Journal of Structural Chemistry. Vol. 49, No. 6, pp. 1090-1097, 2008
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STRUCTURE AND SYNTHESIS OF NITROSORUTHENIUM *trans*-DIAMMINES [Ru(NO)(NH$_3$)$_2$Cl$_3$] AND [Ru(NO)(NH$_3$)$_2$(H$_2$O)Cl$_2$]Cl·H$_2$O

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UDC 542.91:546.96:548.736

A DTA study of thermal decomposition of (NH$_4$)$_2$[Ru(NO)Cl$_5$] in helium atmosphere has been carried out, a synthetic procedure for preparation of the *trans*-diammine complex *mer*-[Ru(NO)(NH$_3$)$_2$Cl$_3$] (**I**) with yield ~70% has been developed. On re-crystallization of **I** from aqueous solution a *trans*-aquanitroso complex [Ru(NO)(NH$_3$)$_2$Cl$_2$(H$_2$O)]Cl·H$_2$O (**II**) has been isolated. The structures of the compounds have been determined by single crystal X-ray diffraction: space group *Pbcn*, $a = 6.607(1)$ Å, $b = 11.255(2)$ Å, $c = 9.878(2)$ Å (**I**) and space group *Ima*2, $a = 8.3032(3)$ Å, $b = 8.0890(2)$ Å, $c = 15.9192(5)$ Å (**II**).

Keywords: ruthenium, nitroso complexes, ammine complexes, chloro complexes, single crystal X-ray diffraction, thermogravimetric analysis.

INTRODUCTION

Discovery of physiological role of nitrogen monoxide has revived the interest to nitroso complexes of transition metals. Amongst the vast variety of nitroso compounds, ruthenium ammine nitroso complexes attract special attention as most stable and least toxic. These compounds and their derivatives already have found successful application as biologically active substances [1-4].

Chemistry of photo-induced processes, rapidly growing during last two decades, also has not ignored ruthenium nitroso compounds [5-9], and the studies on preparation and investigation of ion-radical salts combining conducting (superconducting) and photochromic properties are currently underway [10, 11]. Synthesis and examination of salts comprising photochromic and magnetic ions opens the pathway to design of multifunctional photomagnetic materials based on ruthenium ammine nitroso complexes [12-15]. Stability of ruthenium nitrosoammines in aqueous medium allows their successful application as precursors of metal alloy powders [16].

Up to date, two nitrosoruthenium diammines of the composition [Ru(NO)(NH$_3$)$_2$Cl$_3$] have been reported in the literature [17, 18]. The *fac* isomer, identified by single crystal XRD [19], is formed on interaction of *cis*-[Ru(NO)(NO$_2$)$_2$(NH$_3$)$_2$(OH)] with hydrochloric acid. Heating of the *fac*-[Ru(NO)(NH$_3$)$_2$Cl$_3$] to 325°C results in its isomerization. This second isomer is one of the most stable compounds of ruthenium and occurs as intermediate on thermal decomposition of a whole series of compounds: (NH$_4$)$_2$[Ru(NO)Cl$_5$] (up to 330°C) [17], [Pd(NH$_3$)$_4$][Ru(NO)Cl$_5$] (215°C) [20], [Ru(NO)(NH$_3$)$_3$Cl(H$_2$O)]Cl$_2$ (260°C) [21], [Ru(NO)(NH$_3$)$_5$]Cl$_3$ (310°C) [22, 23], [Ru(NO)(NH$_3$)$_4$OH][MCl$_4$] (M = Pt — 303°C, M = Pd — 327°C [16]). The authors of ref. [17] has isolated this isomer in individual form and characterized it with

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elemental analysis, powder X-ray diffraction, IR and UV-vis spectroscopy. The complex has been obtained with a low yield on heating of $(NH_4)_2[Ru(NO)Cl_5]$ at 320-330°C in a nitrogen stream during 10-15 min. Judging from the data obtained, this isomer has been recognized as highly symmetric and the meridional structure has been assigned (*trans*-square $(NH_3)_2Cl_2$). Nevertheless, according to the authors, final unambiguous conclusion on the structure of this isomer can be formulated only on the basis of a single crystal X-ray diffraction study. The authors of the other works have not aimed at development of preparation of this compound, its formation has been deduced from weight loss data and confirmed by IR spectroscopy and powder XRD.

