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PHYSICAL METHODS OF INVESTIGATION

Reaction of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ with Nitric Acid and Synthesis of Ammine(nitrato)nitrosoruthenium Complexes

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Abstract—The reaction of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ with nitric acid has been studied. Reaction products have been identified by IR spectroscopy, NMR, mass spectrometry, powder and single-crystal X-ray diffraction, and chemical analysis. Synthesis methods have been developed for amminenitrosoruthenium complexes containing outer-sphere and coordinated nitrate ions: *trans*-$[RuNO(NH_3)_4(H_2O)](NO_3)_3$ (**I**), *trans*-$[RuNO(NH_3)_4(NO_3)](NO_3)_2$ (**II**), and *fac*-$[RuNO(NH_3)_2(NO_3)_3]$ (**III**). Complex **II** has two polymorphs: monoclinic and tetragonal. The latter has been studied by X-ray crystallography.

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Aqua nitrate nitrosoruthenium complexes are among the dominating fission ruthenium forms in nitric acid solutions of waste from PUREX reprocessing of spent nuclear fuel (SNF) [1]. Notwithstanding the fact that such solutions have been being studied for more than half a century [2, 3], crystalline phases of ruthenium nitrate complexes have not been isolated from them so far. The composition, structure, and transformations of ruthenium complexes in those solutions have been studied mainly by spectroscopic methods, NMR being most informative among them [4, 5]. The distribution of ruthenium over many complex species in SNF solutions seriously prevents the obtaining of reliable kinetic and thermodynamic information on nitrate coordination to ruthenium. However, such information can also be obtained using model compounds. In our opinion, ammine(nitrato)nitrosoruthenium complexes are most adequate for this purpose [6].

The synthesis of a similar complex, *trans*-$[RuNO(NH_3)_4(NO_3)](NO_3)_2$, was reported in 1974. It was synthesized by long-term heating of a nitric acid solution of *trans*-$[RuNO(NH_3)_4(OH)](NO_3)_2$ in concentrated nitric acid [7]. The activation rate constant ($k = 10^{-4}$ s^{-1}) and the formation constant with respect to nitrate ion ($K \sim 3$) of the *trans*-$[RuNO(NH_3)_4(NO_3)]^{2+}$ complex at 75°C were estimated, and it was stated that the individual character of the compound was confirmed by chemical analysis for Ru and N and IR spectroscopy; however, the corresponding data and detailed synthesis procedure were not reported.

An analogous osmium complex, synthesized by heating *trans*-$[OsNO(NH_3)_4(OH)](NO_3)_2$ in nitric acid for 2 h, has been described in more detail. The resulting compound *trans*-$[OsNO(NH_3)_4(NO_3)](NO_3)_2$ was characterized by chemical and thermal analysis, IR and electronic absorption spectroscopy, and measurements of electric conductivity of its aqueous solutions [8]. The structure of the chloride salt *trans*-$[OsNO(NH_3)_4(NO_3)]Cl_2$ was studied by X-ray crystallography.

It is worth noting that in both cases, the initial compound was available chloride salt *trans*-$[MNO(NH_3)_4(OH)]Cl_2$ (M = Ru, Os), from which the chloride ions were removed prior to the reaction with nitric acid by the reaction of an aqueous solution with silver nitrate [7] or by passing the solution through an anion-exchange resin in the OH form [8]. This procedure makes the synthesis and subsequent purification of the nitrate derivative considerably more laborious, which should inevitably affect its yield (the yield of the target complex has not been reported). The above operation was most likely aimed at avoiding competing complexation with chloride ion (the stability constant of *trans*-$[RuNO(NH_3)_4Cl]^{2+}$ is ~170 [7]). Indeed, the presence of chloride ions in diluted nitric acid solutions of nitrosoruthenium complexes prevents the coordination of nitrate ion and leads to formation of chloro complexes [10]. Nevertheless, using concentrated nitric acid, we have managed to isolate several nitrosoruthenium nitrate derivatives and described their structures [11].

