ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2007, Vol. 52, No. 1, pp. 62–70. © Pleiades Publishing, Inc., 2007.
Original Russian Text © M.A. Il'in, V.A. Emel'yanov, I.A. Baidina, N.I. Alferova, I.V. Korol'kov, 2007, published in Zhurnal Neorganicheskoi Khimii, 2007, Vol. 52, No. 1, pp. 67–75.

COORDINATION COMPOUNDS

Study of Nitrosation of Hexaammineruthenium(II): Crystal Structure of *trans*-$[RuNO(NH_3)_4Cl]Cl_2$

M. A. Il'in, V. A. Emel'yanov, I. A. Baidina, N. I. Alferova, and I. V. Korol'kov

Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
e–mail: maxilyin@ngs.ru

Received December 23, 2005

Abstract—The nitrosation of $[Ru(NH_3)_6]^{2+}$ in hydrochloric acid and alkaline ammonia media has been studied; the patterns of interconversion of ruthenium complexes in reaction solutions have been proposed. In both cases, nitrogen(II) oxide acts as the nitrosation agent. The procedure for the synthesis of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ (yield 75–80%), the main nitrosation product of $[Ru(NH_3)_6]^{2+}$, has been optimized. Thermolysis of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ in a helium atmosphere has been studied; the intermediates have been identified. One of these products is polyamidodichloronitrosoruthenium(II) whose subsequent decomposition gives an equimolar mixture of ruthenium metal and dioxide. The structure of *trans*-$[RuNO(NH_3)_4Cl]Cl_2$, formed in the second stage of thermolysis and as a by-product in the nitrosation of $[Ru(NH_3)_6]Cl_2$, has been determined by X-ray diffraction.

DOI: 10.1134/S0036023607010123

The increased attention of researchers to nitroso compounds of transition metals exhibited in recent years is due to two discoveries made in the 1990s. The first one is participation of nitrogen(II) oxide and compounds containing it in physiological processes, and the second one is the ability of nitroso complexes to undergo a reversible photoinduced transition to a long-lived metastable state. Of particular interest are ruthenium ammine nitroso complexes as the most stable and the least toxic. These compounds are successfully used as biologically active agents [1, 2], to study photochemical transformations [3–5], and in the synthesis of polyfunctional photomagnetic materials [6].

The ruthenium nitroso pentaammine complex [Ru(NO)(NH $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ is characterized by one of the highest temperatures of thermal deactivation of the photoinduced metastable state (260 K) [3, 4]. The synthesis of this compound is faced with certain difficulties. Not more than four ammonia molecules can be introduced into the inner sphere of ruthenium in the reactions of ruthenium nitroso chlorides with a solution of ammonia [7] or with liquid ammonia [8]. The major product formed in these reactions is *trans*-$[Ru(NO)(NH_3)_4OH]Cl_2$. The methods for the synthesis of pentaammine(nitroso)ruthenium known to date are reduced to nitrosation of ruthenium(III) pentaammines [9, 10] or hexaammine [11]. The starting ammine complexes are prepared in several stages from industrial ruthenium trichloride; as a rule, the first stage yields hexaammineruthenium(II) dichloride [10, 12, 13]. The synthesis of $[Ru(NH_3)_5Cl]Cl_2$ directly from $RuCl_3$, which is the most readily available commercial chemical, has been described [14], but the yield of the complex was only 47%. It has been stated [11, 15, 16] that the required ruthenium nitroso pentaammine complex can be obtained by nitrosation of ruthenium(II) hexaammine to reduce the number of required operations; however, no detailed procedures or product yields were reported.

The purpose of this work is to study nitrosation of $[Ru(NH_3)_6]Cl_2$ to optimize the method for the synthesis of the ruthenium(II) pentaammine nitroso complex and to investigate the physicochemical properties of the products formed in this reaction.

EXPERIMENTAL

A solution of $RuCl_3$ in HCl prepared from high-purity grade $RuCl_3$ (46.51% Ru) as described previously [17] was used. Hexaammineruthenium(II) dichloride $[Ru(NH_3)_6]Cl_2$ was obtained in 70—80% yield by a procedure described previously [15]. The other reagents were commercial chemicals, of at least chemically pure grade (Russian state standard).

The IR spectra of polycrystalline samples as mineral and fluorinated oil mulls or KBr pellets were recorded on Specord IR-75 and Scimitar FTS 2000 spectrophotometers in the range 3800–400 cm^{-1}.

Thermogravimetric analysis was carried out on a Q-1000 instrument in a helium atmosphere. A ~150-mg sample of the compound was placed in a quartz crucible; the heating rate was 8 K/min.

X-ray diffraction analysis of ground crystals was carried out on a DRON UM1 diffractometer (R = 192 mm, CuK_α radiation, Ni filter, scintillation detector with amplitude discrimination). The samples were applied as thin layers on the smooth side of a standard quartz cell.

The unit cell parameters and the experimental intensities for solution of the crystal structure of *trans*-$[RuNO(NH_3)_4Cl]Cl_2$ were measured at room temperature on a CAD4 four-circle automated diffractometer (MoK_α radiation, graphite monochromator). The structure was solved by the standard heavy-atom method and refined in the anisotropic–isotropic (for H) approximation; hydrogen atoms were specified geometrically. All calculations were carried out by the SHELX97 program package [18].

Nitrosation in acidic medium. The nitrosation procedure was as follows. A calculated amount of sodium nitrite (Table 1) was added to $[Ru(NH_3)_6]Cl_2$ (~0.6 g, ~2×10^{-3} mol), and the resulting mixture was dissolved in distilled water. Then the required volume of 1 M HCl was added dropwise to the magnetically stirred solution. The overall volume of the reaction mixture was 15–17 mL. Within 5–10 min after the addition of HCl, the reaction mixture was concentrated on a water bath to the beginning of crystallization (2–3 mL) and cooled. The product was collected on a glass filter and washed with a water–ethanol mixture (~1 : 1) and acetone.