Among aquacomplexes of ruthenium nitrosodiammine series only the isomer $[Ru(NO)(NH_3)_2Cl_2(H_2O)]Cl \cdot H_2O$ is known, where coordinated ammonia molecules are in the *cis*-position. Crystal structure of this complex has been elucidated quite recently by single crystal X-ray diffraction [24].

The purpose of this work is the development of synthetic procedure affording the thermally stable isomer $[Ru(NO)(NH_3)_2Cl_3]$ (compound **I**) and determination of its structure by single crystal X-ray diffraction, as well as structural identification of the product of its aquation in water (compound **II**).

EXPERIMENTAL

Ammonium pentachloronitrosoruthenate $(NH_4)_2[Ru(NO)Cl_5]$ used in experiments was prepared from ruthenium trichloride *p* (ruthenium content 46.51%, yield ~97%) according to [25]. The prepared compound was dissolved in a minimal amount of water, added with two volumes of ethanol, and re-precipitated complex was collected on a glass filter. The precipitate was washed with ethanol, acetone, and dried in air.

Thermogravimetric analysis was carried out on a Q-1000 instrument in helium atmosphere. A sample of ~150 mg was placed in a quartz crucible and heated at the rate of 8°C/min.

Synthesis of *mer*-$[Ru(NO)(NH_3)_2Cl_3]$ (complex **I**, *mer*-trichloronitrosodiammine ruthenium). A sample of $(NH_4)_2[Ru(NO)Cl_5]$ (~1 g) was placed at the bottom of a quartz dish to make a uniform layer 1-2 mm thick. The dish was covered with a watch glass and placed in a muffle furnace PT-2 equipped with a digital heat controller VARTA TP 400, furnace temperature being set to 330°C. Optimal exposition in the furnace was 2.5-3 h.

After cooling to ambient temperature, the obtained product was added with ~10 ml of distilled water acidified with 2-3 drops of HCl_{conc}, and the mixture was stirred for 10 min. The residue containing poorly soluble target complex was separated with a Schott filter (porosity 16), washed with 10-15 ml of water, 1-2 ml of ethanol and 1-2 ml of acetone, dried in air and weighted.

For refinement, a sample of the obtained complex (~0.5 g) was dissolved in 300 ml of 0.1 M HCl on heating to ~90°C and under continuous stirring, the hot solution was filtered through a glass filter and concentrated to ~10 ml. The resulting solution was allowed to stand at room temperature. The solution slowly (in 2-3 days) afforded a brick-red precipitate of **I**. It was collected on at Schott filter (porosity 16), washed with acetone and dried in air. Yield of *mer*-$[Ru(NO)(NH_3)_2Cl_3]$ after re-crystallization was ~70% on the starting $(NH_4)_2[Ru(NO)Cl_5]$.

Single crystals of $[RuNO(NH_3)_2Cl_2H_2O]Cl \cdot H_2O$ (complex **II**, 1-nitroso-2,4-dichloro-3,5-diammine-6-aquaruthenium(II) chloride monohydrate). Red-brown mother liquor remaining from the re-crystallization of **I**, was concentrated to ~1 ml at room temperature and left in a beaker covered with a watch glass. In a week the solution yielded X-ray quality orange-red crystals of complex **II**.

The *fac*-isomer of $[Ru(NO)(NH_3)_2Cl_3]$ was prepared according to [17], the material being further re-crystallized from 0.01 M HCl.

IR spectra of the synthesized complexes were registered on Fourier spectrometers Scimitar FTS 2000 (wavenumber range 4000-375 cm^{-1}) and Vertex 80 (600-80 cm^{-1}). The samples were prepared in the usual manner in KBr pellets.