The present work deals with the study of the reaction of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ with nitric acid, as well as with the development of simple and efficient procedures of synthesis of amminenitrosoruthenium

Table 1. Absorption band maxima in the IR spectra of amminenitrosoruthenium complexes

trans-$[RuNO(NH_3)_4(H_2O)](NO_3)_3$ **(I)**	*trans*-$[RuNO(NH_3)_4(NO_3)](NO_3)_2$ **(II)**	*fac*-$[RuNO(NH_3)_2(NO_3)_3]$ **(III)**	Assignment
3277 s	3286 s	3303 s	$\nu(NH_3)$
3195 s*	3206 s	3233 s	
3121 s			$\nu(H_2O)$
1935 vs	1927 s	1937 vs	$\nu(NO)$
	1754 w		$\nu_1 + \nu_4(NO_3)^{outer}$
1601 m br**	1580 (sh) m br	1688 m br	$\delta_d(NH_3)$
	1527 s	1537 vs	$\nu_3(NO_3)^{coord}$
	1265 vs	1501 s	
		1270 vs	
1432 s			
1360 vs	1383 vs	1338 s	$\delta_s(NH_3)$
1327 vs	1353 vs		$\nu_3(NO_3)^{outer}$
1282 vs			
1040 m	1046 w		$\nu_1(NO_3)^{outer}$
	997 s	985 vs	$\nu_1(NO_3)^{coord}$
846 m	848 m br	843 m br	$\rho_r(NH_3)$
823 m	830 s		$\nu_2(NO_3)^{outer}$
			$\nu_2(NO_3)^{coord}$
	789 m	788 s	$\nu_4(NO_3)^{coord}$
	766 w	768 m	
718 m	718 w	712 w	$\nu_4(NO_3)^{outer}$
622 m	613 m	606 w	$\nu(Ru–NO)$
487 m	481 m	509 w	$\nu(Ru–NH_3)$

Notes: * The band is overlapped with $\nu(H_2O)$.
** The band is overlapped with $\delta_d(HOH)$.

complexes containing outer-sphere and coordinated nitrate ions.

EXPERIMENTAL

The initial complex *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ was synthesized in two steps from ruthenium trichloride (pure, 46.51% Ru) as described in [12, 13]. The total yield of the complex was 90–92%. The IR spectra of the complex were identical to the spectrum reported in [14], and the X-ray powder diffraction patterns coincided with that reported for this complex in ICDD/JCPDS PDF [15]. The other reagents used were of no worse than pure for analysis grade.

X-ray diffraction studies were carried out on a DRON-3M diffractometer ($R = 192$ mm, CuK_α radiation, Ni filter, amplitude scintillation detector) in the 2θ range 5°–50° at room temperature. Samples were applied as a thin layer to the smooth surface of a standard quartz cell.

The IR spectra of fine crystalline samples of complexes (Table 1) were recorded as KBr discs on a Scimitar FTS 2000 Fourier transform spectrophotometer in the range 375–3800 cm^{-1}. Assignment was according to [6, 16].

Synthesis of *trans*-$[RuNO(NH_3)_4(H_2O)](NO_3)_3$ (complex **I**, *trans*-aquatetraamminenitrosoruthenium nitrate). A weighed portion of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ (0.17 g, 6.1×10^{-4} mol) was dissolved in 4 mL of water, to which 4.5 mL $HNO_{3(conc)}$ was added. The addition of HNO_3 resulted in deposition of a yellow fine crystalline precipitate.

One day later, the product was filtered off, washed with alcohol and ether, and vacuum dried. The yield of complex **I** was 70%, but could be noticeably increased by evaporation of the mother liquor to a minimal volume at room temperature.

Synthesis of *trans*-$[RuNO(NH_3)_4(NO_3)](NO_3)_2$ (complex **II**, *trans*-tetraamminenitratonitrosoruthenium nitrate). To a sample of 0.13 g (4.4×10^{-4} mol) of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$, 5 mL $HNO_{3(conc)}$ was added, which led to a noticeable change in the morphology of the initial powder and its color changed from pale yellow to bright yellow. This was due to the transformation of the initial compound into complex **I**. The resulting mixture was heated under reflux for

Table 2. Crystallographic data and details of the diffraction experiment for the tetragonal polymorph of complex **II**

Stoichiometric formula	$H_6N_4O_5Ru_{0.50}$
FW	192.62
T, K	296(2)
λ, Å	0.71073
Crystal symmetry system	Tetragonal
Space group	I-4
Unit cell parameters, Å	$a = 7.8209(11)$, $b = 7.8209(11)$, $c = 9.781(2)$
V, Å^3	598.24(17)
Z	4
ρ_{calc}, g/cm^3	2.139
μ, mm^{-1}	1.380
F(000)	384
Crystal size, mm	0.20 × 0.20 × 0.12
θ range, deg	3.34–30.47
hkl range	$-7 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 13$
Number of measured reflections	2814
Number of unique reflections	890 [R(int) = 0.0153]
Data completeness for θ = 25.00°	100.0%
Max and min transmission	0.8519 and 0.7698
Refinement method	Full-matrix least squares on F^2
Number of reflections/constraints/parameters	890/0/86
S on F^2	1.230
R for $[I > 2\sigma(I)]$	$R1 = 0.0243$, $wR2 = 0.0736$
R for all data	$R1 = 0.0243$, $wR2 = 0.0736$
Absolute structure parameter	0.60(14)
Extinction coefficient	0.005(3)
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e/Å^3	0.412 and −0.367

5 min, which led to the compaction of the precipitate and the change in its color to yellow-orange. The color of the mother liquor remained pale yellow. Then, the reaction mixture was cooled to room temperature, the product was filtered off, washed with water (poorly soluble), alcohol, and ether, and vacuum dried. The yield of **II** was 95%. If necessary, the product can be recrystallized from a hot aqueous solution acidified with nitric acid.

