced stable in air crystalline dark brown product **III**, mp 226°C. Te interaction of compounds **I** and L in ethanol or chloroform medium does not lead to the formation of solid products. The interaction of compounds **I** and L in a mixture of ethanol and chloroform in molar ratios of **I**:L = 2:2 and 1:2 leads to complex mixtures of difficultly separable reaction products.



According to the elemental analysis, the metal:ligand ratio in compound **III** is 2:1. Product **III** is readily soluble in acetone. Its high conductivity (52 μS) indicates that compound **III** is an ionic complex.

To determine the stability of complex **III** in solution and to confirm the complexation we considered its electron absorption spectra (EAS) in the UV and visible region. In the EAS of compound L in chloroform there is a band of aromatic absorption with λ_{max} ~276 nm [8–10]. In the EAS of **I** in ethanol there are 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, due probably to their polynuclear structure and the influence of protic solvent [11]. Absorption bands in the visible part of the EAS with λ_{max} ~600, 530, 510, 470, 450, and 430 nm indicate the presence of rhodium ions in the structure of **III** (solution in acetone). These bands evidence the presence of low-spin form of the six-coordinated Rh(III) complex containing in its structure chloride ions and water molecules [9, 12]. In the EAS of **III** in addition to the absorption with λ_{max} ~276 nm appears a second peak with λ_{max} ~283 nm, which indicates the formation of the complex by the aromatic crown ether [8].

To determine the mode of coordination of the donor groups, composition and structure of the synthesized products, we used IR spectroscopy in the near and far regions (see the table), NMR, Raman, and X-ray electron spectroscopy.

The compound L has several donor centers capable of coordination with the rhodium ions: oxygen atoms of the polyether ring (ether, anisole) and P=O group. Therefore, fundamentally the simultaneous coordination of several centers with the metal ions is possible.

It is known that rhodium atom can form a bond with the phosphoryl group oxygen atom [13–15]. The participation of oxygen of the phosphoryl group in the coordination process was confirmed using ^{31}P NMR spectroscopy [16]. In the ^{31}P NMR spectrum of compound L there is a resonance signal of phosphorus nucleus at δ_P 19.64 ppm was also observed. In the ^{31}P NMR spectrum of **III** a resonance signal of phosphorus nucleus (δ_P 14.79 ppm) was shifted upfield compared with the signal in the spectrum of the ligand by 4.85 ppm. This points to the participation of two phosphoryl groups of the macrocycle in the complexation with the formation of the bond of the same type (P=O→Rh) and shows that the coordination of the product has a symmetrical structure. The geminal spin-spin coupling constant $^2J_{PORh}$ 110.26 Hz indicates the formation of the monomeric complex Rh(III) [13, 17]. A somewhat low value of $^2J_{PORh}$ is associated with the formation of the bond via the oxygen of the phosphoryl group.

Compound **I** in the solid state is a mixture of polymers of general formula $(H_3O)_3Rh_nCl_{3n+3}\cdot H_2O$, it has acidic properties and dissociates in weakly acidic and neutral media [11], and therefore a possibility of the formation of the H_3O^+ ion cannot be excluded.

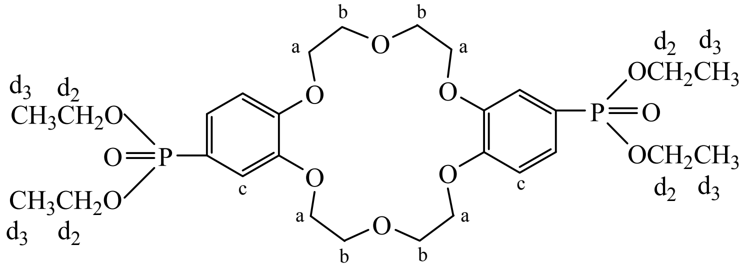
$$[RhCl_n(H_2O)_{6-n}]^{3-n} \rightleftarrows [RhCl_n(OH)(H_2O)_{6-n-1}]^{3-n-1} + H^+.$$

The crown ether complexes may have a structure in which the hydronium ion is directly bound to the crown ring and is stabilized by three hydrogen bonds between H_3O^+ and every second oxygen atom [3, 7, 18, 19]. The nature of the specific interaction of crown ether with the molecules containing O–H bonds is explainable by the formation of either a complex system of hydrogen bonds or electrostatic interaction, as well as by combined interactions of these two types, as seen from the characteristic changes in the ^{1}H NMR and IR spectra. According to [20], the displacement of signals, their splitting and doubling in the ^{1}H NMR spectra of the complexes with macro-cyclic ligands, in particular, crown ethers, is indicative of the complex formation.

