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On Rhodium(III) Chloride Complexes with *N,N*-Dimethylformamide

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Abstract—A prolonged storage of a solution of $RhCl_3 \cdot nH_2O$ in *N,N*-dimethylformamide (DMF) at room temperature is attended by the consecutive formation of two precipitates, which mainly contain the $[(CH_3)_2NH_2][RhCl_5(DMF)]$ complex (**I**) and the complex $[RhCl_3(DMF)_3]$ (**II**) liberates. The addition of PPh_4Cl to an aqueous solution of complex **I** brings about the precipitation of $[PPh_4][RhCl_4(H_2O)_2]$ (**III**). Complex **II** (a mixture of *mer*- and *fac*-isomers) can be obtained also by treatment of $[RhCl_3(CH_3CN)_3]$ with DMF. In the course of the latter reaction, the formation of intermediate complex $[RhCl_3(CH_3CN)_2(DMF)]$ (**IV**) is observed. Complexes **I**–**IV** are characterized by elemental analysis; complexes **I**, **II**, and **IV** are characterized by the IR and ^1H and ^{13}C NMR spectra. The structures of **III** and **IV** are determined by X-ray diffraction analysis.

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N,N-dimethylformamide (**DMF**) has been widely used within the latter four decades as carbonylating agent in the synthesis of Rh(I) carbonyl complexes [1–8]. The authors of [9, 10] returned to the studies of these reactions and, at the same time, characterized some Rh(III) complexes formed on interaction of Rh(III) chloride with DMF. In this publication, we report new data on Rh(III) chloride complexes containing coordinated DMF molecules.

Since the commercial samples of Rh(III) chloride significantly differ in the content of water of crystallization and free HCl, we made an attempt to standardize them to some extent by repeated (two to three times) evaporation of an aqueous solution of commercial grade sample on a water bath. According to the analytical data, the molar ratio Cl : Rh in the samples we used decreased in this case from ~3.6 to 3.1; at the same time, the acidity of their aqueous solutions decreased (from pH ~1.60 to pH ~1.75). The results cited below refer particularly to such standardized samples.

On prolonged storage of Rh(III) chloride solutions in DMF, successive formation of crystalline precipitates with different compositions is observed. Commonly, at sufficient solution concentration (near 0.4 mmol/ml), the precipitate is formed already after 2–3 days, and then its quantity gradually increases. Ten days later, we filtered cherry red precipitate (product 1) and identified it as a demethylammonium salt $[(CH_3)_2NH_2]_2[RhCl_5(DMF)]$ (**I**). The filtrate was retained for further storage. Twenty days after the beginning of the experiment, a new light brown precipitate (product 2) was separated from the solution and identified as $[RhCl_3(DMF)_3]$ (**II**). The compositions of both precipitates varied slightly from experiment to experiment. Although the elemental analyses of products 1 and 2, which precipitated from a solution of $RhCl_3 \cdot nH_2O$ in DMF can be considered satisfactory, the detailed comparison of the IR and ^1H NMR spectra with the analytical data shows that each product contains small quantities of another product as an impurity and also contains admixtures of the other related compounds, for example, $[(CH_3)_2NH_2][RhCl_4(DMF)(H_2O)]$, $[(CH_3)_2NH_2][RhCl_4(DMF)_2]$, etc. (Obviously, the precipitate with the molar ratio Cl : Rh = 4.2, which formed in small quantity and was filtered off 15 days after the beginning of the experiment, also belongs to this type of salts.) In 40 days, one more portion of the precipitate was filtered off; its composition and spectrum coincided with those of salt **I**, separated at the beginning of the process. The dimethylammonium cation, contained in the above salt products, is likely to be resulted from the of known reaction of gradual decomposition of DMF [11] under the action of the acid agents present in the solution (excess hydrochloric acid, the acidity of hydrated Rh chloride itself): $(CH_3)_2N(CO)H + H^+ \longrightarrow (CH_3)_2NH_2^+ + CO$.

The observations presented in this article should be regarded not as the recommended procedure of the synthesis of individual complexes **I** and **II**, but only as the characteristics of the main products formed as a result of slow processes spontaneously occurring at room temperature in solutions of Rh(III) chloride hydrate in DMF.

The ^1H NMR spectrum of product 1 (a solution in D_2O) contains singlet signals from methyl protons of the dimethylammonium cation (2.72 ppm), from the methyl (2.85 and 3.01 ppm) and formyl (7.93 ppm) protons of DMF. On the basis of the spectrum of a solution of DMF in D_2O we measured and the literature data [12], we assigned these signals to a free DMF and, hence, can conclude that on dissolution of the complex, the DMF molecules contained in the anion almost quantitatively pass into the solution and are replaced by water molecules. In addition to the indicated intense singlets, the spectrum contains some close but weak signals, which are likely to be due to the above admixtures contained in product 1.

The ^{13}C NMR spectrum of product 1 exhibits singlets from the methyl carbons of dimethylammonium (35.4 ppm), methyl (32.0 and 37.6 ppm) and formyl (165.5 ppm) carbons of a DMF molecule. As in the case with the proton spectrum, the chemical shifts of DMF almost coincide with their values in the spectrum of DMF in D_2O we measured and with the data of [12].