Synthesis of *fac*-[RuNO(NH_3)$_2$(NO_3)$_3$] (complex **III**, *fac*-diamminetrinitratonitrosoruthenium). To a sample of 0.52 g (1.8 × 10^{-3} mol) of *trans*-[RuNO(NH_3)$_4$(OH)]Cl_2, 15 of $HNO_{3(conc)}$ was added. The resulting mixture was heated under reflux for 50 min. In the course of the first 5 min, a successive transformation of the initial compound into complexes **I** and **II** was observed. Further refluxing led to a slow (in 35–40 min) dissolution of the precipitate of **II**, which was accompanied by a change in solution color to red. During the final 5–10 min of heating, a red fine crystalline precipitate of complex **III** started depositing. The precipitate amount considerably increased after the heating was switched off and the reaction mixture was allowed to cool to room temperature. The product was filtered off, washed with a minimal amount of water, alcohol, and ether, and vacuum dried. The dry fine crystalline powder of complex **III** was red-brown. An additional amount of the product was separated by evaporation of the mother liquor on a water bath to a minimal volume. The overall yield of **III** was ~65%.

The composition of gaseous reaction products was studied on a Scimitar FTS 2000 Fourier spectrophotometer in the range 400–3800 cm^{-1} in a gas cell and on a QMS 100 Series gas analyzer. For sampling, the reaction system was connected through a reflux condenser with a gas syringe. Before sampling, the system was blown with argon. To study the products of the reaction yielding complex **II**, the gas mixture was collected during the first 10 min of heating, and for the reaction resulting in complex **III**, the gas mixture was collected in the time interval 20–50 min of heating.

The ^{14}N NMR spectra of aqueous solutions were recorded on a Bruker MSL-300 spectrometer operating at a frequency of 21.68 MHz. Chemical shifts (δ scale, ppm) were measured from the signal of the external reference, 1 M $NaNO_3$. The spectra were processed with the Nuts Pro 6.0 program package [17].

Atomic absorption analysis of the ruthenium content in preliminarily prepared samples was carried out on a Hitachi Z-8000 spectrophotometer. Samples were prepared as follows: To dissolve complex **II**, it was heated with $HNO_{3\ (conc)}$. Solutions of complex **II** and samples of complex **III** were poured with 1–2 M HCl and heated on a boiling water bath for 1 h. The resulting solutions were diluted to a ruthenium concentration of 30–40 μg/mL and analyzed. Hydrochloric acid solutions of chloronitrosoruthenium complexes were used as reference samples.

Elemental CHN analysis was carried out on a Euro EA 3000 automated analyzer. To carry out analysis for nitrogen, samples were preliminarily mixed with glucose.

X-ray diffraction analysis of a single crystal of the tetragonal polymorph of complex **II** was carried out on a Bruker X8Apex automated diffractometer (MoK_α radiation, graphite monochromator). The structure was solved by the heavy-atom method and refined in the anisotropic (isotropic for H) approximation. In structure **II**, some of the hydrogen atoms were located from a difference synthesis, and some of them were introduced in geometrically calculated positions. All calculations were performed with the SHELX-97 program package [18]. Crystallographic characteristics and selected experimental and refinement details are shown in Table 2, and the coordinates of basis atoms, excluding hydrogen atoms, and equivalent thermal parameters are listed in Table 3.

RESULTS AND DISCUSSION

Complex I. The X-ray diffraction patterns of complex **I** are completely indexed on the basis of the single-crystal structure of *trans*-[RuNO$(NH_3)_4(H_2O)$]$(NO_3)_3$ [11], which is evidence of the single-phase character of the product. The IR spectrum of this complex (Table 1) is consistent well with the spectra of the known aquatetraamminenitrosoruthenium complexes [13, 19, 20]. However, it is worth noting that the ν(NO) band in the spectrum of complex **I** is observed at a considerably shorter wavelength (1935 cm^{-1}) than it is typical of the complexes containing the *trans*-coordinate H_2O–Ru–NO (~1910–1920 cm^{-1}).