TABLE 1. Crystal Data and Experimental Details

Parameter	**I**	**II**
Temperature, K	293(2)	296(2)
a, *b*, *c*, Å	6.607(1), 11.255(2), 9.878(2)	8.3032(3), 8.0890(2), 15.9192(5)
Space group	*Pbcn*	*Ima*2
Z	4	4
V, Å^3	734.5(2)	1069.21(6)
ρ_x, g/cm^3	2.455	1.910
μ, mm^{-1}	3.142	2.184
F(000)	520	600
θ range, deg	3.58—24.96	4.35—30.01
h, *k*, *l* range	$-7 \le h \le 7, -13 \le k \le 13, 0 \le l \le 11$	$-11 \le h \le 11, -9 \le k \le 11, -22 \le l \le 15$
Measured reflections	1924	4577
Independent reflections [*R*(int)]	624 [0.0374]	1505 [0.0163]
Data completeness	96.6%	98.5%
Refinement	Full matrix on F^2	
Number of parameters	40	66
GOOF on F^2	0.960	1.260
$R1$ [$I > 2\sigma(I)$]	0.0444	0.0311
$wR2$ [$I > 2\sigma(I)$]	0.1047	0.0797
$R1$ (all data)	0.0745	0.0353
$wR2$ (all data)	0.1122	0.0907

Powder X-ray diffraction patterns of the compounds were recorded on a diffractometer DRON-3M (R = 192 mm, CuK_α radiation, Ni-filter, scintillation detector with amplitude discrimination) in 2θ interval 5-50° at room temperature. The patterns of all synthesized complexes were completely indexed using the single crystal data, thus evidencing phase purity of the products obtained.

Unit cell parameters and intensity data were measured at room temperature on automated four-circle diffractometers (MoK_α radiation, graphite monochromator) CAD-4 (for **I**) and Bruker-Nonius X8 Apex, equipped with a 2-D CCD detector (for **II**).

Both structures were solved by the standard heavy atom method and refined in anisotropic-isotropic (for H) approximation, hydrogen atoms were set in geometrical positions. All calculations were performed with SHELX-97 program package [26].

Crystal data and selected refinement details are given in Table 1, atom coordinates and equivalent thermal parameters — in Table 2.

RESULTS AND DISCUSSION

Thermal decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ and synthesis of *mer*-$[Ru(NO)(NH_3)_2Cl_3]$. The data on thermal decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ available from the literature are somewhat contradictory. Reference [27] reports a DTA curve of this compound in air; it is stated that on heating of $(NH_4)_2[Ru(NO)Cl_5]$ to 300°C two NH_4Cl molecules are lost at once, i.e., no diammine complex is formed during the thermolysis. Intermediate products were not studied, and ruthenium dioxide appeared to be the final product of decomposition. At the same time, the authors of [17] succeeded in preparation of $[Ru(NO)(NH_3)_2Cl_3]$ by heating of $(NH_4)_2[Ru(NO)Cl_5]$ in nitrogen atmosphere at 320-330°C during 10-15 min, but the yield was not reported.

TABLE 2. Coordinates of Independent Atoms and Equivalent Thermal Parameters (Å^2)