The ^{1}H NMR spectrum of compound L in $CDCl_3$, according to [5], has the following characteristics (δ, ppm): 1.09 t (12H, $OCH_2C\underline{H}_3$), 3.69 m (8H, $OC\underline{H}_2CH_3$), 3.75 m (8H, OCH_2), 3.89 m (8H, OCH_2), 6.98 d, 7.25 d.d, 7.40 d.d (2H, ArH). The signals in the ^{1}H NMR spectrum of the product **III** were assigned using the data of ^{1}H and ^{1}H–{^{31}P} NMR spectroscopy. The changes in the shape of the signals at the decoupling from the phosphorus nucleus makes it possible to identify the signals corresponding to the various protons of the ligand. The number of signals in the ^{1}H NMR spectrum of compound **III**, their chemical shifts, relative intensities, and multiplicity confirmed the fact that coordination with the metal left unchanged the structure of the ligand L in the complex compared with the free ligand.

In the region of 10.36–11.0 ppm in the ^{1}H NMR spectrum of compound **III** in CD_3COCD_3 there is a broad singlet [δ 10.87 ppm (6H, H_3O^+)], which is characteristic of the complexes of hydronium ion with crown ethers [3, 21] .

In the ^1H NMR spectrum of product **III** a marked change in shape (doubling and the multiplicity) of the signal belonging to the aryl protons at δ 6.6–6.9 ppm was recorded.



The largest shifts and splitting occur in the signals belonging to the protons of methyl (d$_3$) and methylene (d$_2$) groups of the $P(O)(OCH_2CH_3)_2$ fragments and methylene groups of the crown-ether ring (a). The signals belonging to the protons of methyl groups (d$_3$) in the $P(O)(OCH_2C\underline{H}_3)_2$ fragments are split and appear at δ 0.86–0.89 ppm (5H, $OCH_2C\underline{H}_3$), 1.209-1.27 ppm (5H, $OCH_2C\underline{H}_3$), 1.632-1.634 ppm (2H, $OCH_2C\underline{H}_3$). The signals of the methylene group protons (a) of the crown ether ring are split, and some of them are overlapped with the signals of protons of the methylene groups (d$_2$) of the $P(O)(OCH_2CH_3)_2$ fragment as a multiplet band at δ 3.45-3.74 ppm (8H, $OC\underline{H}_2CH_3$; 4H, OCH_2). The signals of the methylene groups protons (b) in the crown ether ring also are split, and overlap with the signals of protons of the methylene groups (a) of the crown ether ring (δ, ppm): 4.19–4.21 t (3H, OCH_2), 4.04–4.06 t (3H, OCH_2), 2.87 s (1H, OCH_2), 2.46–2.44 m (4H, OCH_2), 2.18 s (1H, OCH_2). Thus, differences in the shifts and splitting of the signals belonging to protons of the methylene groups of the crown-ether ring (a, b), as well as methylene (d$_2$) and methyl (d$_3$) groups of the $P(O)(OCH_2CH_3)_2$ fragments, indicate the formation by these fragments of the bonds with various complexing particles.

The main analytical bands in the IR spectrum of the ligand L are the absorption bands associated with vibrations of the phosphoryl group and its surrounding [10, 22–25], as well as the absorption band of ethylene glycol groups of the crown ether ring [26–28]. The shift of the vibration frequency of ethylene glycol group of crown ethers in the IR spectra is known to indicate the formation of a complex [26, 29]. The most significant changes at the complex formation in the IR spectrum of benzocrown ethers occur in the region of 1300–1000 cm^{-1} [27, 30].