Complex II. The IR spectrum of complex **II** (Table 1) is in good agreement with the spectrum of the diamminedinitrato- and acidotetraamminenitrosoruthenium complexes [6, 13, 20, 21].

In the X-ray powder diffraction pattern of **II** (Fig. 1), reflections belonging to two polymorphs of *trans*-[RuNO$(NH_3)_4(NO_3)$]$(NO_3)_2$, monoclinic and tetragonal. The structure of the former was described in [11] and that of the latter is determined in the present work by X-ray crystallography.

The results of chemical analysis are the following:

For [RuNO$(NH_3)_4(NO_3)$]$(NO_3)_2$ anal. calcd. (%): Ru, 26.3; N, 29.1; H, 3.1.

Found (%): Ru, 26.9 ± 0.8; N, 29.2 ± 0.3; H, 3.3 ± 0.5.

Table 3. Coordinates of basis atoms and isotropic thermal parameters for the tetragonal modification of **II**

Atom	*x/a*	*y/b*	*z/c*	U^*_{eq}, Å^2
Ru(1)	1	0	0	0.03464(15)
N(1)	0.8097(4)	0.1913(4)	0.006(2)	0.0621(13)
N(2)	1	0	0.2971(15)	0.081(12)
N	1	0	0.1747(14)	0.048(3)
O(21)	0.937(4)	0.026(7)	0.2050(15)	0.066(8)
O(23)	0.822(2)	0.001(3)	0.2963(18)	0.070(4)
N(3)	0.5	0	0.25	0.057(4)
O(22)	1	0	0.4186(11)	0.26(2)
N(4)	0.5	0	–0.215(3)	0.099(11)
O(41)	0.409(6)	–0.121(5)	–0.252(2)	0.103(10)
O(43)	0.5	0	–0.0751(12)	0.069(3)
O(31)	0.526(3)	0.146(2)	0.222(2)	0.046(3)
O(32)	0.466(3)	0.1440(19)	0.2307(19)	0.047(3)
O(33)	0.497(3)	0.120(4)	0.178(3)	0.076(6)
O(34)	0.500(4)	0.046(3)	0.128(3)	0.083(7)
O	1	0	0.301(2)	0.072(8)

Crystal structure of the tetragonal modification of *trans*-[RuNO$(NH_3)_4(NO_3)$]$(NO_3)_2$. The compound has an island structure composed of *trans*-[RuNO$(NH_3)_4(NO_3)$]$^{2+}$ cations (Fig. 2) and outer-

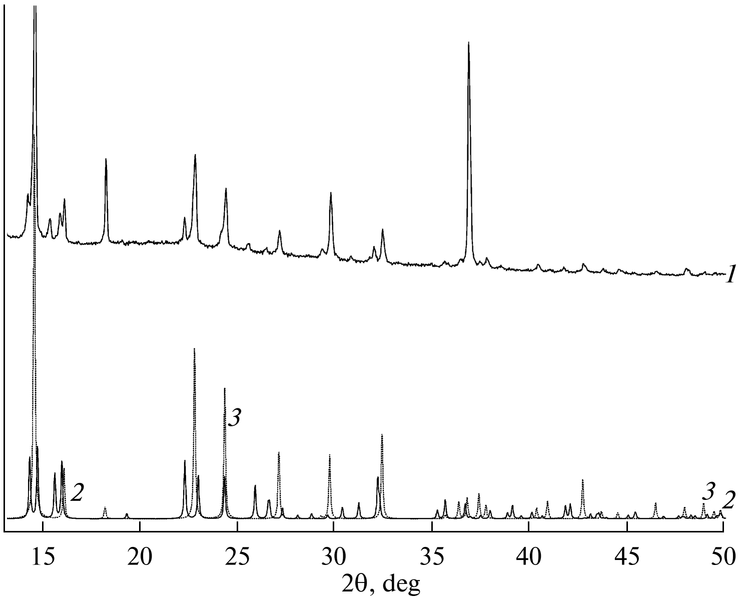

Fig. 1. (*1*) X-ray powder diffraction pattern of complex **II** and the theoretical X-ray diffraction patterns of the (*2*) monoclinic and (*3*) tetragonal phases of *trans*-[RuNO$(NH_3)_4(NO_3)$]$(NO_3)_2$.