Atom	x/a	y/b	z/c	U_{eq}
		mer-$[Ru(NO)(NH_3)_2Cl_3]$ (**I**)		
Ru(1)	0.0000	0.13177(8)	0.7500	0.0250(3)
Cl(1)	0.2710(3)	0.1281(3)	0.9075(2)	0.0359(5)
Cl(2)	0.0000	–0.0758(3)	0.7500	0.0433(8)
N	0.0000	0.2956(12)	0.7500	0.034(2)
O	0.0000	0.3814(11)	0.7500	0.065(3)
N(1)	–0.2097(11)	0.1200(9)	0.9083(7)	0.0404(17)
		$[RuNO(NH_3)_2Cl_2H_2O]Cl{\cdot}H_2O$ (**II**)		
Ru(1)	–0.2500	–0.26664(3)	–0.484450(18)	0.02383(12)
Cl(1)	0.03263(12)	–0.25229(9)	–0.49205(19)	0.0375(4)
N(1)	–0.2500	–0.0644(8)	–0.4001(4)	0.0343(13)
O(1W)	–0.2500	–0.0902(7)	–0.5757(4)	0.0323(10)
N	–0.2500	–0.4105(8)	–0.4047(4)	0.0350(13)
O	–0.2500	–0.4958(8)	–0.3492(4)	0.0671(14)
N(2)	–0.2500	–0.4409(8)	–0.5823(4)	0.0353(12)
Cl	–0.0242(3)	–0.8623(3)	–0.24520(16)	0.0465(5)
O(2W)	0.0000	–0.5000	–0.1697(3)	0.0403(8)

We examined thermal decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ in helium atmosphere. Generally, DTA curves (Fig. 1) are in good accord with the data given in [27] for thermal decomposition of this compound in air. The complex decomposes in three poorly separated steps with the maximums of endothermic effects at 370°C, 394°C, and 414°C. In air the first two effects are observed at somewhat lower temperatures (by 40°C and 29°C, respectively), the third — at 420°C, and thermolysis ends with a strong exothermic effect at 455°C. We examined the intermediate product obtained by the following procedure: heating of $(NH_4)_2[Ru(NO)Cl_5]$ to 340°C, exposure to this temperature during 30 min, and subsequent slow cooling to room temperature in helium atmosphere. Powder diffraction pattern and IR spectrum of the product, after washing with water and drying, basically correspond to those given in refs. [17, 18] for *mer*-$[Ru(NO)(NH_3)_2Cl_3]$. Thus, the first weight loss at the TG curve of $(NH_4)_2[Ru(NO)Cl_5]$ corresponds to elimination of two HCl molecules and can be described with the following equation:

$$(NH_4)_2[Ru(NO)Cl_5] \rightarrow [Ru(NO)(NH_3)_2Cl_3] + 2HCl\uparrow.$$

The behavior of the diammine complex on further heating agrees well with that described by us for $[Ru(NO)(NH_3)_2Cl_3]$ [23] developing during thermal decomposition of $[Ru(NO)(NH_3)_5]Cl_3{\cdot}H_2O$, which has been studied in detail. The minor difference lays in a slight shift of the maximums of two subsequent endothermic effects. For the product forming on thermolysis of $(NH_4)_2[Ru(NO)Cl_5]$, they are shifted to higher temperatures by 27°C and 13°C, correspondingly. According to [23], at the fist of these stages occurs elimination of one hydrogen chloride molecule and one ammonia molecule, thus affording polymeric nitrosoruthenium amidochloride $[Ru(NO)Cl(\mu\text{-}NH_2)(\mu\text{-}Cl)]_n$. At the last stage (maximum at 414°C) the complex completely decomposes with elimination of the nitroso-group. As evidenced by powder XRD, the product of complete decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ in inert atmosphere is a mixture ruthenium metal and its dioxide. The weight of the residue is 29.9%, slightly larger than calculated for pure metal (29.4%), but essentially less than expected for the equimolar mixture RuO_2 + Ru (34.0%), which results from thermal decomposition of $[Ru(NO)(NH_3)_5]Cl_3{\cdot}H_2O$.

Using the data of the DTA studies, we performed a number of experiments resulted in optimization of the preparation of $[Ru(NO)(NH_3)_2Cl_3]$ by thermal decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ in air. Three parameters were varied in the course of the experiments: temperature of the furnace, exposure, and mass transfer in the system. The extent of conversion was monitored by periodical weighting of samples (calculated weight loss 21.2%).