Salt **I** was previously characterized in [10], and the values of the chemical shifts we established for the ^1H and ^{13}C signals in its NMR spectra satisfactorily agree with the data reported in [10]. Note that although these shifts correspond to free molecules [12], the authors of [10] discovered the doublet splitting of a signal of formyl C at $\delta^{13}C$ 165.2 ppm with the spin-spin coupling constant $^2J(CRh)$ 17 Hz.

The addition of $[PPh_4]Cl$ to an aqueous solution of product 1 gives cherry red crystalline precipitate $[PPh_4][RhCl_4(H_2O)_2] \cdot H_2O$ (**III**). This fact suggests that the aquation of the $[RhCl_5(DMF)]^{2-}$ anion is attended by removal from its coordination sphere of a portion of chloride ions, in addition to the DMF molecule. The pH value of an aqueous solution of a salt (~4.0) indicates the high degree of acid dissociation of the coordinated water molecules. The results of X-ray diffraction analysis of complex **III** revealed that in its anion, the coordinated water molecules are *cis* to one another. Previously [13], the *trans*-diaqua anion $[RhCl_4(H_2O)_2]^-$ in the composition of the salt $[NMe_4][RhCl_4(H_2O)_2]$ was described.

The ^1H NMR spectrum of product 2 (a solution in D_2O) contains intense signals from the methyl (3.08 and 3.18 ppm) and formyl (7.92 ppm) protons of the coordinated DMF. In addition to these signals, the spectrum exhibits also the signals from the protons of a free DMF (3.01, 2.85; a signal at 7.92 ppm is overlapped by the signal of the coordinated DMF), and the signal from the methyl protons of the dimethylammonium cation in salt admixtures, which, as was indicated above, are always present in product 2. Close to the signals from the coordinated DMF protons (both methyl and formyl), the additional signals are commonly recorded with δ^1H, which slightly differ (by 0.01–0.03 ppm) from the above signals. We assumed that these signals are due to the DMF molecules in the products of the complex aquation. The significant and increasing with the storage time degree of aquation of $[RhCl_3(DMF)_3]$ is confirmed by the signals in the spectra of these solutions corresponding to a free DMF and by the intensity of these signals increasing with time.

The ^{13}C NMR spectrum of an aqueous solution of product 2 fully agrees with such interpretation of its proton spectrum. The highest intensities are shown by singlets from the coordinated DMF molecules at 34.0, 39.5 ppm (the methyl carbon) and 170.1 ppm (the formyl carbon); the splitting of the signal from the formyl C as a result of interaction $^{13}C–^{103}Rh$ was not detected.

As with the proton spectra of product 2, these intense singlets lie close to the additional weak signals, which probably correspond to the DMF molecules in the other isomeric form of the complex or the products of its partial aquation. The spectrum also contains weak signals that we assigned to a free DMF and the dimethylammonium cation.

We obtained complex **II** free from the admixtures by interaction of DMF with the known acetonitrile Rh(III) complex $[RhCl_3(CH_3CN)_3]$ [14–17]. Judging from the number and position of the absorption maxima ν(CN) in the IR spectra of several compounds $[RhCl_3(CH_3CN)_3]$, we synthesized following the procedures [15, 17], they were the mixtures of the *mer*- and *fac*-isomers in the quantitative ratio that changed from experiment to experiment. As noted in [17], the relative content of the isomers in a particular compound $[RhCl_3(CH_3CN)_3]$ depends on peculiarities of the composition of the initial Rh(III) chloride and on details in the synthesis procedures. As was expected, the heating of a solution of this complex in DMF gives the $[RhCl_3(DMF)_3]$ complex in a good yield as a mixture of the *mer*- and *fac*-isomers. We believe that the relative content of the isomers in the reaction product depends on the isomeric composition of the initial acetonitrile complex. Typical examples of the ^1H and ^{13}C NMR spectra of the complex thus obtained are presented in Fig. 1. The ^1H spectrum consists of three groups of signals: one group in the region of resonances of the formyl proton and two groups in the region of the methylprotons, each groups containing three singlets with different intensities (Fig. 1a). We assigned the signals as follows. In each group, the most intense singlet cor-