The resulting product was dissolved in a minimum amount of 1 M HCl (~10 mL). The insoluble fraction (fraction 1, $[Ru(NH_3)_5Cl]Cl_2$ + $[Ru(NO)(NH_3)_4Cl]Cl_2$) was collected on a glass filter, washed with ethanol and acetone, dried in air, and weighed.

A double volume of ethanol was added to the mother liquor and the reprecipitated apricot-colored complex (fraction 2) was separated on a glass filter. The precipitate was washed with ethanol and acetone, dried in air, and weighed.

Nitrosation in an alkaline ammonia medium. A solution of $[Ru(NH_3)_6]Cl_2$ in ammonia was prepared by a known procedure [15] by the reaction of $RuCl_3$ (~4×10^{-3} mol) with aqueous NH_3 and Zn metal in the presence of NH_4Cl. The solution was filtered, conc. NH_3 (~20 mL) was added (to pH 10.5–11), and ammonium peroxodisulfate (~4.6 g, 2×10^{-2} mol) was added in small portions under magnetic stirring. During the addition, the solution warmed up and changed color from greenish-yellow to red-orange. At the end of the reaction, acrid odor of nitrogen oxides was clearly perceived together with the strong smell of ammonia. The resulting orange precipitate of $[Ru(NO)(NH_3)_5](SO_4)(S_2O_8)_{0.5}$ was collected on a filter and washed with 1–2 mL of conc. NH_3 and 1–2 mL of H_2O.

The minor amount of ruthenium left in the mother liquor can be isolated as the *trans*-tetrammine(chloro)nitrosoruthenium dichloride $[Ru(NO)(NH_3)_4Cl]Cl_2$. This was done by adding conc. HCl (~10 mL) followed by heating for 2–3 h. The yellow-orange precipitate was filtered off and washed with a water–ethanol mixture (~1 : 1) and acetone. The yield of $[Ru(NO)(NH_3)_4Cl]Cl_2$ was up to ~20%.

Table 1. Effect of sodium nitrite concentration and hydrochloric acid on the ruthenium recovery to the solid phase (c_{Ru} = 1.7×10^{-3} to 2.1×10^{-3} mol/l)

Entry	The molar ratio Ru : $NaNO_2$: HCl	Yield, %		
		1st fraction	2nd fraction	total
1	1.0 : 1.0 : 3.0	13.4	77.3	90.7
2	1.0 : 1.0 : 4.0	14.1	74.0	88.1
3	1.0 : 1.0 : 5.0	22.2	74.6	96.8
4	1.0 : 1.3 : 3.9	6.6	73.6	80.2
5	1.0 : 1.3 : 5.2	6.4	78.4	84.8
6	1.0 : 1.3 : 6.5	6.1	80.6	86.7
7	1.0 : 1.3 : 9.75	8.1	79.5	87.6
8	1.0 : 1.5 : 4.5	6.1	77.0	83.1
9	1.0 : 1.5 : 6.0	6.0	79.5	85.5
10	1.0 : 1.5 : 7.5	5.7	81.9	87.6
11*	1.0 : 1.5 : 4.5	17.9	68.9	86.8
12*	1.0 : 3.0 : 4.5	44.6	39.8	84.4

* The experiments were carried out at elevated temperature (~95°C).

The complex $[Ru(NO)(NH_3)_5](SO_4)(S_2O_8)_{0.5}$ was treated with conc. HCl (~10 mL) with heating on a water bath for 20–30 min. The reaction mixture was cooled to ~5°C and the resulting precipitate of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ was collected on a filter and washed with a water–ethanol mixture (~1 : 1) and acetone.

The complex $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ was purified by reprecipitation from a saturated aqueous solution by conc. HCl. The yield of purified $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ was ~75% based on $RuCl_3$.

RESULTS AND DISCUSSION

Nitrosation in acidic medium. The introduction of a nitroso group by means of $NaNO_2$ in HCl is widely used to prepare ruthenium nitroso chloro complexes in high yields. The key mechanistic features of this process were described in detail [17]. The results of hexaammineruthenium(II) nitrosation experiments, which we carried out at different reactant ratios, are summarized in Table 1. During nitrosation, some ruthenium separates as a poorly soluble yellow precipitate that remains on the filter after reprecipitation (fraction 1). According to IR spectroscopy and powder

X-ray diffraction, fraction 1 is either a mixture of $[Ru(NH_3)_5Cl]Cl_2$ (major component) and *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ (when nitrosation is carried out at room temperature) or only *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ (when nitrosation is carried out at elevated temperature).

The data of Table 1 demonstrate that, even at a $[Ru(NH_3)_6]Cl_2 : NaNO_2 : HCl$ ratio of 1 : 1 : 3 (entry 1), the yield of pure pentaammine(nitroso)ruthenium (fraction 2) is more than 75%. An increase in the $NaNO_2$ or HCl concentration hardly affects the yield of fraction 2 and slightly increases the proportion of *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ in fraction 1. A temperature rise results in almost quantitative nitrosation of ruthenium but markedly decreases the yield of the target complex (entries 11, 12). Our experiments substantiate the conclusion that the formation of the pentaammine nitroso complex under these conditions can basically be described by the following equation:

$$[Ru(NH_3)_6]Cl_2 + NaNO_2 + 3HCl \longrightarrow [RuNO(NH_3)_5]Cl_3 \cdot H_2O + NaCl + NH_4Cl,$$

however, it is complicated by a number of side reactions that decrease the yield of this complex.