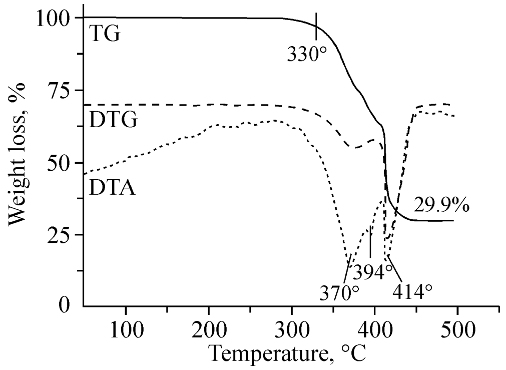

Fig. 1. DTA curves of $(NH_4)_2[RuNOCl_5]$ in helium atmosphere.

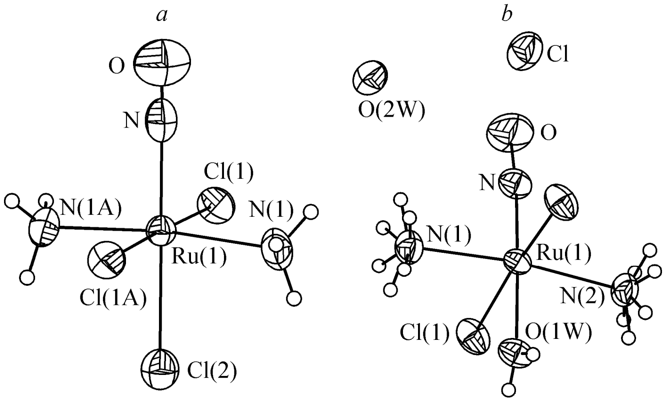

Fig. 2. Structure of complex moieties in the *trans*-diammine complexes of nitrosoruthenium: (*a*) — **I**, (*b*) — **II**.

It was found that the best yields of compound **I** (~70% after re-crystallization) are achieved when heating of $(NH_4)_2[Ru(NO)Cl_5]$ is carried out in a “semi-closed” system (a dish covered with a watch glass) at the temperature of 330°C during 2.5-3 h. Temperature lowering results in essential elongation of the process. Temperature rise by 5-10°C or employment of an open system strongly shortens the time required to reach the calculated weight loss, but worsens the yield of the target product. The samples thus obtained contain appreciable amounts of both the starting $(NH_4)_2[Ru(NO)Cl_5]$ and the decomposition product of compound **I** — $[Ru(NO)Cl(\mu\text{-}NH_2)(\mu\text{-}Cl)]_n$, as evidenced by powder XRD, IR and NMR spectroscopies. Such an influence of temperature on the course of the process is not surprising, for the decomposition stages of $(NH_4)_2[Ru(NO)Cl_5]$ are quite poorly separated (Fig. 1). Operation in “semi-closed” systems ensures that the thermolysis occurs in hydrogen chloride atmosphere, thus shifting back the equilibrium of the reaction of decomposition of the target product with formation of unwanted polymeric nitrosoruthenium amidochloride.

Description of crystal structures. The structures of complexes **I** and **II** was established by single crystal X-ray diffraction. The crystal structure of **I** comprises neutral complexes $[Ru(NO)(NH_3)_2Cl_3]$, the structure of **II** — complex cations $[Ru(NO)(NH_3)_2Cl_2H_2O]^+$, outer-sphere anions Cl^-, and water molecules of crystallization. The structures of the complex moieties with atomic labeling and thermal ellipsoids are shown in Fig. 2, selected interatomic distances and bond angles being listed in Table 3. The coordination polyhedron of ruthenium in both structures is a distorted octahedron having in the equatorial plane two pairs of *trans* chlorines and *trans* nitrogen atoms of ammonia molecules. The axial positions are occupied with the nitroso-group and the coordinated chloride ion (in **I**) or water molecule (in **II**).