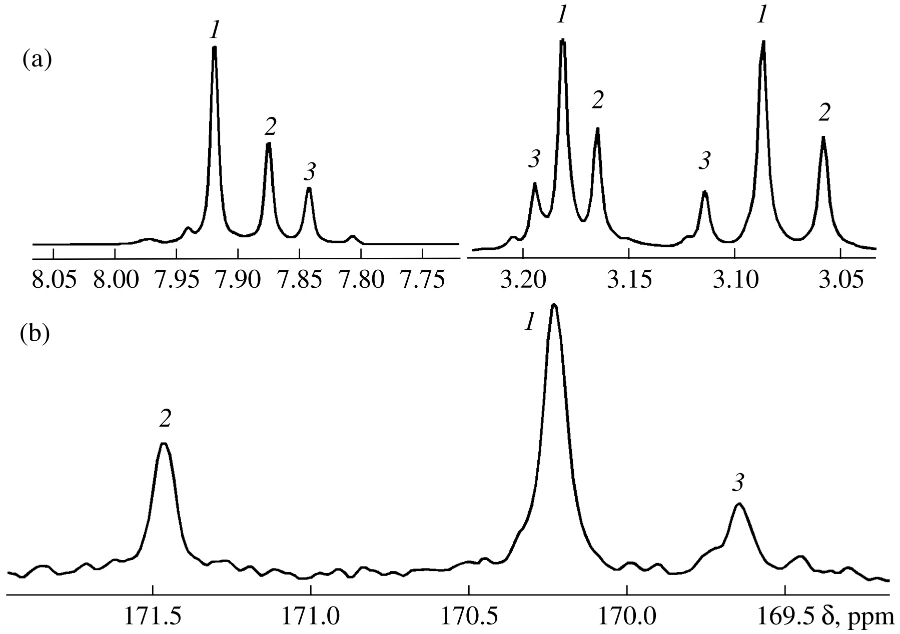

Fig. 1. The NMR spectra of the complex $[RhCl_3(DMF)_3]$ (**II**) obtained from $[RhCl_3(CH_3CN)_3]$ (D_2O solvent): (*1*) *fac*-isomer, (*2*) *mer*-isomer (DMF *trans*-DMF), (*3*) *mer*-isomer (DMF *trans*-Cl). (a) 500 MHz ^1H (fourfold increase in the vertical scale of the formyl protons 8.05–7.75 ppm as compared with the methyl region 3.20-3.05 ppm); (b) 125 mHz ^{13}C; the signals of the formyl carbon nuclei.

responds to three equivalent DMF molecules in the *fac*-isomer; the second (in intensity) singlet corresponds to two equivalent DMF molecules that are *trans* to one another in the *mer*-isomer; finally, the weakest singlet corresponds to the DMF molecule in the *mer*-isomer in the *trans*-position to the chloride ligand. The ^{13}C NMR spectrum of this complex in a region of the formyl carbon has the same shape (Fig. 1b). The signals from the methyl carbons appear as singlets, most likely, due to the fact that the chemical shifts corresponding to different positions of the DMF molecules in the isomeric forms of $[RhCl_3(DMF)_3]$ isomers are very close. Note that in this spectrum, we did not observe the splitting of the signals from the formyl carbon due to the interaction ^{13}C–^{103}Rh either, although in this case, all the signals under consideration correspond to the coordinated DMF molecules.

On the basis of the above data one can conclude that product 2 spontaneously precipitated from the solutions of Rh chloride in DMF consists almost fully of the *fac*-$[RhCl_3(DMF)_3]$.

Commonly, at the initial stage of the heating of a solution of $[RhCl_3(CH_3CN)_3]$ in DMF, an intermediate salmon red precipitate is formed that is dissolved on further heating and transforms to the final product, i.e., a mixture of the *mer*- and *fac*-isomers of $[RhCl_3(DMF)_3]$. According to the elemental analysis data, the composition of the intermediate precipitate corresponds to the formula $[RhCl_3(CH_3CN)_2(DMF)]$ (**IV**). The results of the study of its molecular structure are given below. Compound **IV** is insoluble in common organic solvents; its IR spectrum contains the absorption bands due to the coordinated molecules CH_3CN and DMF. The ^1H NMR spectrum of an aqueous solution of complex **IV** contains signals from a free and coordinated DMF, coordinated CH_3CN, and a number of signals that are likely to be assigned to the products of transformation of the coordinated acetonitrile [18] that we did not identify. Note that complex **IV** can be obtained also at room temperature. Its crystals precipitate on storage of a solution of $[RhCl_3(CH_3CN)_3]$ in DMF already in 1–2 h.

We performed X-ray diffraction analysis of complexes **III** and **IV**. In the anionic complex **III**, the coordinated water molecules are in the *cis*-position to one another (Fig. 2).The anions form infinite chains due to hydrogen bonds involving the coordinated and solvate water molecules and the chloride ligands (Fig. 3). The bond lengths and bond angles in complex **III** are listed in Tables 1, 2. The Rh–Cl and Rh–O bond lengths are in a good agreement with the values found previously in [13, 19, 20] for the anions *trans*-$[RhCl_4(H_2O)_2]^-$ and $[RhCl_5(H_2O)]^{2-}$ and reflect the same geometric *trans*-effect of the ligands: the bonds Rh–Cl and Rh–O in the *trans*-position to the chloride ligands are longer than those in the *trans*-position to the water molecules:

	cis-$[RhCl_4(H_2O)_2]^-$	*trans*-$[RhCl_4(H_2O)_2]^-$ [13]	$[RhCl_5(H_2O)]^{2-}$ [20]
$r(Rh–Cl)_{av.}$-*trans*-Cl	2.336	2.329	2.347
r(Rh–Cl)-*trans*-O	2.300 (av.)		2.304
r(Rh–O)-*trans*-Cl	2.080 (av.)		2.090
r(Rh–O)-*trans*-O		2.032	

The structure of complex **IV** is presented in Fig. 4. The bond lengths and bond angles are given in Table 3. The comparison of the values r(Rh–Cl) and r(Rh–O) in **IV** and in the related complex *cis*-$[RhCl_3(DMSO)_2(DMF)]$ [21] also indicated that these bond lengths depend on the nature of the *trans*-ligand:

	trans-O	*trans*-Cl	*trans*-S
r(Rh–Cl)	2.2868 (**IV**)	2.3204 (**IV**); 2.336 (средн.) [21]	2.366 [21]
r(Rh–O)		2.060 (**IV**)	2.112 [21]