On the basis of analysis of the data on nitrosation of ruthenium chloro complexes [17] resorting to the published data [11, 19, 20] and relying on our results (Table 1), one can propose the following set of processes taking place in HCl solutions containing the $[Ru(NH_3)_6]^{2+}$ complex cation and the nitrite ion:

$$H^+ + NO_2^- \rightleftharpoons HNO_2, \quad (1)$$

$$[Ru(NH_3)_6]^{2+} + HNO_2 + H^+ \longrightarrow [Ru(NH_3)_6]^{3+} + NO + H_2O, \quad (2)$$

$$3HNO_2 \xrightarrow{\sim 90^\circ C} HNO_3 + 2NO + H_2O, \quad (3)$$

$$NH_4^+ + HNO_2 \xrightarrow{\sim 90^\circ C} N_2\uparrow + 2H_2O + H^+, \quad (4)$$

$$[Ru(NH_3)_6]^{2+} + H_2O + H^+ \longrightarrow [Ru(NH_3)_5(H_2O)]^{2+} + NH_4^+, \quad (5)$$

$$[Ru(NH_3)_5(H_2O)]^{2+} + HNO_2 + H^+ \longrightarrow [Ru(NH_3)_5(H_2O)]^{3+} + NO + H_2O, \quad (6)$$

$$[Ru(NH_3)_6]^{3+} + NO + H^+ \longrightarrow [Ru(NO)(NH_3)_5]^{3+} + NH_4^+, \quad (7)$$

$$[Ru(NH_3)_5(H_2O)]^{3+} + NO \longrightarrow [Ru(NO)(NH_3)_5]^{3+} + H_2O, \quad (8)$$

$$[Ru(NH_3)_5(H_2O)]^{3+} + Cl^- \rightleftharpoons [Ru(NH_3)_5Cl]^{2+} + H_2O, \quad (9)$$

$$[Ru(NH_3)_5Cl]^{2+} + 2Cl^- \longrightarrow [Ru(NH_3)_5Cl]Cl_2\downarrow, \quad (10)$$

$$[Ru(NO)(NH_3)_5]^{3+} + HNO_2 \longrightarrow trans\text{-}[Ru(NO)(NH_3)_5]^{3+} + N_2\uparrow + H_2O, \quad (11)$$

$$trans\text{-}[Ru(NO)(NH_3)_4(H_2O)]^{3+} + Cl^- \rightleftharpoons trans\text{-}[Ru(NO)(NH_3)_4Cl]^{2+} + H_2O, \quad (12)$$

$$trans\text{-}[Ru(NO)(NH_3)_4Cl]^{2+} + 2Cl^- \longrightarrow trans\text{-}[Ru(NO)(NH_3)_4Cl]Cl_2\downarrow. \quad (13)$$

In acidic medium, nitrous acid formed from the nitrite ion (reaction 1) acts as an oxidant ($HNO_2 + H^+ + \bar{e} \longrightarrow NO + H_2O$, $E^0 = 0.99$ B, [21]); redox reaction (2) is single-electron; therefore, no kinetic hindrance occurs in this reaction. The standard electrode potential for $[Ru(NH_3)_6]^{3+} + \bar{e} \longrightarrow [Ru(NH_3)_6]^{2+}$ is ~ –0.05 V at 25°C [22].

In addition, at elevated temperature (heating in a water bath) HNO_2 disproportionates (reaction (3)) to give an additional amount of NO. Nitrous acid is also consumed in comproportionation with the ammonium ion present in the solution (reaction(4)).

In acidified aqueous solutions, preactivation of the $[Ru(NH_3)_6]^{2+}$ cation (reaction (5)) ($k^{298} = (1.24 \pm 0.03) \times 10^{-3}$ L mol^{-1} s^{-1} [22]) followed by oxidation by nitrous acid ($[Ru(NH_3)_5(H_2O)]^{3+} + \bar{e} \longrightarrow [Ru(NH_3)_5(H_2O)]^{2+}$, $E^0 \sim -0.07$ V [22]) may occur.

The mechanism of nitrosation of the $[Ru(NH_3)_6]^{3+}$ ion with nitrogen(II) oxide in an acidified aqueous solution has been studied [11]. It was found that the reaction is bimolecular, does not require preactivation of the ammine complex, and gives the pentaammine(nitroso)ruthenium cation $[Ru(NO)(NH_3)_5]^{3+}$ (reaction(7)). The same complex may form upon the displacement of coordinated water molecules in the aqua complex $[Ru(NH_3)_5(H_2O)]^{3+}$ by nitrogen(II) oxide (reaction (8)), as in the case of Ru(III) aqua chloro complexes [17].

The formation of fraction 1 components is due to the following reactions. In hydrochloric acid solutions containing $[Ru(NH_3)_5(H_2O)]^{3+}$, the coordinated water molecules are replaced by chloride ions (reaction 9, $K \sim$ 70–240 L/mol [22, 23]), the resulting $[Ru(NH_3)_5Cl]^{2+}$ cation being precipitated as poorly soluble $[Ru(NH_3)_5Cl]Cl_2$ (10). The *trans*-tetraammine(chloro)nitrosoruthenium cation is formed upon oxidation of the coordinated ammonia molecules present in the $[Ru(NO)(NH_3)_5]^{3+}$ cation by nitrous acid (reaction 11) with subsequent displacement of the coordinated water molecules by chloride ions (reaction 12, $K \sim$ 170 L/mol) [24]. Its chloride salt is also poorly soluble [19], which ensures a shift of equilibrium (12) and almost quantitative precipitation of *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ (13).

A temperature rise entails a decrease in the yield of the target $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ (Table 1, entry 11), and only *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ is formed as the by-product, its yield increasing to ~45% upon an increase in the nitrite ion concentration (Table 1, entry 12). Thus, at room temperature fraction 1 is formed via processes (9), (10) (mainly), and (11)–(13), while temperature rise results in quantitative nitrosation and in a noticeable relative increase in the rates of processes (11) and (12).