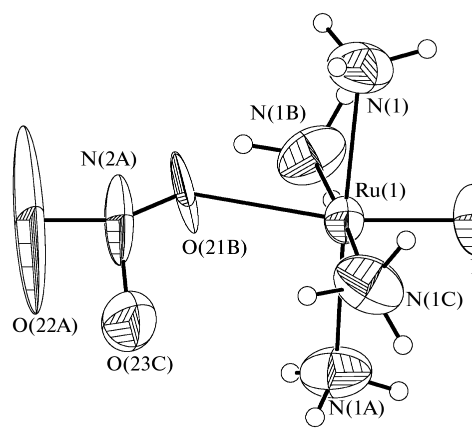

Fig. 2. Structure of the complex cation in the tetragonal structure of **II** with the atom numbering scheme and thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg) in structure **II**: Ru(1)–N, 1.709(14); Ru(1)–O(21), 2.075(14); Ru(1)–N(1), 2.111(3); N(2)–O(21), 1.05(2); N(2)–O(22), 1.188(19); N(2)–O(23), 1.394(17); N–O, 1.23(3); N(3)–O(32), 1.171(15); N(3)–O(33), 1.17(3); N(3)–O(31), 1.192(17); N(4)–O(41), 1.235(18); N(4)–O(43), 1.37(3); NRu(1)N(1), 88.5(5); O(21)Ru(1)N(1), 74.7(8); O(21)N(2)O(22), 149.3(10); O(21)N(2)O(23)#2, 118(2); ONRu(1), 180.00(1); O(41)N(4)O(43), 106.8(17).

sphere nitrate anions. All ions in the structure are disordered.

The ruthenium coordination polyhedron is a distorted octahedron located on axis –4. The equatorial plane contains four ammonia molecules related by the symmetry axis, and the axial positions are occupied by the nitroso group and the coordinated nitrate ion. The nitroso group is located on axis –4 and is disordered over two positions, and the Ru(1)NO angle is linear. The nitrato group is coordinated to the ruthenium atom through one oxygen atom and is disordered over four positions. The bond lengths in the complex cation (Fig. 2) differ from those in the structure of the monoclinic polymorph by no more than 0.03 Å [11]. The deviations of the bond angles at the Ru atom from 90° are considerable being as large as 15.3°. In the coordinated and outer-sphere nitrate ions, which are also disordered, there is a considerable scatter of bond lengths and angles. The shortest distance between the centers of anions N···N is 4.55 Å.

Each complex cation in the structure is surrounded by 12 neighboring cations at Ru···Ru distances within 7.382–7.821 Å.

Study of the composition of the gas phase formed in the course of synthesis of II. The IR spectrum of gaseous reaction products formed on heating *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ in $HNO_{3(conc)}$ for 10 min shows strong ν_{N-O}(NOCl) (1810 and 1790 cm^{-1}) and ν_{N-Cl}(NOCl) (605 and 586 cm^{-1}) bands. In addition, the spectrum shows weaker bands due to the $2\nu_{N-O}$(NOCl) (3572 and 3554 cm^{-1}), $\nu_s(H_2O)$ (3492 and 3468 cm^{-1}), $\nu_{N-O}(N_2O)$ (2237 and 2211 cm^{-1}), $\nu_{as}(NO_2)$ (1628 and 1602 cm^{-1}), and $\nu_{N-N}(N_2O)$ (1301 and 1270 cm^{-1}). The mass spectrum shows strong signals of N_2, O_2, NO, and Cl, as well as weak signals of NO_2, H_2O, and N_2O.

Thus, major gaseous products evolved upon the formation of complex **II** in the system are NOCl and Cl_2. The presence of N_2 and O_2 signals is caused by the residual pressure of these gases after pumping out air from working chambers, and the presence of NO and NO_2 signals is due to NOCl dissociation, which is almost complete at the working pressure of the mass spectrometer (~10^{-9} atm). The presence of small amounts of N_2O is caused by partial oxidation of the coordinated ammonia by concentrated nitric acid.

Complex III. The IR spectra of complex **III** (Table 1) are consistent with the spectra of *trans*-diamminedinitratonitrosoruthenium and *cis*-diamminetrichloronitrosoruthenium complexes [6, 22], as well as with the spectrum of complex **II**. It is worth noting that the spectrum shows pronounced vibrations of coordinated NO, NH_3, and NO_3 groups and lacks vibrations of outer-sphere NO_3^-.

The X-ray powder diffraction patterns of complex **III** coincide with that of *fac*-$[RuNO(NH_3)_2(NO_3)_3]$, for which the tentative structure was described by us on the basis of EXAFS data [11].

The results of chemical analysis are the following:

For $[RuNO(NH_3)_2(NO_3)_3]$ anal. calcd. (%): Ru, 28.8; N, 23.9; H, 1.7.

Found (%): Ru, 28.9 ± 0.9; N, 23.9 ± 0.3; H, 2.1 ± 0.5.