EXPERIMENTAL

All the reactions were carried out in the atmosphere of dry argon using traditional Schlenk technique. DMF was used as received. Special purity grade acetonitrile was distilled over calcium hydride. Diethyl ether was kept over potassium hydroxide and then over calcium hydride and was distilled over calcium hydride. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer at 500 and 125 Mhz, respectively. The signals of the ^1H and ^{13}C nuclei of the DMF methyl group at 2.85 and 32.0 ppm, respectively, were used as internal standards [12]. The IR spectra (mineral oil mulls, solutions in $CHCl_3$) were measured on a Specord 75IR spectrometer. The pH of the solutions was measured using galvanic cell consisting of the pH-metric electrode (a ESL-63 glass hydrogen electrode) and a EVL-M3 silver chloride reference electrode. The emf was measured with a pH-120.1 high-resistance voltmeter.

Interaction of Rh(III) chloride with DMF at room temperature. The commercial sample of Rh(III) chloride hydrate was dissolved in water and evaporated on a water bath to dryness; this procedure was repeated 2–3 times. In Rh(III) chloride (standardized in this way), the ratio Cl : Rh = 3.10 (Rh 40.26%, Cl 42.8%). Such standardized sample (5.0 g) was dissolved in commercial DMF (45 ml). The solution obtained (c_{Rh} = 0.44 mmol/ml) was stored in the atmosphere of argon for 3 months. Several days later, the formation of a precipitate was observed.

In 10 days, crystals of red color were filtered, washed with acetone, and dried in a vacuum (the mass of product 1was 0.68 g).

For $[(CH_3)_2NH_2]_2[RhCl_5(DMF)]$ ($C_7H_{23}N_3ORhCl_5$)

anal. calcd. (%): Rh, 23.10; Cl, 39.79; C, 18.87; H, 5.16; N, 9.42.

Found (%): Rh, 23.46; Cl, 39.82; C, 19.58; H, 5.25; N, 9.47.

The IR spectrum (mineral oil mull), ν cm^{-1}: 1640–1644 vw, 1580, 1564, 1490, ~1450, 1438, $\underline{1428}$, 1366, 1262, 1250 sh, 1114, 1062, $\underline{1014}$, $\underline{890}$, $\underline{823}$, $\underline{812}$, 708. Underlined wave numbers of the absorption maxima are supposed to be due to the cation $(CH_3)_2NH_2^+$. The ^1H NMR (D_2O), δ, ppm: 2.72(12H) ($(C\underline{H}_3)_2NH_2^+$), 3.01(3H), and 2.85 (3H) ($(C\underline{H}_3)_2NCOH$), 7.93(1H) ($(CH_3)_2NCO\underline{H}$). The ^{13}C NMR (D_2O), δ, ppm: 35.4 ($(\underline{C}H_3)_2NH_2^+$), 37.6 and 32.0 ($(\underline{C}H_3)_2NCOH$), 165.5 ($(CH_3)_2N\underline{C}OH$). The complex is soluble in water and insoluble in organic solvents.

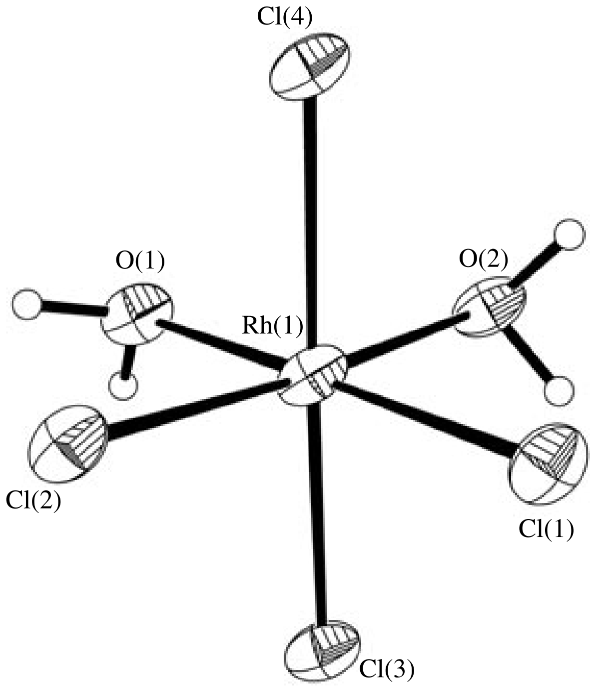

Fig. 2. The structure of the $[RhCl_4(H_2O)_2]^-$ anion in the composition of **III** (50% probability ellipsoids).