Substitution of water for the coordinated chloride ion in the *trans*-position to NO on transition from **I** to **II** results in the following changes in IR spectra (Table 4). The maximum of the stretching vibrations of the nitroso group ν(NO) is blue-shifted by 20 cm^{-1}, a wide band with the maximum at 3445 cm^{-1} appears in the region of stretching vibrations of water $\nu(H_2O)$. The band of degenerated deformation vibrations of ammonia $\delta_d(NH_3)$ at 1625 cm^{-1} is somewhat broadened and blue-shifted by 15 cm^{-1}, what is caused by its overlap with the deformation band δ(HOH). In general, IR spectrum of compound **I** is in agreement with the spectra described in [17, 18] for *trans*-diammine $[Ru(NO)(NH_3)_2Cl_3]$, but there are minor discrepancies in positions of maximums and the number of bands. The most important distinction is the absence in the cited works of the band $\delta_d(NH_3)$ near 1620-1630 cm^{-1}, clearly discernible in the spectrum of **I**. This band is also absent in the reported spectra of *cis*-diammine $[Ru(NO)(NH_3)_2Cl_3]$, what is surprising as it has lower symmetry. To resolve this problem, we synthesized the *fac*-isomer (*cis*-diammine) $[Ru(NO)(NH_3)_2Cl_3]$ and recorded its IR spectrum. As evident from Table 4, this spectrum also does manifest the band $\delta_d(NH_3)$ with the maximum at 1630 cm^{-1}. The same Table lists the data for the product of aquation of this complex studied in ref. [24]. Substitution of the coordinated chloride ion with water in the *cis*-isomer results in the same changes in the spectrum as in the case of the *trans*-isomer, and the spectra of the *trans*-diammines are characterized by considerably fewer number of bands.

TABLE 3. Interatomic Distances (Å) and Valence Angles (deg) in **I** and **II**

Distance *d*	**I**	**II**	Distance *d*	**I**	**II**
Ru(1)–N	1.844(13)	1.722(6)	Ru(1)–Cl(1)	2.372(2)	2.353(1)
N–O	0.966(15)	1.122(7)	Ru(1)–Cl(2)	2.336(3)	
Ru(1)–N(1)	2.093(7)	2.116(7)	Ru(1)–O(1W)		2.037(5)
Ru(1)–N(2)		2.100(7)			
Angle ω	**I**	**II**	Angle ω	**I**	**II**
N–Ru(1)–N(1)	93.6(3)	93.2(3)	N(1)–Ru(1)–Cl(1A)	89.4(2)	
N–Ru(1)–N(2)		95.3(2)	N(2)–Ru(1)–Cl(1)		89.71(5)
N–Ru(1)–Cl(1)	91.00(8)	94.09(6)	Cl(1)–Ru(1)–Cl(2)	89.00(8)	
N–Ru(1)–Cl(2)	180		Cl(1)–Ru(1)–O(1W)		85.91(6)
N–Ru(1)–O(1W)		178.0(3)	N(1)–Ru(1)–Cl(2)	86.4(3)	
O–N–Ru(1)	180	175.4(6)	N(1)–Ru(1)–O(1W)		84.9(2)
N(1)–Ru(1)–N(1A)	172.8(6)		N(2)–Ru(1)–O(1W)		86.6(3)
N(1)–Ru(1)–N(2)		171.5(3)	Cl(1)–Ru(1)–Cl(1A)	178.00(16)	171.83(12)
N(1)–Ru(1)–Cl(1)	90.5(2)	89.68(5)			

Note. Symmetry operations generating equivalent atoms Cl(1A): **I** $-x, y, -z + 3/2$; **II** $-x - 1/2, y, z$.

TABLE 4. Positions of Maximums of Absorption Bands (cm^{-1}) in IR Spectra of Nitrosoammine Complexes of Ruthenium