Complex **III** poorly soluble in cold water is readily soluble on heating its suspension in water. The ^{14}N NMR spectrum of such a solution is shown in Fig. 3. The spectral characteristics required for our discussion are listed in Table 4. The table also shows for comparison the spectra of a solution of *trans*-diamminedinitratonitrosoruthenium complex whose synthesis and crystal structure were described by us in [6]. The spectra are very similar: the spectra each contains four signals with the integrated intensity ratio $I_{NO} : I_{NH_3} : I_{NO_3}^{coord} : I_{NO_3}^{-}$ corresponding to the average composition of complexes in a solution of $[RuNO(NH_3)_2(H_2O)_{3-x}(NO_3)_x](NO_3)_{3-x}$, where $x = 0.6$ and 1.3, respectively.

The existence of free nitrate ion in the solution of complex **III**, which is absent according to IR data, is due to the fact that heating the complex in water leads to the substitution of water for the coordinated nitrate ion:

$$[RuNO(NH_3)_2(NO_3)_3] + H_2O$$
$$= [RuNO(NH_3)_2(H_2O)(NO_3)_2]^+ + NO_3^-;$$

$$[RuNO(NH_3)_2(H_2O)(NO_3)_2]^+ + H_2O$$
$$= [RuNO(NH_3)_2(H_2O)_2(NO_3)]^{2+} + NO_3^-.$$

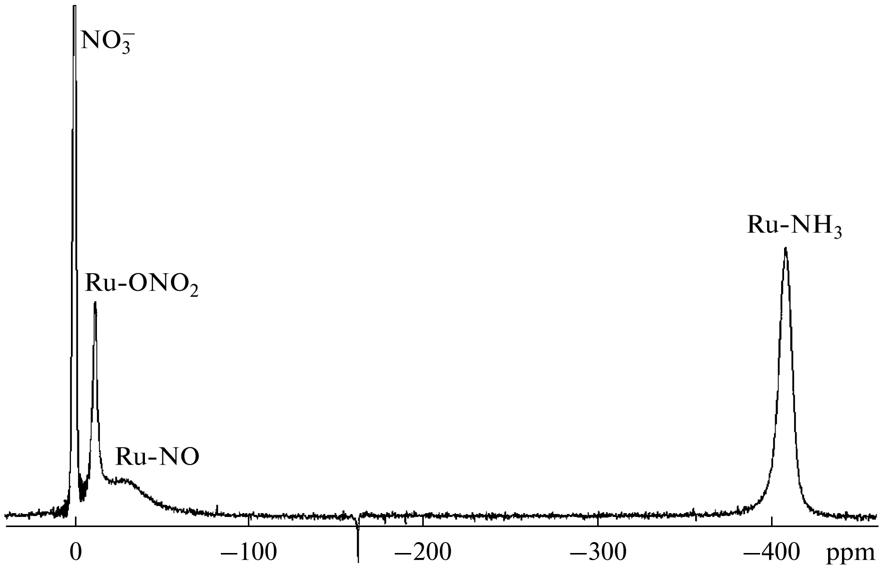

Fig. 3. Fragment of the ^{14}N NMR spectrum of solution prepared by dissolving a sample of complex **III** in water on heating, c_{Ru} = 0.14 mol/L.

In a *trans*-$[RuNO(NH_3)_2(H_2O)(NO_3)_2]NO_3$ solution not subjected to heating, the degree of aquation is noticeably lower.

The chemical shift of the coordinated nitroso group (−27 to −29 ppm) in both solutions is intermediate between the shifts typical of the *trans* coordinates ON−Ru−OH_2 (−17 to −21 ppm) and ON−Ru−OH (−34 to −38 ppm) [5, 23, 24], which is explained by that aquanitrosoruthenium complexes in an aqueous solution are subjected to partial deprotonation:

$$[RuNO(NH_3)_2(H_2O)_2(NO_3)]^{2+}$$
$$= [RuNO(NH_3)_2(H_2O)(NO_3)(OH)]^+ + H^+$$

(see, e.g., [13]).

In the above spectra, the largest difference is observed in the position of signals of coordinated ammonia molecules. The spectrum of a solution of *trans*-diammine, the chemical shift of NH_3^{coord} is −396.8 ppm and is close to the chemical shift of *trans*-tetraamminenitrosoruthenium complexes (−400 ppm [13]). In the spectrum of a solution of complex **III**, this signal is shifted upfield by 12.2 ppm. Such a difference between the positions of signals of identical ligands for complexes with a similar ligand composition is almost always caused by the change in the *trans* partner [25]. This means that we can state with a high degree of confidence that, in ruthenium species existing in a solution of complex **III**, the NH_3^{coord} ligand is *trans* to coordinated water molecules and nitrate ions. Isomerization of the complex in the course of solution preparation can be ruled out since the evaporation of this solution in the presence of concentrated nitric acid leads to initial complex **III**. In addition, no cases of *cis*−*trans* isomerization are known for amminenitrosoruthenium complexes, whereas opposite examples are available [26].