By varying the acidity, the nitrite ion concentration, and nitrosation temperature, we selected conditions for the preparation of the pentammine nitroso complex $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ (fraction 2) in the highest yield (82%, Table 1, entry 10). Nitrosation of $[Ru(NH_3)_6]Cl_2$ by sodium nitrite in acidic medium should be carried out at room temperature and at the molar ratio Ru : $NaNO_2$: HCl = 1.0 : 1.5 : 7.5.

Nitrosation in an alkaline ammonia medium. When $[Ru(NH_3)_6]Cl_2$ is prepared by the reported procedure [15], up to 30% of ruthenium added as the trichloride remains in the reaction solution due to the solubility of the hexaammine complex. In order to increase the yield of the target complex $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ based on commercial ruthenium trichloride, we decided to perform the nitrosation of ruthenium ammine complexes in alkaline ammonia medium without intermediate isolation of solid hexaammine.

It was found experimentally that nitrosation of ammonium peroxodisulfate takes place within pH 10.5–11 in the presence of aqueous ammonia. The reaction carried out at pH 8–10 or above 11 yields black colloid solutions, while the yield of the target complex decreases appreciably, in some cases, down to 0%.

The results of nitrosation of $[Ru(NH_3)_6]^{2+}$ with ammonium peroxodisulfate in the absence of free ammonia (pH was brought to 10.5–11 by adding aqueous NaOH) were also unsatisfactory.

The experimental data and the presence of nitrogen oxides in ammonia solutions detected by smell suggest the following process scheme.

The peroxodisulfate ion oxidizes the hexaammineruthenium(II) cation:

$$2[Ru(NH_3)_6]^{2+} + S_2O_8^{2-} \longrightarrow 2[Ru(NH_3)_6]^{3+} + 2SO_4^{2-}.$$

In the presence of ruthenium ammine complexes, ammonia molecules are oxidized in the reaction solution at pH 10.5–11 to nitrogen(II) oxide [9]:

$$12NH_3 + 2H_2O + 5S_2O_8^{2-} \xrightarrow{[Ru(NH_3)_x]} 2NO + 10SO_4^{2-} + 10NH_4^+.$$

The unsuccessful nitrosation experiments without addition of aqueous ammonia confirm the absence of direct oxidation of coordinated ammonia molecules to give nitroso complexes.

The NO molecules formed react with hexaammineruthenium(III) cation

$$[Ru(NH_3)_6]^{3+} + NO \longrightarrow [Ru(NO)(NH_3)_5]^{3+} + NH_3.$$

The resulting $[Ru(NO)(NH_3)_5]^{3+}$ is eliminated from the reaction solution as a poorly soluble double salt [9]:

$$[Ru(NO)(NH_3)_5]^{3+} + 1/2\ S_2O_8^{2-} + SO_4^{2-} \longrightarrow [Ru(NO)(NH_3)_5](SO_4)(S_2O_8)_{0.5}\downarrow.$$

On treatment with concentrated hydrochloric acid, the peroxodisulfate ion is reduced

$$[Ru(NO)(NH_3)_5](SO_4)(S_2O_8)_{0.5} + 4HCl + H_2O \longrightarrow [Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O + 1/2Cl_2\uparrow + 2H_2SO_4.$$

According to IR spectroscopy, the precipitate obtained after treatment with HCl contains, together with pentaamminenitrosoruthenium, a minor amount of sulfate ions and *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$.

Complexes of the nitrosotetraammine series result from the following side processes. In alkaline medium, the coordinated NH_3 molecules in the $[Ru(NO)(NH_3)_5]^{3+}$ cation are replaced by hydroxo groups [9, 22]:

$$[Ru(NO)(NH_3)_5]^{3+} + OH^- \longrightarrow [Ru(NO)(NH_3)_4OH]^{2+} + NH_3. \quad (14)$$

On heating of $[Ru(NO)(NH_3)_4OH]^{2+}$ with concentrated HCl, the coordinated hydroxy group is protonated ($K \sim 10^3$ L/mol [25]):

$$[Ru(NO)(NH_3)_4OH]^{2+} + H^+ \rightleftharpoons [Ru(NO)(NH_3)_4(H_2O)]^{3+},$$

the coordinated water molecule in the aqua complex $[Ru(NO)(NH_3)_4(H_2O)]^{3+}$ is replaced by the chloride ion, and poorly soluble $[Ru(NO)(NH_3)_4Cl]Cl_2$ precipitates (reactions (12) and (13)).

The main nitrosation product was purified by reprecipitation by concentrated HCl. The complex obtained in 75% yield was pure $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$.

Physicochemical studies of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$. IR spectra of the isolated $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ samples coincided in band positions and intensities with the spectrum reported in the literature [26]; the X-ray diffraction patterns were completely indexed based on the reported data from a single crystal study [27].

The thermolysis of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ was studied in a helium atmosphere. The thermogram (Fig. 1) is generally in good agreement with that reported previously [28] for thermolysis of this compound in air. The first two endotherms are observed in a helium atmosphere at somewhat lower temperatures than in air (by 20°C and 15°C, respectively) and also correspond to the removal of a water molecule of crystallization