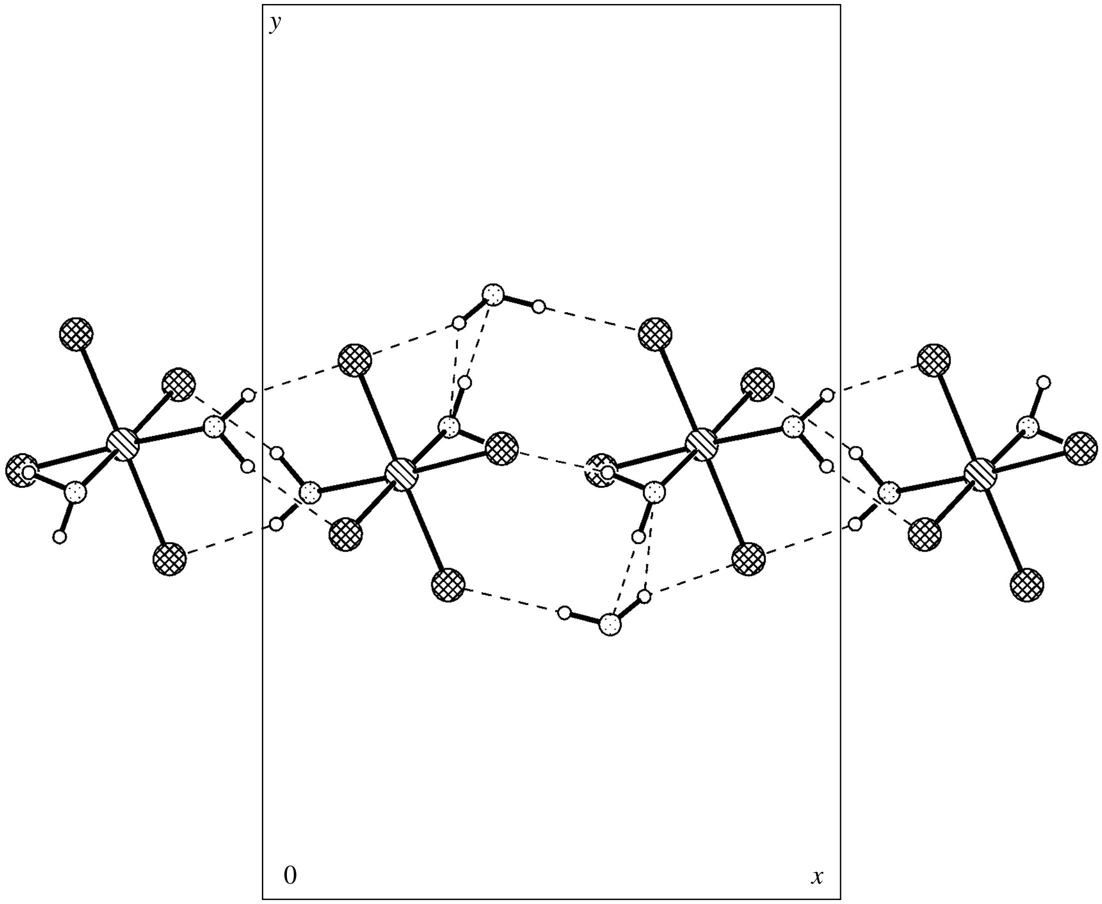

Fig. 3. H-bonded chains along the *x*-axis of the$[RhCl_4(H_2O)_2]^-$ anions and solvate water molecules (hydrogen bonds are shown in the dashed lines).

In 20 days, fine crystalline precipitate of a light brown color was filtered off, washed with acetone, and dried in a vacuum (the mass of product 2 was 1.24 g).

For $[RhCl_3(DMF)_3]$ $(C_9H_{21}N_3O_3RhCl_3)$
anal. calcd. (%): Rh, 24.01; Cl, 24.81; C, 25.22; H, 4.90; N, 9.80.
Found (%): Rh, 24.23; Cl, 25.23; C, 24.82; H, 4.91; N, 9.91.

The IR spectrum (mineral oil mull), ν cm^{-1}: 1635 vw, br, 1490, ~1450, 1438, 1364, 1256, 1118, 1062, 706. The spectrum contains very weak maxima at 1013, 890, 822, 819 cm^{-1} (the cation $(CH_3)_2NH_2^+$). The ^1H NMR (D_2O), δ, ppm: 3.18(3H) and 3.08(3H) $((C\underline{H}_3)_2NCOH)$, 7.92(1H) $((CH_3)_2NCO\underline{H})$. In addition to these signals, the spectrum contains the signals from the protons of a free DMF (3.01, 2.85, 7.92 ppm), sometime the signals at ~3.17, 3.09, 7.97 ppm from the isomeric and/or aquated forms of the complex, and a weak signal at 2.72 ppm (the $(CH_3)_2NH_2^+$ cation in the salt admixtures). The ^{13}C NMR, (D_2O), δ, ppm: 39.5, 34.0 $((\underline{C}H_3)_2NCOH)$, 170.1 $((CH_3)_2N\underline{C}OH)$; weak signals at 37.5, 32.0 and 165.5 ppm (free DMF) and 35.4 ppm (the dimethylammonium cation). The compound is soluble in water, DMF, chloroform and is insoluble in benzene, diethyl ether, hexane. The dissolution of the compound in chloroform, filtration of the obtained solution, and the treatment of a residue with benzene give the product, whose ^1H NMR spectrum does not contain the signal from $(C\underline{H}_3)_2NH_2^+$.