The facial structure of complex **III** was also supported by the results of studying its interaction with hydrochloric acid. The process that occurs in the system is completely described by the equation

$$[RuNO(NH_3)_2(NO_3)_3] + 3HCl\ (2\ M)$$
$$= [RuNO(NH_3)_2Cl_3]\downarrow + 3HNO_3.$$

The X-ray powder diffraction pattern and IR spectrum of the product coincide with the characteristics of *fac*-$[RuNO(NH_3)_2Cl_3]$ described in [15, 22]. Inas-

Table 4. Chemical shifts (δ, ppm) and assignment of lines in the ^{14}N NMR spectra of aqueous solutions of amminenitratonitrosoruthenium complexes

Sample	NO_3^{outer}	NO_3^{coord}	NO^{coord}	NO_3^{coord}	NH_4^+
0.14 M solution of **III**	−0.7(2.3)*	−12.0(0.6)	−27.1(1.0)	−409.2(2.0)	
0.08 M solution of *trans*-$[RuNO(NH_3)_2(NO_3)_2(H_2O)]NO_3$	−0.7(1.7)	−13.2(1.3)	−28.8(0.9)	−396.8(2.0)	
Mother liquor after precipitation of **III**	−22.8(3.4)HNO_3	−11.8(0.08)		−408(0.04)	−356.7

* Relative signal intensities are parenthesized.

much as *trans*-diammine $[RuNO(NH_3)_2Cl_3]$ is thermodynamically more stable [27], the formation of the *cis*-diammine in this reaction is convincing evidence in favor of the facial structure of the initial diammine trinitrato complex.

Study of the composition of the gas phase formed in the course of synthesis of complex III. The IR spectrum of the gaseous reaction products forming on heating *trans*-$[RuNO(NH_3)_4(NO_3)](NO_3)_2$ in $HNO_{3(conc)}$ shows strong $\nu_{N-O}(N_2O)$ (2236 and 2214 cm^{-1}) and $\nu_{N-N}(N_2O)$ (1299 and 1273 cm^{-1}) bands, as well as weak $\nu_s(H_2O)$ (3494 and 3467 cm^{-1}) and $\delta_d(N_2O)$ (589 cm^{-1}) bands. The mass spectrum shows strong lines of N_2, N_2O, H_2O, O_2, and NO, as well as weak lines of NO_2 and Cl_2.

Thus, the major gaseous product accompanying the formation of complex **III** in the system under consideration is N_2O formed in the course of oxidation of coordinated ammonia molecules by concentrated nitric acid. The presence of noticeable amounts of NO in the mass spectrum (and its absence in the IR spectrum) can be associated with partial disproportionation of N_2O at the working pressure of the mass spectrometer ($\sim 10^{-9}$ atm): $2N_2O = 2NO + N_2$.

Study of the composition of a mother liquor after precipitation of complex III. The ^{14}N NMR parameters of the mother liquor after evaporation to a volume of 2 mL and separation of the second fraction of complex **III** are listed in Table 4. The strongest signal at -22.8 ppm is due to the $NO_3^- - HNO_3$ exchange signal [28]. The signal of NO^t on the *trans* coordinate ON–Ru–OH_2, with a close chemical shift and considerably weaker intensity, is not detected against the background of the former signal. The NH_3^{coord} signal is observed as a shoulder of this line at -11.8 ppm. The spectrum also shows the line of NH_3^{coord} (-408 ppm) and the strong signal at -356.7 ppm (quintet with SCC = 53.4 Hz) arising from the NH_4^+ cation [29].

On the basis of the total concentration of nitrate ions in this solution (~16 mol/L), the intensity ratio of the signals in the ^{14}N NMR spectrum, and material balance equations, we estimated the concentrations of nitrogen-containing species and their degrees of conversion in the chemical reactions of the process. The average composition of the ruthenium complex species contained in the mother liquor is close to $[RuNO(NH_3)(H_2O)_2(NO_3)_2]^+$. About two-thirds of the total ammonia removed from the ruthenium inner sphere remains in solution as the NH_4^+ cation, whereas one-third of ammonia is oxidized by concentrated nitric acid and removed from the solution.