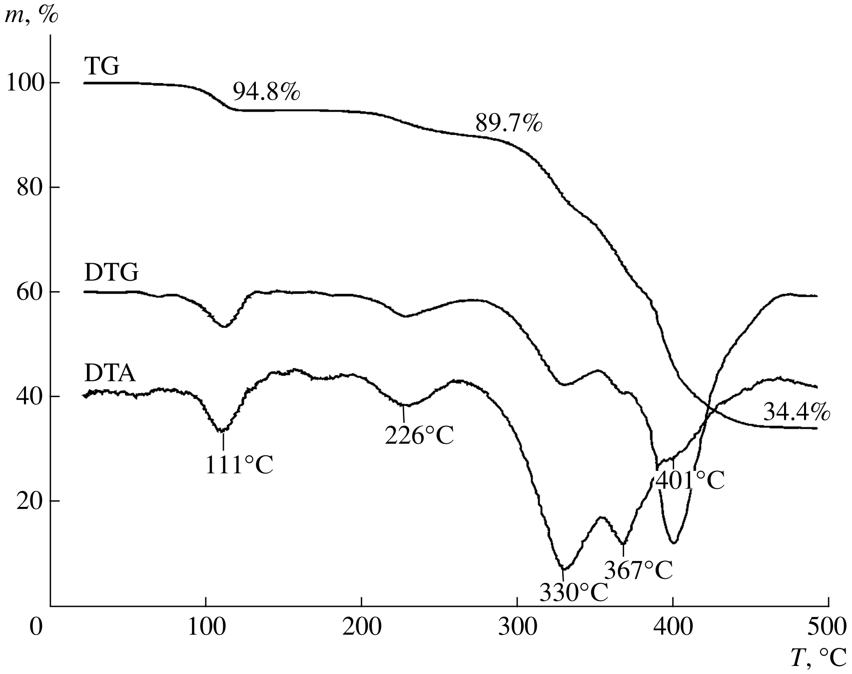

Fig. 1. Thermoanalytical curves of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$.

and one ammonia molecule (calculated, 5.3 + 5.0%; found from the weight loss curve, 5.2 + 5.1%). We studied the intermediates obtained by heating of the initial compound to 130 (**1**) and 270°C (**2**) and subsequent cooling to room temperature under helium. The removal of the water molecule is reversible; on storage in air, the anhydrous product is again converted gradually into the crystal hydrate. This is confirmed by X-ray diffraction and IR spectroscopy; the stretching (3420 cm^{-1}) and bending (1625 cm^{-1}) bands for the water molecule of crystallization, which are absent from the IR spectrum of compound **1**, appear again when the compound is stored in air.

The positions and the intensities of the IR bands of product **2** fully coincide with reported data [26] for *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$. The X-ray diffraction pattern of the sample recrystallized from 0.1 M HCl coincides with that of *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ we obtained in nitrosation experiments.

Further destruction of the complex occurs as three poorly resolved stages with endothermic peaks at 330, 367, and 401°C (in air, these temperatures are 310, 365, and 425°C [28, 29]). The first one, according to published data [29], corresponds to the loss of two ammonia molecules, while the last one was reported [28] to reflect complete destruction of the complex (the destruction products were not identified in the study cited). We studied the products obtained by heating of the complex to 325.5 (**3**), 369.5 (**4**), and 500°C (**5**) followed by slow cooling to room temperature in a helium atmosphere. The X-ray diffraction pattern and the IR spectrum of product **3** mainly correspond to those reported previously [30] for *mer*-$[Ru(NO)(NH_3)_2Cl_3]$ obtained upon thermolysis of $(NH_4)_2[RuNOCl_5]$. The loss of mass with respect to the initial $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ was 20.5% (calculated for $[Ru(NO)(NH_3)_2Cl_3]$, 20.3%).

The next stage is assumed, most reasonably, to involve elimination of two more ammonia molecules to give a rather stable ruthenium nitroso trichloride. According to published data [8], this is formed from the monohydrate at 360°C and decomposes at 440°C. However, apart from the bands for the coordinated nitroso group ($\nu(NO) = 1889$ cm^{-1}, $\nu(Ru–NO) = 610$ cm^{-1}), the IR spectrum of product **4** clearly contains bands that are usually assigned to coordinated ammonia molecules ($\nu(NH_3)$ = 3287 and 3178 cm^{-1}; $\delta(NH_3)$ = 1613 and 1292 cm^{-1}, $\rho(NH_3)$ = 795 cm^{-1}) and strong bands at 3233, 1508, 1068, and 670 cm^{-1}. The theoretical weight of the residue calculated for $RuNOCl_3$ is 69.7% of the initial complex; however, the weight of product **4** was only 63.1%. This means that the fragment eliminated at ~370°C is heavier than this was suggested. The calculation taking into account the retention of the ruthenium charge shows that this fragment is NH_4Cl (the calculated weight of the residue is 64%). Thus, the composition of product **4** is best described by the molecular formula $[Ru(NO)(NH_2)Cl_2]$. Due to the requirement of retaining the coordination number of six, which is most typical of ruthenium nitroso complexes, polymeric structure with two bridging ligands can be suggested

Table 2. Crystal data and X-ray experiment details for *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$

Parameter	Value
Temperature	293(2) K
Wavelength	0.71073 Å
Space group	*P*2(1)
Unit cell parameters	$a = 6.7270(13)$ Å $\alpha = 90°$
	$b = 10.444(2)$ Å $\beta = 100.49(3)°$
	$c = 6.7394(13)$ Å $\gamma = 90°$
volume	465.59(16) Å^3
Z	2
Density (calcd)	2.180 g/cm^3
Absorption coefficient	2.497 mm^{-1}
F(000)	300
θ range	3.08°–24.98°
Range of *h*, *k*, *l*	$-6 \le h \le 7$, $-12 \le k \le 12$, $-6 \le l \le 7$
The number of measured reflections	1732
The number of independent reflections	1624 [*R*(int) = 0.0821]
The data collection completeness for θ = 24.98°	99.9 %
Refinement method	full-matrix least-squares on F^2
	1624/1/95
S on F^2	0.981
$R\ [I > 2\sigma(I)]$	$R1 = 0.0569$, $wR2 = 0.1430$
R (all data)	$R1 = 0.0747$, $wR2 = 0.1565$
Absolute structure parameter	–0.1(2)
Max. and min. of the residual electron density	1.402 and –0.708 e/Å^3

for this compound. According to published data [31], the bridging amido group in the polymeric mercury amido chloride is responsible of bands at 3200, 3175 cm^{-1} ($\nu(NH_2)$), 1530 cm^{-1} ($\delta(NH_2)$), and 1022, 688 cm^{-1} ($\rho(NH_2)$), which is in satisfactory agreement with the IR spectrum of complex **4**. The following structure appears to be the most likely: $[Ru(NO)Cl(\mu\text{-}NH_2)(\mu\text{-}Cl)]_n$.