The stretching vibration frequency of the phosphoryl group is governed by the electronegativity of the substituents at the phosphorus atom [22]. In the IR spectrum of ligand L these bands appear in the same region as those of ethylene glycol units in the form of a strong multiplet band: $\nu(P{=}O)$ ~1240 cm^{-1}, $\nu_s(Ar–OC)$ ~1264 cm^{-1}, $\tau(CH_2)$ ~1246 cm^{-1}, and $\nu_{as}(Ar–OC)$ ~1220 cm^{-1} [23–25, 27]. In the IR spectrum of product **III** these vibrations appear as a doublet band with a more intense high-frequency component at ~1264 cm^{-1} and less intense low-frequency component at ~1224 cm^{-1}. Thus, the position of the band $\nu_s(Ar–OC)$ is preserved. This fact indicates that the anisole oxygen atoms are not involved in the complex formation. Thus, the coordination of rhodium atoms occurs at the oxygen of the phosphoryl group.

In the IR spectrum of product **III** in the region below 500 cm^{-1} there is a broad band $\nu(Rh–Cl_{term.})$ ~329 cm^{-1}. The position of the band $\nu(Rh–Cl_{term.})$ depends on the *trans*-ligand, the oxidation state, and the coordination number of the central metal atom of the complex. For octahedral monomeric complexes of the Rh^{3+} ion the band $\nu(Rh–Cl_{term.})$ is located in the region of 325–340 cm^{-1} [13, 31, 32]. The intraligand vibrations in the region below 600 cm^{-1} are of low intensity compared with the band $\nu(Rh–Cl_{term.})$ indicating the outer-sphere coordination of the rhodium-containig fragment with the crown ring. The binding energy of $3d_{5/2}$ bond, according to X-ray photoelectron spectroscopy, corresponds to the complex of Rh(III) (310.8 eV) [33].

Vibrations $\nu_{as}(COC)$ of the ethylene glycol units in crown ethers are very sensitive to the conformation of the OCH_2CH_2O fragment. Their frequency varies at the coordination within rather a wide limit depending on the torsion angle and the type of the chemical bond [26, 28, 29]. Therefore, changes of the bands of the conformation-sensitive vibrations $\nu_{as}(COC)$ are due to the conformational rearrangement of the polyethylene glycol chains of the ligand at the complexation and are an indication of the complex formation.

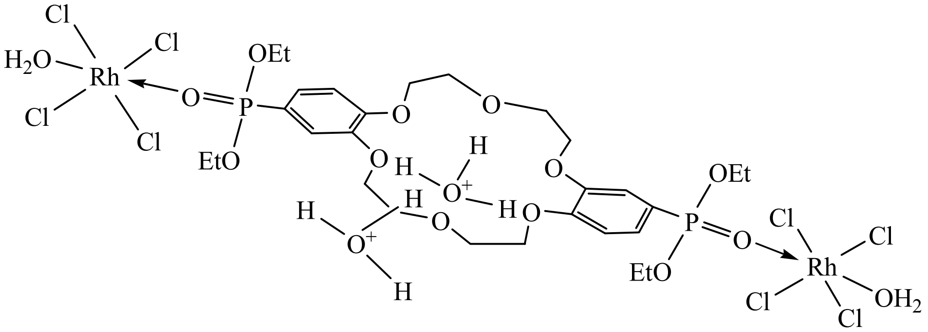
In the region of 1200–1100 cm^{-1} of the IR spectrum of ligand L there is a strong multiple band ν_{as}(COC) at ~1119, 1110 cm^{-1}. The existence of two different absorption bands ν_{as}(COC) indicates the conformational heterogeneity of the OCH_2CH_2O links forming the crown-ether ring of the ligand L. It was found in [34] in the case of benzocrown compounds thet the ν_{as} (COC) occurred at1100 ± 10 cm^{-1} for the TGT conformation of the OCH_2CH_2O link, at 1120–1130 cm^{-1} for TGG, and at 1110–1120 cm^{-1} for TGS conformation, which is intermediate between the TGT and TGG. Note that the conformation of the OCH_2CH_2O link is governed by a set of torsion angles at O–C, C–C, and C–O bonds, denoted by the symbols T (~180°), S (~120°), G (~60°), and C (0°). Negative angles are designated as T^-, G^-, S^-, and C^-, respectively. The symbol G relates to torsion angles from 30° to 90°, etc.