On the basis of our study of the compositions of solutions and crystalline and gaseous products formed by the interaction of *trans*-$[RuNO(NH_3)_4(OH)]Cl_2$ with nitric acid under different conditions (varying the HNO_3 and complex concentrations, reaction mixture temperature, and heating duration), we can suggest the following scheme of the processes that occur in the system:

$$\begin{gathered}[RuNO(NH_3)_4(OH)]^{2+} + H^+ \\ = [RuNO(NH_3)_4(H_2O)]^{3+},\end{gathered} \tag{1}$$

$$\begin{gathered}[RuNO(NH_3)_4(H_2O)]^{3+} + 3NO_3^- \\ = [RuNO(NH_3)_4(H_2O)](NO_3)_3\downarrow,\end{gathered} \tag{2}$$

$$3Cl^- + 4H^+ + NO_3^- = NOCl\uparrow + Cl_2\uparrow + 2H_2O, \tag{3}$$

$$\begin{gathered}[RuNO(NH_3)_4(H_2O)]^{3+} + NO_3^- \\ = [RuNO(NH_3)_4(NO_3)]^{2+} + H_2O,\end{gathered} \tag{4}$$

$$\begin{gathered}[RuNO(NH_3)_4(NO_3)]^{2+} + 2NO_3^- \\ = [RuNO(NH_3)_4(NO_3)](NO_3)_2\downarrow,\end{gathered} \tag{5}$$

$$\begin{gathered}[RuNO(NH_3)_4(NO_3)]^{2+} + H^+ + H_2O \\ = [RuNO(NH_3)_3(H_2O)(NO_3)]^{2+} + NH_4^+,\end{gathered} \tag{6}$$

$$NH_4^+ + NO_3^- = N_2O\uparrow + 2H_2O, \tag{7}$$

$$\begin{gathered}[RuNO(NH_3)_3(H_2O)(NO_3)]^{2+} + NO_3^- \\ = [RuNO(NH_3)_3(NO_3)_2]^+ + H_2O,\end{gathered} \tag{8}$$

$$\begin{gathered}[RuNO(NH_3)_3(NO_3)_2]^+ + H^+ + H_2O \\ = [RuNO(NH_3)_2(H_2O)(NO_3)_2]^+ + NH_4^+,\end{gathered} \tag{9}$$

$$\begin{gathered}[RuNO(NH_3)_2(H_2O)(NO_3)_2]^+ + NO_3^- \\ = [RuNO(NH_3)_2(NO_3)_3]\downarrow + H_2O,\end{gathered} \tag{10}$$

$$\begin{gathered}[RuNO(NH_3)_2(H_2O)(NO_3)_2]^+ + H^+ + H_2O \\ = [RuNO(NH_3)(H_2O)_2(NO_3)_2]^+ + NH_4^+.\end{gathered} \tag{11}$$

The processes involve the protonation of the coordinated hydroxo group (1), formation of crystalline phase **I** (2), oxidation of the outer-sphere chloride ion resulting in formation and release of gaseous NOCl and Cl_2 (3), substitution of a nitrate ion for the water molecule in the inner sphere of nitrosoruthenium ((4), (8), (10)), formation of poorly soluble crystalline phases **II** (5) and **III** (10), protonation of the coordinated ammonia molecules and their replacement by water molecules ((6), (9), (11)), and comproportionation of NH_4^+ and NO_3^- (7).

At room temperature, reactions (1) and (2) occur at any concentration of nitric acid to give complex **I**. When developing the synthesis method for this complex, we preferred a homogeneous process since the use of $HNO_{3(conc)}$ entails the problem of purification of the product from a concentrated acid.

When the complex is refluxed in 8 M HNO_3, reactions (1)–(5) occur in the system, and a mixture of complexes **I** and **II** is deposited.

An increase in the nitric acid concentration leads to partial destruction of the tetraammine complex by reaction (6)–(10), and the reaction products are mixtures of poorly soluble complexes **II** and **III**. The oxidation of ammonia molecules is preceded by their passing into the solution volume at high acidity and temperature ((6), (9)). The resulting NH_4^+ cation is oxidized by reaction (7).

The use of concentrated nitric acid makes it possible to separate the reactions of formation of complexes **II** and **III** in time and isolate them as individual compounds. The insufficiently high yield of complex **III** is caused by the occurrence of reaction (1).

Attempts to stop the process at the stage of formation of triamminenitrosoruthenium complexes (reactions (6) and (8)) by varying the HNO_3 concentration and heating duration were unsuccessful. In these runs, the products are mixtures of complexes **II** and **III**. The treatment of mother liquors with hydrochloric acid on heating also leads to mixtures of tetra- and diamminenitrosoruthenium complexes *trans*-$[RuNO(NH_3)_4Cl]Cl_2$ and *fac*-$[RuNO(NH_3)_2Cl_3]$. This is most likely caused by the fact that the rate of reaction (9) is considerably higher than the rate of reaction (6).

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