Complete destruction of the complex with removal of the nitroso group starts at 375°C (the peak is at 401°C). According to X-ray diffraction, product **5** is a mixture of ruthenium metal and dioxide. The weight of the residue is 34.4%, which exactly coincides with the value calculated for the equimolar mixture $RuO_2 + Ru$ (34.4%). Note that ruthenium nitroso trichloride decomposes under inert atmosphere at 440°C to ruthenium dioxide and trichloride [8]. Decomposition of ruthenium trichloride into elements, i.e. the reduction of Ru(III) with the chloride ion, occurs in the temperature range of 655–840°C [32]. In all probability, under our experimental conditions ($T \sim 400°C$), chlorine is removed as hydrogen chloride, and the last stage of thermolysis can be described by the equation

$$2[Ru(NO)Cl(\mu\text{-}NH_2)(\mu\text{-}Cl)]_n \longrightarrow nRu + nRuO_2 + 2nN_2 + 4nHCl.$$

The chemistry of this stage is elimination of HCl from polyamidodichloronitrosoruthenium(II) and redox disproportionation of Ru^{2+} to Ru and Ru^{4+} and comproportionation of N^{3+} and N^{3-} to give N_2.

Crystal structure of *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$. The structure of the tetraammine complex formed in the second stage of thermolysis $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ and as the main impurity during nitrosation of $[Ru(NH_3)_6]Cl_2$ was determined by X-ray diffraction. The crystal data and X-ray diffraction experiment details are summarized in Table 2, and selected interatomic distances and bond angles in the complex cation *trans*-$[Ru(NO)(NH_3)_4Cl]^{2+}$ are in Table 3. The structure of the complex cation with atom numbering and ellipsoids of thermal vibrations is shown in Fig. 2.

The central Ru atom has a somewhat distorted octahedral environment formed by the chlorine atom and

Table 3. Interatomic distances and angles in *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$

Distance	*d*, Å	Angle	ω, deg	Angle	ω, deg
Ru–N	1.799(12)	NRuN(1)	95.7(17)	N(2)RuN(4)	86.6(10)
Ru–N(1)	2.15(2)	NRuN(2)	91.1(5)	N(3)RuN(4)	89.2(10)
Ru–N(2)	2.112(9)	NRuN(3)	92.3(5)	NRuCl(1)	177.9(15)
Ru–N(3)	2.093(9)	NRuN(4)	88.8(18)	N(1)RuCl(1)	86.4(6)
Ru–N(4)	2.039(16)	N(1)RuN(2)	92.9(9)	N(2)RuCl(1)	88.6(3)
Ru–Cl(1)	2.376(3)	N(1)RuN(3)	91.1(10)	N(3)RuCl(1)	87.9(3)
N–O	1.026(12)	N(1)RuN(4)	175.5(4)	N(4)RuCl(1)	89.1(8)
		N(2)RuN(3)	174.5(9)	ONRu	176(6)

Table 4. Atomic coordinates and isotropic displacement parameters (Å^2) for *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Ru	0.26585(12)	0.2203	0.76603(12)	0.0315(3)	O	–0.0616(13)	0.223(4)	0.4378(14)	0.051(2)
Cl(1)	0.5417(4)	0.2205(15)	1.0421(4)	0.0470(7)	N(1)	0.280(3)	0.015(2)	0.784(2)	0.035(5)
Cl(2)	–0.2224(17)	0.4603(7)	–0.2731(14)	0.051(3)	N(2)	0.4763(15)	0.229(3)	0.5691(15)	0.044(3)
Cl(3)	0.2264(15)	0.4605(7)	0.2794(14)	0.047(2)	N(3)	0.0724(14)	0.226(3)	0.9765(15)	0.045(3)
N	0.0579(18)	0.226(5)	0.5564(18)	0.044(4)	N(4)	0.273(4)	0.4155(15)	0.766(3)	0.051(7)

five nitrogen atoms belonging to four ammonia molecules and the nitroso group. The geometric characteristics of the Cl–Ru–NO fragment are usual for ruthenium complexes containing a coordinated chloride ion in the *trans* position to the nitroso group [33, 34]. The bond angles at the Ru atom deviate by ±5.7° from 90°. The Ru–N(NH_3) distances are in the range of 2.04–2.15 Å (average 2.098 Å), the ruthenium atom deviates from the root-mean-square equatorial plane N_4 by 0.075 Å toward the nitroso group. These values are quite consistent with published data for the known ruthenium ammine nitroso complexes [2, 27, 35–39]. The atom coordinates and isotropic parameters of atom displacements are given in Table 4.