The ν_{as}(COC) band in the IR spectrum of complex **III** is recorded as an asymmetric band with the main absorption at ~1126 cm^{-1}. Reduced number of the ν_{as}(COC) bands points to the conformational changes in the OCH_2CH_2O links and is an indication of the complex formation.

In the IR spectrum of product **III** the absorption bands characteristic of stretching and bending vibrations of $(H_3O)^+$ at 3100–3200, 2000–1990, 1700–1670, 1570–1502, 1175–1050 cm^{-1} are also observed [7, 35, 36]. The closeness of the frequencies of stretching vibrations ν_1, ν_2 and of hydronium cations leads to their registration as a broad doublet band of medium intensity at 3190, 3210 cm^{-1}. The bands at 1737 and 1710 cm^{-1} are due to the asymmetric bending vibrations ν_4 of the $(H_3O)^+$ ions, whereas the position of the band ν_2 of symmetric bending vibrations is not observed owing to the presence of intense intraligand vibration bands of the macrocycle in its characteristic region around 1100 cm^{-1}. At ~1990, 2000 cm^{-1} the bands of the first overtone $2\nu_2(H_3O)^+$ are observed.

It should be noted also that the coordination at the phosphoryl and ether oxygen atoms leads to very significant changes in the entire IR spectrum. There is a lot of other bands, a rigorous assignment of which is hardly possible and necessary. The table shows the assignment of the fundamental vibration frequencies in the IR spectra of compounds L and **III**.

The results of physicochemical studies and elemental analysis, taking into account conformation of the ligand, suggest that at the complexation of **I** with ligand L in ethanol–chloroform medium a structural unit of the supramolecular ensemble is compound **III**, whose assumed structure is shown below.



The interaction of compounds **II** and L in a molar ratio of 2:1 in ethanol resulted in a stable in air, finely dispersed powder product **IV** of blue color, mp 200°C. Carrying out the synthesis in a mixture of ethanol and chloroform leads to the formation of finely dispersed red-black powder. The composition of this multicomponent substance could not be determined.

According to the elemental analysis, the metal–ligand ratio in compound **IV** is 2:1. Product **IV** is well soluble in acetone. When dissolved in dimethyl sulfoxide or chloroform, the solution color changed to red and yellow-green, respectively, due, apparently, to the resolvation and decomposition of product **IV**. The low value of electrical conductivity (5.35 μS) indicates that this complex is of neutral type.

To determine the stability of complex **IV** in solution and to confirm the complexation, we studied its EAS in the UV and visible regions. In the EAS of compound **II** in acetone in the UV region a pronounced absorption maximum at λ_{max} ~223 nm and low maximum at λ_{max} ~250 nm (the metal–ligand charge transfer band) was observed, in the visible region, at λ_{max} ~590 and 446 nm [the $\pi^*(Rh)\rightarrow\sigma^*(Rh)$ and $\pi^*(Rh)\rightarrow\delta^*(Rh)$ transitions] [37]. In the EAS of