Compound	ν (H_2O)	ν (NH_3)	ν (NO)	δ_d (NH_3)	δ_s (NH_3)	ρ (NH_3)
mer-[Ru(NO)(NH_3)$_2$$Cl_3$] (**I**)		3290	1882	1625	1286	795
		3240		1545		761
		3195				
[RuNO(NH_3)$_2$$Cl_2$$H_2O$]Cl·$H_2O$ (**II**) (*trans*-diammine)	3445	3310	1901	1640*	1300	824
		3260		1575		784
		3160				
fac-[Ru(NO)(NH_3)$_2$$Cl_3$]		3320 sh.	1884	1630	1322	813
		3270		1560	1299	780 sh.
		3190		1530	1272	720 sh.
[RuNO(NH_3)$_2$$Cl_2$$H_2O$]Cl·$H_2O$ (*cis*-diammine) [24]	3540	3280	1915	1630*	1335	820
	3365	3260	1875	1550	1315	780
		3200				720
		3140				

Compound	ν (Ru–NO)	δ (Ru–NO)	ω (H_2O)	ν (Ru–NH_3)	ν (Ru–Cl_{eq})	ν (Ru–Cl_{ax})
mer-[Ru(NO)(NH_3)$_2$$Cl_3$] (**I**)	606	587		484	330	289
[RuNO(NH_3)$_2$$Cl_2$$H_2O$]Cl·$H_2O$ (**II**) (*trans*-diammine)	603	583	522	481	346	
fac-[Ru(NO)(NH_3)$_2$$Cl_3$]	605	590		490 sh.	342,	288
				477	318,	
					310	
[RuNO(NH_3)$_2$$Cl_2$$H_2O$]Cl·$H_2O$ (*cis*-diammine) [24]	620	610	510	490 sh.	—	—
			460	480		

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*Overlapped with δ_d(HOH).

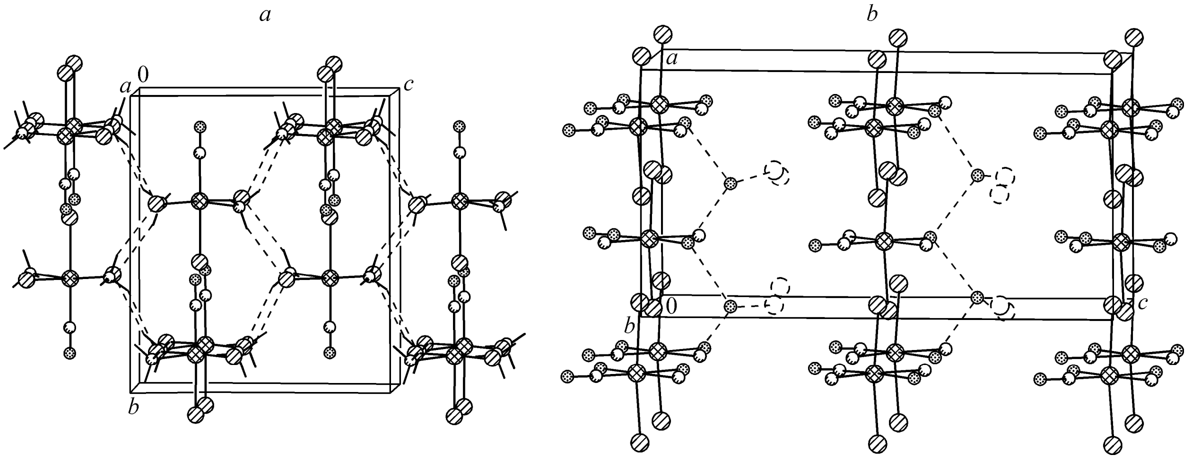

Fig. 3. Packing of the molecules of complexes **I** (*a*) and **II** (*b*) in the crystal and the scheme of hydrogen bonding.

In the structures of complexes **I** and **II** both equatorial bonds Ru–Cl are equivalent (2.372(2) Å for **I**, 2.353(1) Å for **II**). The distance to the chlorine atom located at the *trans*-coordinate Cl(2)–Ru(1)–$N_{(NO)}$ in the structure of **I** is somewhat shorter (2.336(3) Å) than the distance Ru–Cl_{eq}. This phenomenon is observed in all structurally characterized nitroso chloro complexes of ruthenium, as noted in ref. [28]. In the long-wavelength region of IR spectrum of complex **II** there is observed a single intense band of stretching vibrations Ru–Cl at 346 cm^{-1}, while in the spectrum of compound **I**, in agreement with its structure, — two bands (at 330 cm^{-1} and 289 cm^{-1}). The more intensive wide band (330 cm^{-1}), shifted by 16 cm^{-1} in respect to the ν(Ru–Cl_{eq}) in **II**, we also attribute to ν(Ru–Cl_{eq}), while the weaker band strongly shirted to longer wavelengths (at 289 cm^{-1}) — to ν(Ru–Cl_{ax}).