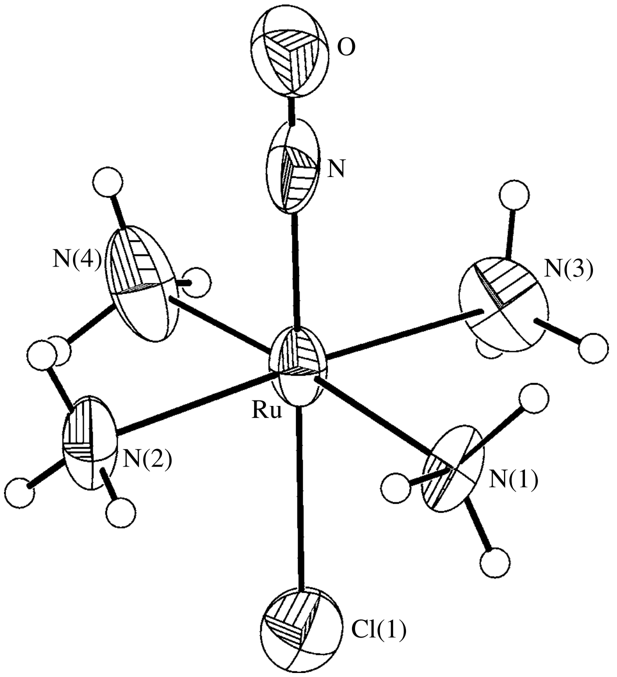

Fig. 2. Structure of the complex cation in $[Ru(NO)(NH_3)_4Cl]Cl_2$.

The structure projected along z direction is shown in Fig. 3. The unit cell contains two crystallographically independent chloride anions, which are connected to the $[Ru(NO)(NH_3)_4Cl]^{2+}$ complex cations by N–H···Cl type hydrogen bonds (N–Cl, 3.21–3.49 Å). The shortest distances between the central Ru atom and the chloride anion vary from 4.10 to 4.42 Å. The shortest Ru···Ru distance in the structure is 6.597 Å. The scheme of hydrogen bonds involving ammine groups of the complex is shown in Fig. 3 by dashed lines.

Thus, the complex $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ can be prepared in high yield by nitrosation of hexaammineruthenium(II) by both sodium nitrite in hydrochloric acid and ammonium peroxodisulfate in alkaline ammonia medium. In the former case, the highest yield is ~80% based on ruthenium(II) hexaammine, while in the latter case, this is ~75% based on the initial commercial ruthenium trichloride. Thus, the latter method should be preferred for large-scale preparation of the pentammine nitroso complex. Both processes are complicated by a number of side reactions that decrease the yield of the target product and result in its contamination by *trans*-tetrammine(chloro)nitrosoruthenium chloride, whose structure was determined by X-ray diffraction.

The thermal decomposition of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ goes through the formation of $[Ru(NO)(NH_3)_5]Cl_3$, *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$, *mer*-$[Ru(NO)(NH_3)_2Cl_3]$,

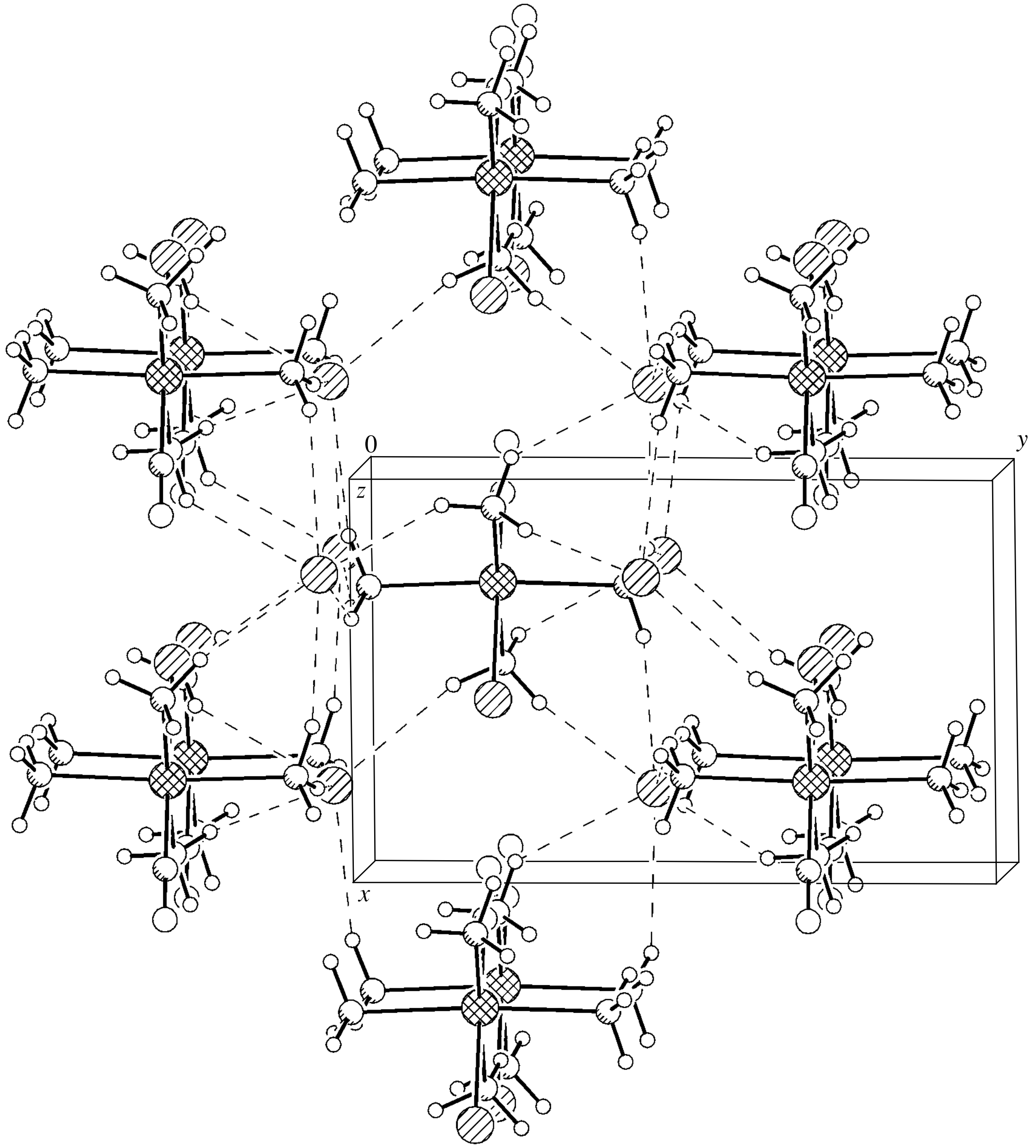

Fig. 3. Packing of the structure and hydrogen bonds for *trans*-[Ru(NO)$(NH_3)_4$Cl]Cl_2.

and [Ru(NO)Cl(μ-NH_2)(μ-Cl)]$_n$, and results in an equimolar mixture of ruthenium metal and dioxide.