Interaction of $[(CH_3)_2NH_2]_2[RhCl_5(DMF)]$ with $[PPh_4]Cl$. A solution of $[PPh_4]Cl$ (0.37 g, 0.99 mmol) in water (3 ml) was added to a solution of product 1 (0.4 g, 0.9 mmol) in water (3 ml) and the mixture was allowed to stand. In 4 h, the obtained crystals of red color were washed with water and acetone. The yield was 0.48 g (85%).

For $[PPh_4][RhCl_4(H_2O)_2] \cdot H_2O$ $(C_{24}H_{26}O_3PRhCl_4)$
anal. calcd. (%): Rh, 16.12; Cl, 22.22; C, 45.16; H, 4.07.
Found (%): Rh, 16.29; Cl, 22.48; C, 44.92; H, 3.97.

Table 1. Selected bond lengths and bond angles in the $[RhCl_4(H_2O)_2]^-$ anion of complex **III**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Rh(1)–O(2)	2.074(4)	O(2)Rh(1)O(1)	86.85(15)	Cl(1)Rh(1)Cl(4)	93.91(5)
Rh(1)–O(1)	2.086(4)	O(2)Rh(1)Cl(1)	91.36(11)	Cl(2)Rh(1)Cl(4)	90.04(5)
Rh(1)–Cl(1)	2.2980(14)	O(1)Rh(1)Cl(1)	177.12(11)	O(2)Rh(1)Cl(3)	88.69(11)
Rh(1)–Cl(2)	2.3025(14)	O(2)Rh(1)Cl(2)	175.74(11)	O(1)Rh(1)Cl(3)	89.48(11)
Rh(1)–Cl(4)	2.3314(14)	O(1)Rh(1)Cl(2)	90.17(11)	Cl(1)Rh(1)Cl(3)	88.23(5)
Rh(1)–Cl(3)	2.3407(14)	Cl(1)Rh(1)Cl(2)	91.74(5)	Cl(2)Rh(1)Cl(3)	94.33(5)
		O(2)Rh(1)Cl(4)	86.83(11)	Cl(4)Rh(1)Cl(3)	175.08(5)
		O(1)Rh(1)Cl(4)	88.24(11)		

Table 2. Hydrogen bonds in the structure of $[PPh_4][RhCl_4(H_2O)_2] \cdot H_2O$ (**III**)

D–H···A	Distance, Å			DHA angle, deg	Symmetry transformation
	D–H	H···A	D···A		
O(1)–H(1O*A*)···Cl(3)	0.91	2.26	3.116(5)	157	[–*x* + 1, –*y*, –*z* + 1]
O(1)–H(1O*B*)···Cl(2)	0.98	2.22	3.126(5)	153	[–*x* + 1, –*y*, –*z* + 1]
O(2)–H(2O*A*)···Cl(1)	0.93	2.12	3.026(5)	162	[–*x* + 2, –*y*, –*z* + 1]
O(2)–H(2O*B*)···O(3)	0.90	1.73	2.632(6)	176	
O(3)–H(3O*A*)···Cl(4)	0.89	2.24	3.130(5)	177	[–*x* + 2, –*y*, –*z* + 1]
O(3)–H(3O*B*)···Cl(3)	0.97	2.32	3.257(5)	163	

The compound has a limited solubility in DMF; it is insoluble in water, acetone and the other organic solvents.

Synthesis of complex II. A suspension of the complex $[RhCl_3(CH_3CN)_3]$ [15, 17] (1.3 g, 3.9 mmol) in DMF (13 ml) was stirred at 80°C. The initial complex dissolved quickly to form a brown-red solution. In ~10 min, the precipitate of a salmon-red color was formed that was identified as $[RhCl_3(CH_3CN)_2(DMF)]$ (**IV**). On further heating of the reaction mixture, the precipitate dissolved fully.[1] The solvent was removed in a vacuum at 60°C. Then, DMF (4 ml) was added to an oily residue and heated at 100°C for 10 min. The solvent was again removed in a vacuum at 60°C; evacuation was continued for 3–4 h, the product was separated by trituration of an oily residue with some portions of benzene. The powdered light brown solid was filtered off, washed with acetone, and dried in a vacuum for 5 h. The yield was 1.34 g (80%). The compound is soluble is water, DMF and insoluble in benzene, diethyl ether, hexane.

For $[RhCl_3(DMF)_3](C_9H_{21}N_3O_3RhCl_3)$	
anal. calcd. (%):	Rh, 24.01; Cl, 24.82; C, 25.22; H, 4.90; N, 9.80.
Found (%):	Rh, 24.11; Cl, 24.75; C, 25.25; H, 4.91; N, 9.64.

The IR spectrum (mineral oil mull), ν cm^{-1}: 1635 vw, br, 1486, 1430, 1364, 1255, 1154 vw, 1116, 1060 w, 704. The ^1H NMR (freshly prepared solution in D_2O), δ, ppm: 3.18, 3.08 ($((C\underline{H}_3)_2NCOH)$), 7.92 ($((CH_3)_2NCO\underline{H})$) (presumably the *fac*-isomer); 3.20, 3.11 ($((C\underline{H}_3)_2NCOH)$), 7.88 ($((CH_3)_2NCO\underline{H})$) (presumably DMF *trans*-Cl in the *mer*-isomer); 3.17, 3.05 ($((C\underline{H}_3)_2NCOH)$), 7.84 ($((CH_3)_2NCO\underline{H})$) (presumably DMF *trans*-DMF in the *mer*-isomer). In addition to these signals, the spectrum contains also the signals from the protons of a free DMF (3.01, 2.85, a signal at 7.92 ppm is overlapped by a signal from the coordinated DMF). The ^{13}C NMR (freshly prepared solution in D_2O), δ, ppm: 170.2

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[1] The duration of this stage depends on the ratio of the *mer*- and *fac*-isomers in the initial acetonitrile complex; if the precipitate did not dissolv fully in 1 h, the reaction mixture was heated again for another 10 min at 100°C. In the case of pure *fac*-$[RhCl_3(CH_3CN)_3]$, no precipitate can be observed.