Parameters of IR spectra of compounds L, **III** and **IV**

Comp. no.	ν, cm^{-1}
L	3020 (C–H, Ar); 2854, 2924 (CH$_2$, CH$_3$); 1591, 1513 (C=C, Ar); 1460, 1406 [δ(CH$_2$) + ν(P–Ar)]; 1374, 1364, 1326 [ω(CH$_2$) + ν(P–Ar)]; 1264 [ν$_s$(Ar–OC)]; 1246, 1240, 1220 [τ(CH$_2$) + ν(P=O) + ν$_{as}$(Ar–OC)]; 1160 [δ(CH)$^{sh}_{Ar}$]; 1140 (P–O–Et); 1119, 1110 [ν$_{as}$(COC)]; 1082, 1060, 1045 [δ(CH)$^{sh}_{Ar}$]; 1026, 959, 908 [ν$_s$(COC) + ν(CC)$_{CR}$ + ρ(CH$_2$)]; 867, 844 [ν$_{pulse}$, ρ(CH$_2$) + ν(CO)]; 795 (P–C); 766, 675, 645 [δ(CH)$^{sh}_{Ar}$]; 608, 582, 551 [δ(COC) + δ(CCO)]; 532, 502 [δ(ArPO) + δ(CPO)]; 482, 465, 419 [δ(COC) + δ(CCO)]
III	3440 (O–H); 3190, 3210 [ν$_1$(H$_3$O)$^+$ + ν$_2$(H$_3$O)$^+$]; 2978, 2933 (CH$_2$, CH$_3$); 1990, 2000 [2ν$_2$(H$_3$O)$^+$]; 1737, 1710 [ν$_4$(H$_3$O)$^+$]; 1588, 1514 (C=C, Ar]; 1440, 1415 [δ(CH$_2$) + ν(P–Ar)]; 1357, 1325 [ω(CH$_2$) + ν(P–Ar)]; 1263 [ν$_s$(Ar–OC)]; 1224 [τ(CH$_2$) + ν(P=O) + ν$_{as}$(Ar–OC)]; 1126 [ν$_{as}$(COC)]; 1044 [δ(CH)$^{sh}_{Ar}$]; 1020, 962 [ν$_s$(COC) + ν(CC)$_{CR}$ + ρ(CH$_2$)]; 846 [ν$_{pulse}$, ρ(CH$_2$) + ν (CO)]; 787 (P–C); 700 [δ(CH)$^{sh}_{Ar}$]; 626, 581, 554 [δ(COC) + δ(CCO)]; 512 [δ(ArPO) + δ(CPO)]; 427, 414 [δ(COC) + δ (CCO)]; 443 (Rh–O, P=O]; 329 (Rh–Cl$_{term}$)
IV	2981, 2930 (CH$_2$, CH$_3$); 1637, 1650 [δ(H$_2$O)]; 1593, 1558, 1511 [ν(C=C)$_{Ar}$ + ν$_{as}$(COO)]; 1455, 1407 [δ(CH$_2$) + ν(P–Ar) + ν$_s$(COO)]; 1362, 1327 [ω(CH$_2$) + ν(P–Ar)]; 1263 [ν$_s$(Ar–OC); 1223 [τ(CH$_2$) + ν(P=O) + ν$_{as}$(Ar–OC)]; 1127 [ν$_{as}$(COC)]; 1050, 1048 [δ(CH)$^{sh}_{Ar}$]; 1023, 960 [ν$_s$(COC) + ν(CC)$_{CR}$ + ρ(CH$_2$)]; 867 [ν$_{pulse}$, ρ(CH$_2$) + ν(CO)]; 793 (P–C); 763, 675, 644 [δ(CH)$^{sh}_{Ar}$]; 611, 582, 553 [δ(COC) + δ(CCO)]; 524, 502 [δ(ArPO) + δ(CPO)]; 487, 465, 414 [δ(COC) + δ(CCO)]; 440 (Rh–O, P=O); 382 [ν$_{as}$(Rh–O)$_{COO}$]; 343 [ν$_s$(Rh–O)$_{COO}$]

the product **IV** in acetone also there are absorption bands in the region of 400–600 nm with λ$_{max}$ ~439 and 585 nm characteristic of binuclear complexes of rhodium(II**)**. These facts indicate the retention of the Rh–Rh bond in the complex **IV**. In the UV region of the EAS of compound **IV** in addition to the bands with λ$_{max}$ ~220 and 245 nm there is an absorption band of aromatic ring with λ$_{max}$ ~ 278 nm characteristic of aromatic crown ethers, and a second peak at λ$_{max}$ ~285 nm, which indicates the involvement of the crown ether into the complex formation [8].