Average distances Ru–$N_{(NH_3)}$ in both structures fall within a narrow interval 2.093-2.116 Å characteristic of the majority of ammine complexes of nitrosoruthenium [29-32]. The distances Ru(1)–N and N–O in the structure of **II** are 1.722(6) Å and 1.122(7) Å, respectively, the angle Ru(1)–N–O equals to 175.4(6)°. These values are common for most ruthenium nitroso complexes. In the structure of **I** the fragment Ru(1)–N–O is linear, and the nitrogen atom is shifted by ~0.1 Å towards the oxygen atom resulting in some elongation of the distance Ru(1)–N (1.844(13) Å) and shortening of the distance N–O (0.966(15) Å), as compared to usual values. Such phenomenon already has been noted for some nitroso complexes of ruthenium [33], and can be related to thermal motion of the nitrogen atom.

Bond angles at the atom Ru(1) deviate from 90° by ±3.6° for **I** and ±5.3° for **II**. In both structures the ruthenium atom is shifted from the equatorial plane toward the nitroso-group by 0.07 Å (for **I**) and 0.16 Å (for **II**). The non-coordinated anion Cl^- in the structure of **II** is disordered over two positions.

The structure of compound **I** is of island type, 12 shortest distances Ru...Ru fall within 5.761-6.607 Å. Structural units are joined by hydrogen bonds N–H...Cl (N...Cl 3.36-3.43 Å) involving coordinated atoms Cl(1) and Cl(1A) and hydrogen atoms of ammonia molecules N(1) and N(1A). Chlorine atoms Cl(2), located in the *trans*-positions to NO, do not participate in hydrogen bonding and are directed to the nitroso-groups of neighboring complexes (the shortest distance Cl(2)...$O_{(NO)}$ 3.33 Å). Crystal packing and the scheme of hydrogen bonds in complex **I** are shown in Fig. 3*a*.

Figure 3*b* illustrates the packing in the structure of **II** as viewed along the *Y* direction. In general, the structure of **II** is of layered nature, interlayer distance is 7.96 Å. The complex cations form square nets in the plane *xy* with the distances 5.611-5.987 Å between the Ru central atoms within the layer. The length of the hydrogen bond O–H...O between the coordinated water molecule and the crystallization water molecule is O...O 2.66 Å. The bonds O–H...Cl of 3.17 Å and N–H...Cl falling within 3.39-3.57 Å should be noted.

Thus, thermal decomposition of $(NH_4)_2[Ru(NO)Cl_5]$ in air affords the meridional isomer (*trans*-diammine) $[Ru(NO)(NH_3)_2Cl_3]$, as supposed by the authors of ref. [17]. In order to obtain this complex with a good yield (~70%)

thermolysis should be carried out in a "semi-closed" system at 330°C during 2.5-3 h. On heating of this compound in aqueous solution acidified with HCl followed by concentration of the resulted solution at room temperature, *trans*-dichlorodiammino complex $[Ru(NO)(NH_3)_2Cl_2(H_2O)]Cl \cdot H_2O$ can be isolated, which has a coordinated water molecule in the *trans*-position to the nitroso group. The structures of the complexes have been established by single crystal X-ray diffraction.

The authors are grateful to N. V. Kuratieva and I. V. Korol'kov for assistance in X-ray diffraction experiments, to N. I. Alferova and L. A. Sheludaykova for registration of IR spectra, and to P. E. Plyusnin for carrying out the DTA experiment.

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