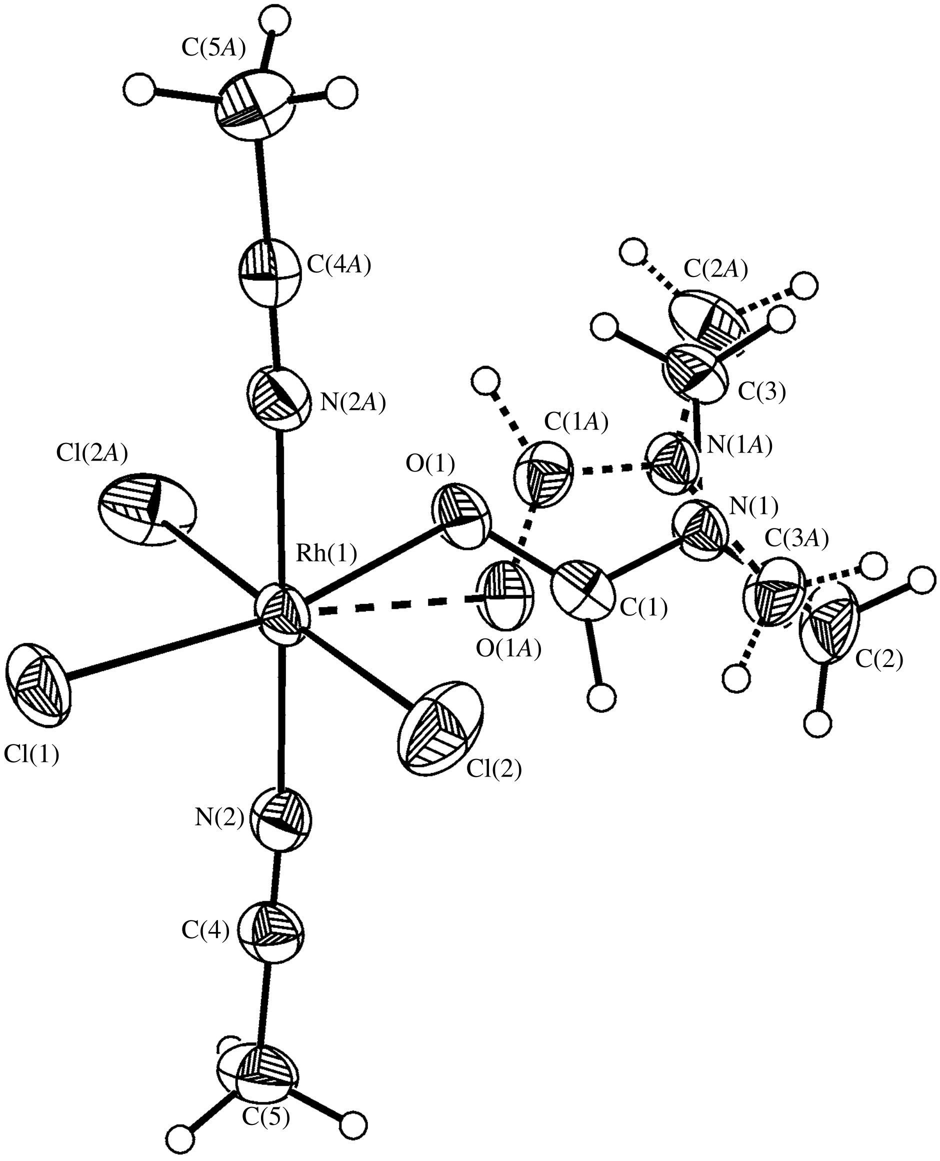

Fig. 4. The structure of complex **IV** (40% probability ellipsoids, the alternative position of the DMF molecule is shown in the dot-and-dash line).

($(CH_3)_2N\underline{C}OH$) (the *fac*-isomer) 169.7, 171.5, ($(CH_3)_2N\underline{C}OH$) (the *mer*-isomer). The ^{13}C nuclei of all methyl groups are presented in the spectrum by two singlets at 39.6 and 34.1 ppm.

Synthesis of complex IV. In some experiments, the above reaction between $[RhCl_3(CH_3CN)_3]$ and DMF was terminated at the stage of formation of an intermediate precipitate, which was isolated and studied. A suspension of $[RhCl_3(CH_3CN)_3]$ (0.5 g, 1.5 mmol) in DMF 5 ml) was stirred at 80°C. The initial complex dissolved quickly and in 10–15 min, the precipitate of a salmon-red color appeared. The precipitate was filtered, washed with acetone, and dried in a vacuum. The yield of the precipitate varies within wide limits (up to 70%). The compound is insoluble in common organic solvents.