The comparison of IR absorption spectra of free ligand L and complex **IV** shows that complexation leads to changes in the position and intensity of the main analytical bands. In the IR spectrum of product **IV** there are absorption bands corresponding to the stretching vibrations ν$_s$(Ar–OC), ν$_{as}$(Ar–OC), τ(CH$_2$), ν(P=O), observed as a doublet band of high intensity at ~1263, 1223 cm^{-1}. Thus, the position of the band corresponding to the stretching vibrations ν$_s$(Ar–OC) remains virtually unchanged. The band with maximum absorption at ~1223 cm^{-1} is rather complex, and it includes the bands corresponding to the stretching vibrations ν$_{as}$(Ar–OC), τ(CH$_2$) and ν(P=O) [22–25, 27]. The participation of the phosphoryl group oxygen in the coordination is confirmed also by ^{31}P NMR spectroscopy of complex **IV** [16]. In the ^{31}P NMR spectrum one resonance signal of the phosphorus nucleus, δ$_P$ = 18.01 ppm is observed, shifted upfield compared with the signal of the ligand L (δ$_P$ 19.64 ppm) by 1.63 ppm, which indicates the equivalent participation of both phosphoryl groups of the macrocycle in the complex formation. The low upfield shift of the resonance signals of the phosphorus nucleus in the ^{31}P NMR spectrum of complex **IV** in comparison with complex **III** (1.63 ppm) indicates a weak interaction and a less strong bonding.

It is known that the rhodium atoms in compound **II** may form bonds with the oxygen atom of the phosphoryl group [38]. The absorption bands of the Rh–O stretching vibration in the case of phosphoryl group are observed at ~440 cm^{-1} [13, 32]. The absorption bands of the stretching vibrations of the Rh–O characteristic of the acetate group are observed in the infrared absorption spectrum below 400 cm^{-1} [ν$_{as}$(Rh–O) ~382 cm^{-1}, ν$_s$(Rh–O) ~343 cm^{-1}] [39]. The stretching and bending vibrations of the bridging acetate groups appearing in the region of 1300–1600 cm^{-1} could be superimposed with the skeletal vibrations of aromatic bonds ν(C–C)$_{Ar}$. Note that all the bands in this area have asymmetrical blurred contour with a slight splitting, indicating a superposition of vibrations ν$_{as}$(CCO) and ν$_s$(CCO) of the bridging acetate groups with the ν(C–C)$_{Ar}$, since these vibrations in the IR spectra appear as an intense singlet band. The absorption bands ν$_{as}$(COO) are observed together with the bands of ν(CC)$_{Ar}$ vibrations at ~1593, 1558, 1511 cm^{-1}, the ν$_s$(COO) vibrations are observed together with δ(CH_2) and ν(P–Ar) at ~1455, 1407 cm^{-1} [10, 39]. The ν(Rh–Rh) vibrations of the rhodium binuclear complexes with acetate bridges are estimated to occur in the Raman spectra in the region of 300–350 cm^{-1} [37]. In the Raman spectrum the bands of medium intensity are recorded at ~349, 318 cm^{-1}, belonging to the ν(Rh–Rh) vibrations. Thus, these data support the retention of the binuclear *lantern* structure with a Rh–Rh bond and its incorporation into product **IV.**