REFERENCES

1. M. J. Clarke, Coord. Chem. Rev. **232**, 69 (2002).
2. E. Tfouni and M. Krieger, et al., Coord. Chem. Rev. **236**, 57 (2003).
3. P. Coppens, D. V. Fomitchev, M. D. Carducci, and K. Culp, J. Chem. Soc., Dalton Trans., No. 6, 865 (1998).
4. D. V. Fomitchev, I. Novozhilova, and P. Coppens, Tetrahedron **56**, 6813 (2000).
5. D. Schaniel, T. Woike, B. Delley, et al., Phys. Chem. Chem. Phys. **7** (6), 1164 (2005).
6. L. A. Kusch, L. S. Plotnikova, Yu. N. Shvachko, et al., J. Phys. IV France **114**, 459 (2004).
7. N. M. Sinitsyn, G. G. Novitskii, I. A. Khartonik, et al., Zh. Neorg. Khim. **27** (8), 2042 (1982).
8. M. B. Fairy and R. J. Irving, J. Am. Chem. Soc. **18** (5), 475 (1966).
9. K. Gleu and I. Buddecker, Z. Anorg. Allg. Chem. **268** (4), 202 (1952).
10. F. Bottomley, J. Chem. Soc. Dalton **19**, 2145 (1972).
11. J. N. Armor, H. A. Scheidegger, and H. Taube, J. Am. Chem. Soc. **90** (21), 5928 (1968).
12. L. H. Vogt, J. L. Katz, S. E. Wiberley, et al., Inorg. Chem. **4** (8), 1157 (1965).

13. A. D. Allen, F. Bottomley, R. O. Harris, et al., J. Am. Chem. Soc. **89** (25), 5595 (1967).
14. A. D. Allen and C. V. Senoff, Can. J. Chem. **45** (12), 1337 (1967).
15. F. M. Lever and A. R. Powell, J. Chem. Soc. A **9** (10), 1477 (1969).
16. N. M. Sinitsyn and O. E. Zvyagintsev, Zh. Neorg. Khim. **10** (11), 2571 (1965).
17. V. A. Emel'yanov, S. P. Khranenko, and A. V. Belyaev, Zh. Neorg. Khim. **46** (3), 404 (2001) [Russ. J. Inorg. Chem. **46** (3), 346 (2001)].
18. G. M. Sheldrick, *SHELX97, Release 97-1* (Univ. of Göttingen, Göttingen, 1997).
19. A. F. Schreiner, S. W. Lin, P. J. Hauser, et al., Inorg. Chem. **11** (4), 880 (1972).
20. S. Pell and J. N. Armor, Inorg. Chem. **12** (4), 873 (1973).
21. Yu. Yu. Lur'e, *Handbook on Analytical Chemistry* (Khimiya, Moscow, 1967) [in Russian].
22. E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium* (Elsevier, Amsterdam, 1984).
23. J. F. Endicott and H. Taube, Inorg. Chem. **4** (4), 437 (1965).
24. N. M. Sinitsyn and V. V. Borisov, Zh. Neorg. Khim. **19** (6), 1688 (1974).
25. C. W. B. Bezerra, S. C. Da Silva, M. T. P. Gambardella, et al., Inorg. Chem. **38** (25), 5660 (1999).
26. E. E. Mercer, W. A. McAlister, and J. R. Durig, Inorg. Chem. **5** (11) (1966).
27. F. Bottomley, J. Chem. Soc. Dalton Trans., No. 15, 1600 (1974).
28. N. M. Sinitsyn and O. E. Zvyagintsev, Dokl. Akad. Nauk SSSR **145** (1), 109 (1962).
29. N. M. Sinitsyn and A. A. Svetlov, Koord. Khim. **2** (10), 1381 (1976).
30. N. M. Sinitsyn, A. A. Svetlov, and N. V. Brykova, Koord. Khim. **2** (5), 662 (1976).
31. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed. (Wiley-Interscience, New York, 1997), part B, p. 13.
32. N. M. Sinitsyn, A. S. Kozlov, and V. V. Borisov, Zh. Neorg. Khim. **27** (11), 2854 (1982).
33. V. A. Emel'yanov, I. A. Baidina, S. A. Gromilov, et al., Zh. Strukt. Khim. **43** (2), 327 (2002).
34. V. A. Emel'yanov, I. A. Baidina, S. P. Khranenko, et al., Zh. Strukt. Khim. **44** (1), 48 (2003).
35. A. S. Salomov, N. A. Parpiev, Kh. T. Sharipov, et al., Zh. Neorg. Khim. **29** (11), 2853 (1984).
36. V. A. Emel'yanov, I. A. Baidina, S. A. Gromilov, et al., Zh. Strukt. Khim. **41** (6), 1242 (2000).
37. A. S. Salomov, N. A. Parpiev, Kh. T. Sharipov, et al., Zh. Neorg. Khim. **29** (10), 2608 (1984).
38. S. I. Gorelsky, S. C. Da Silva, A. B. P. Lever, and D. W. Franco, Inorg. Chim. Acta **300–302**, 698 (2000).
39. V. A. Emel'yanov, S. A. Gromilov, and I. A. Baidina, Zh. Strukt. Khim. **45** (5), 923 (2004).