For $[RhCl_3(CH_3CN)_2(DMF)]$ ($C_7H_{13}N_3ORhCl_3$)

anal. calcd. (%): Rh, 28.23; Cl, 29.18; C, 23.07; H, 3.57; N, 11.52.
Found (%): Rh, 28.30; Cl, 29.29; C, 23.24; H, 3.58; N, 11.62.

The IR spectrum (mineral oil mull), ν cm^{-1}: 2310 w, 1634 w, 1496, 1438, 1428 sh, 1416 sh, 1364, 1244, 1126, 1062, 1032, 1010, 708.

X-ray diffraction analysis of $[PPh_4][RhCl_4(H_2O)_2] \cdot H_2O$ (III) and $[RhCl_3(CH_3CN)_2(DMF)]$ (IV). The unit cell parameters and reflection intensities for compounds **III** and **IV** were measured on automated Bruker SMART 1000 CCD diffractometer (λMoK_α radiation, graphite monochromator, φ and ω scan mode). The absorption correc-

Table 3. Selected bond lengths and bond angles in the structure of [$RhCl_3(CH_3(CN)_2(DMF)$] (**IV**)

Bond	*d*, Å	Bond	*d*, Å
Rh(1)–N(2)	1.983(3)	N(1)–C(1)	1.351(7)
Rh(1)–O(1)	2.060(4)	N(1)–C(2)	1.470(7)
Rh(1)–Cl(1)	2.2868(11)	N(1)–C(3)	1.470(7)
Rh(1)–Cl(2)	2.3204(10)	N(2)–C(4)	1.127(4)
O(1)–C(1)	1.260(7)	C(4)–C(5)	1.446(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(2)Rh(1)N(2*A*)	178.67(12)	Cl(2)Rh(1)Cl(2*A*)	178.08(6)
N(2)Rh(1)O(1)	97.19(16)	C(1)O(1)Rh(1)	120.6(2)
N(2)Rh(1)Cl(1)	89.34(6)	C(1)N(1)C(2)	120.57(13)
O(1)Rh(1)Cl(1)	168.41(9)	C(1)N(1)C(3)	120.55(12)
Cl(2)Rh(1)N(2*A*)	89.43(8)	C(2)N(1)C(3)	118.9(2)
N(2)Rh(1)Cl(2)	90.59(8)	C(4)N(2)Rh(1)	175.9(2)
O(1)Rh(1)Cl(2)	98.50(14)	O(1)C(1)N(1)	123.30(14)
Cl(1)Rh(1)Cl(2)	90.96(3)	N(2)C(4)C(5)	179.2(3)

Table 4. The main crystallographic parameters for complex **III** and **IV**

Parameter	Value	
	III	**IV**
M	638.13	364.46
Temperature, K	100(2)	290(2)
Space group	$P2_1/n$	$C2/c$
Crystal size, mm	0.32 × 0.24 × 0.18	0.12 × 0.10 × 0.08
a, Å	10.7960(19)	7.2079(8)
b, Å	16.420(3)	16.6545(19)
c, Å	14.865(3)	11.4052(13)
α, deg	90	90
β, deg	99.705(4)	100.650(2)
γ, deg	90	90
V, Å^3	2597.4(8)	1345.5(3)
Z	4	4
ρ(calcd.), g cm^{-3}	1.632	1.799
F(000)	1288	720
μ_{Mo} cm^{-1}	11.55	18.44
T_{max}; T_{min}	0.819; 0.709	0.866; 0.809
Scan interval on 2θ, deg	1.86–27.04	2.45–28.02
Total number of reflections	23037	6645
Number of independent reflections (R_{int})	5615 (R_{int} = 0.035)	1600 (R_{int} = 0.030)
Number of reflections with $I > 2\sigma(I)$	4916	1342
Number of refined parameters	298	93
R_1 (for reflections with $I > 2\sigma(I)$)	0.0621	0.0301
wR_2 (for all reflections)	0.1544	0.0757
GOOF	1.040	1.041
ρ_{max}/ρ_{min}, eÅ^{-3}	2.051/–0.867	1.050/–0.606

tion was applied for the data obtained using the SADABS program [22]. The main crystallographic characteristics and summary of data collection and refinement are given in Table 4. The structures were solved by the direct method and refined by the full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms. Crystal **III** contains one solvate water molecule in a unit cell. Complex **IV** in crystal occupies partial position on axis 2, while DMF molecule is disordered over two positions with respect to this axis. The hydrogen atoms of water molecules in structure **III** and of acetonitrile molecules in structure **IV** were localized objectively in the Fourier difference syntheses and refined with the fixed positional and thermal parameters. The positions of the remaining H atoms in structures **III** and **IV** were calculated geometrically and refined in isotropic approximation with the fixed positional (rider model) and thermal ($U_{iso}(H) = 1.2U_{eq}(C)$) parameters. All the calculations were performed with the SHELXTL PLUS program package (version 5.10) [23]. The coordinates of the atoms, bond lengths, bond angles, and anisotropic thermal parameters for compounds **III** and **IV** are deposited with the Cambridge Structural Database.

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