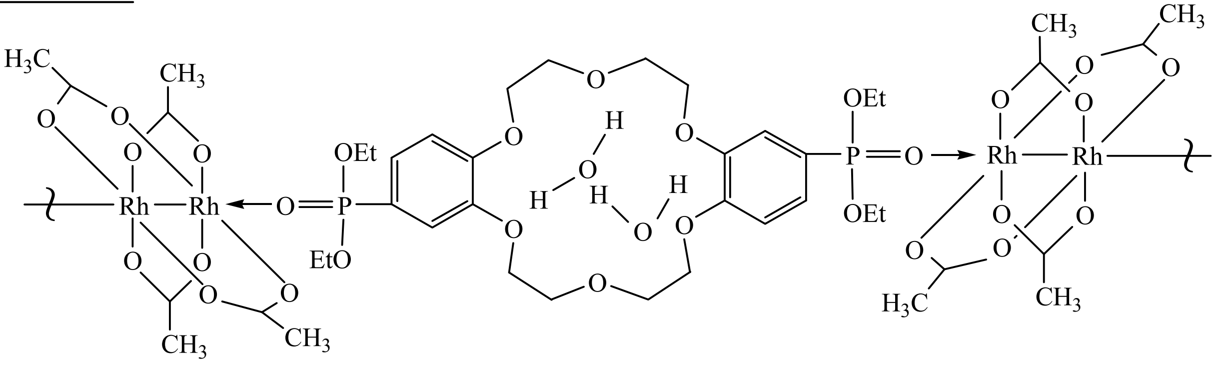
The biggest changes in the spectrum of complex **IV** compared with the spectrum of free ligand L are observed in the region below 1150 cm^{-1}. Thus, a significantly different pattern of the absorption spectrum of complex **IV** is registered in the region of the frequency of conformationally sensitive vibration ν_{as}(COC) appearing at 1127 cm^{-1} as an asymmetric band of high intensity. Conformational rearrangement of ethylene glycol chains of the ligand L at the coordination leads to significant changes in the region of 800–1000 cm^{-1}, where appear complex stretching-bending vibrations [ν_s(COC) + ρ(CH_2) + ν$(CC)_{CR}$] and [ν_{puls},ρ(CH_2) + ν(CO)], observed at ~959 and ~867 cm^{-1} respectively as two weak bands. The displacement of the bands of bending vibrations [δ(ArPO) + δ(CPO)] at ~ 524, 502 cm^{-1} indicates certain deformation of the ligand L structure caused by the coordination. These data suggest conformational rearrangements of ethylene glycol chains and the complex formation [10, 25, 27].

The molecules of crown ethers can form complexes with water molecules, the crown ether skeleton with the cavity filled with a water molecule is fixed mainly by hydrogen bonds [18]. In the IR spectrum of the product **IV** the ν(OH) stretching vibrations of coordinated water molecules are represented by a broad band with the main absorption at ~3440 cm^{-1}, the δ(H_2O) vibration by a medium intensity band at ~1637 cm^{-1} and a shoulder at ~1650 cm^{-1} [32]. The corresponding parameter of the ^{1}H NMR spectrum of compound **IV** in CD_3COCD_3 is typical of the molecular complexes of crown ethers with water of the *host-guest* type [40]: in the region of 4.50–5.36 ppm there is a broad singlet at δ 4.95 ppm (4H, H_2O).

In the ^{1}H NMR spectrum of product **IV**, the complexation results in a noticeable change in the form (doubling and multiplicity) of aryl proton signal [δ 6.3–6.6 ppm (6H, ArH)]. The signals of methyl protons (d_3), methylene groups of $P(O)(OCH_2CH_3)_2$ fragments (d_2), and the methylene groups of the crown-ether ring (a) undergo the largest shifts and splitting. The signals of the methyl groups protons (d_3) of $P(O)(OCH_2CH_3)_2$ fragments are split (δ, ppm): 0.84–0.87 m (5H, $OCH_2C\underline{H}_3$), 1.21–1.27 m (5H, OCH_2C_{H3}), 1.632–1.634 d (2H, $OCH_2C\underline{H}_3$). The signals of the methylene groups protons of crown ether ring (a) also are split, and some of them are overlapped with the signals of protons of the methylene groups (d_2) of $P(O)(OCH_2CH_3)_2$ fragment as a multiplet band at δ 3.42–3.71 (8H , $OC\underline{H}_2CH_3$; 4H, OCH_2). The signals of protons of the methylene groups (b) of the crown ether ring also are split and overlap with the signals of protons of the methylene groups (a) of the crown ether ring (δ, ppm): 4.15–4.19 m (3H, OCH_2), 4.01–4.03 t (3H, OCH_2), 2.84 s (1H, OCH_2), 2.41–2.43 m (4H, OCH_2), 2.16 s (1H, OCH_2) [20, 40]. These observations indicate that various fragments of the ligand L form bonds with various complexing species.

The binding energy $3d_{5/2}$, according to the data of X-ray electron spectroscopy, corresponds to the rhodium(II) binuclear complex (309.6 eV) [33].

These physicochemical studies and elemental analysis, taking into account the conformation of the ligand, allow a conclusion that at the complexation of compound **II** with ligand L in ethanol medium the structural unit of the supramolecular ensemble is compound **IV**, the assumed structure of which is shown below.



Thus, the presence in the molecule of the ligand L of oxygen atoms of three types differing by their donor properties leads to differentiation at the complex formation. The most effective are the phosphoryl oxygen atoms. The rhodium(III) and dirhodium(II) ions mainly form bonds with the oxygen atoms of the phosphoryl groups, because of the high electronegativity of the P=O group. For the ether oxygen atoms of the ethylene glycol chain and the anisole oxygen atoms the hydrogen bonding is more typical.

EXPERIMENTAL

We used compound **I** of analytical grade. The compounds L and **II** were prepared according to [5, 41]. Solvents were purified and dried by standard techniques just before use. Preparatory operations and the syntheses were carried out in an atmosphere of dry argon. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (400.13 and 166.93 MHz, respectively). The δ values were calculated using the shifts relative to residual proton signals of solvent (^{1}H) and 85% H_3PO (^{31}P) as external reference. IR spectra in the region 600–200 cm^{-1} were recorded using a FTIR UFS 113-V instrument, in the region of 4000–450 cm^{-1} on a Bruker Fourier spectrometer Vector 22. Crystalline substances were investigated as suspendsions in mineral oil. Raman spectra were recorded on a Bruker FT-Raman RAMI spectrometer. The electron absorption spectra were recorded on a SF-16 instrument in the range 200–350 nm and Specol in the range 350–700 nm (l 1 cm, c 1×10^{-3} mol l^{-1}). The ESR spectra were recorded on a Radiopan SE/X-2544 spectrometer. The X-ray electron spectra were obtained on a VIEE-15 instrument using MgK_α-radiation at 10^{-2} Pa. Ionic conductivity of solutions of the complexes in acetone at 25°C was measured on a LM-301 conductometer (standard cell LM-3000). Determination of carbon and hydrogen was carried out by the microanalytical method on a Carlo Erba analyzer, the metal content was determined by the method of X-ray fluorescence analysis on a VRA 20L instrument, the phosphorus content was deterined by photocolorimetric method on a FEK-56m-C4-2 photocolorimeter, the chlorine content was determined according to [42].

Synthesis of octachlorodiaqua[*trans*-4,4'-bis(diethoxyphosphoryl)dirhodium(III) (III). Compound **I,** 0.1 g, was dissolved in 10 ml of ethanol within 15 min while passing argon (dark red solution). Then, under argon, while stirring, was added a solution of 0.12 g of the ligand L in 10 ml of chloroform. The solution color changed to brown. The mixture was stirred at 60–65°C for 6 h. The reaction completion was determined by the end of color change of the reaction mixture and the formation of a brown precipitate. The reaction mixture was cooled with ice. The fine brown crystals separated from the reaction mixture were filtered off and washed with chloroform and ethanol, then with benzene, and dried in a vacuum at 40°C (0.06 Torr) over Al_2O_3 to the constant weight. Yield 0.1 g (~43.5%). Found, %: C 28.19, H 4.39, Cl 23.50, P 5.24, Rh 17.32. $C_{28}H_{52}Cl_8O_{16}P_2Rh_2$. Calculated, %: C 28.09, H 4.35, Cl 23.75, P 5.18, Rh 17.22.

Synthesis of octaacetato[*trans*-4,4'-bis(diethoxyphosphoryl)biphenyl-18-crown-6-(diaqua)]tetrarhodium(II) (IV). Compound **II**, 0.1 g, was dissolved in 10 ml of ethanol within 15 min while passing argon (dark green solution). Then 0.07 g of ligand L was added while stirring, and the stirring was continued at 50–55°C for 3 h. The reaction completion was determined by the end of the color change of the reaction mixture (blue). The reaction mixture was left in a vacuum desiccator. From the reaction mixture separated a blue crystalline precipitate, which was filtered off, washed with ethanol and benzene, and dried in a vacuum at 40°C (0.06 Torr) over Al_2O_3 to constant weight. Yield 0.08 g (~47%). Found, %: C 26.58, H 4.29, P 3.91, Rh 26.62. $C_{44}H_{70}O_{30}P_2Rh_4$. Calculated, %: C 26.55, H 4.25, P 3.99, Rh 26.55.

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