

**SYNTHESIS AND CRYSTAL STRUCTURE OF
TRANS-[Ru(NO)(NH₃)₄SO₄]ClO₄ AND
[Ru(NO)(NH₃)₄SO₄][Ru(NO)(NH₃)₃Cl(SO₄)]HSO₄·H₂O**

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After the addition of the saturated NaClO₄ solution to a solution of *trans*-[Ru(NO)(NH₃)₄SO₄]HSO₄·H₂O, *trans*-[Ru(NO)(NH₃)₄SO₄]ClO₄ perchlorate salt (**I**) is obtained with the yield of ~80%. The heating of *trans*-[Ru(NO)(NH₃)₄(H₂O)](HSO₄)SO₄ at a temperature of ~220 °C results in a complete removal of coordination water and a partial removal of ammonia molecules. Successive treatment of the thermolysis product with sulfuric and hydrochloric acids yields [Ru(NO)(NH₃)₄SO₄][Ru(NO)(NH₃)₃Cl(SO₄)]HSO₄·H₂O crystals (**II**). The single crystal X-ray diffraction method is used to determine the structure of the compounds obtained. For **I**: space group *P2₁/c*, *a* = 6.6949(9) Å, *b* = 13.7049(19) Å, *c* = 12.8641(17) Å, β = 101.028(4)°; for **II**: space group *P2₁/c*, *a* = 14.1304(4) Å, *b* = 12.4908(3) Å, *c* = 11.6264(3) Å, β = 94.1980(10)°.

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INTRODUCTION

One of the most actively developing aspects of the chemistry of ruthenium nitroso complexes is concerned with their ability to form long-lived metastable isomers [1-3]. These isomers differ in nitroso group coordination to the ruthenium atom. In the stable state, the NO group is coordinated through the nitrogen atom to transition metal. Under visible light irradiation of the initial nitroso complex isomers form in which NO is coordinated either by the oxygen atom (MS1 state) or simultaneously by the oxygen and nitrogen atoms (MS2 state). Reversible photoisomerization provides the possibility to produce hybrid materials combining the properties such as conductivity or magnetism, apart from photochromic, in the same crystal lattice [4, 5]. In order to develop this aspect, first of all, it is important to collect more detailed information on synthesis methods, structure, and properties of the initial nitroso complexes. The present work describes the synthesis and determination of the crystal structure of compounds containing the complex *trans*-[Ru(NO)(NH₃)₄SO₄]⁺ cation.

Initial [Ru(NO)(NH₃)₄(H₂O)](SO₄)HSO₄ and [Ru(NO)(NH₃)₄SO₄]HSO₄·H₂O were obtained from *trans*-[Ru(NO)(NH₃)₄(OH)]Cl₂ according to the procedures described in the literature [6, 7].

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EXPERIMENTAL

Synthesis of *trans*-[Ru(NO)(NH₃)₄(SO₄)]ClO₄ (I). About ~0.5 g (1.2·10⁻³ mol) of *trans*-[Ru(NO)(NH₃)₄(SO₄)]HSO₄·H₂O was dissolved in ~1 ml of distilled water. To the obtained solution, ~1 ml of the saturated NaClO₄ solution was added. In ~1 h, the bright-yellow precipitate of **I** was filtered off, washed with 1-2 ml of cold water and the same volume of acetone, and dried in the air flow (the yield was ~80%). Single crystals suitable for the single crystal X-ray diffraction (XRD) analysis were obtained by slow evaporation of the aqueous solution of **I**.

Synthesis of [Ru(NO)(NH₃)₄(SO₄)] [Ru(NO)(NH₃)₃Cl(SO₄)]HSO₄·H₂O (II). A weighed sample of ~1 g (2.4·10⁻³ mol) of *trans*-[Ru(NO)(NH₃)₄(H₂O)](SO₄)HSO₄ was placed in a quartz cup covered with a watch glass and heated in a muffle furnace at a temperature of 220 °C for ~4 h. The obtained product was dissolved in ~2 M of H₂SO₄ and the precipitate of *trans*-[Ru(NO)(NH₃)₄(SO₄)]HSO₄·H₂O was isolated. The remained mother liquor was treated with concentrated hydrochloric acid on heating, and the solution was evaporated to the minimum volume (1-2 ml). The precipitate (~0.1 g) was isolated on a glass porous filter, and dissolved in the minimum amount of water. Red-orange crystals of [Ru(NO)(NH₃)₃Cl(SO₄)]·2H₂O and orange crystals of **II** suitable for the XRD analysis were obtained by slow evaporation of a part of the solvent from the aqueous solution.

IR spectra of the samples in pellets with KBr were recorded on a Scimitar FTS 2000 Fourier spectrometer in the range 4000-375 cm⁻¹.

X-ray investigations of the compounds were carried out on a DRON-3M diffractometer ($R = 192$ mm, CuK_α radiation, Ni filter, scintillation detector with the amplitude discrimination) in the range 5° ≤ 2θ ≤ 50° at room temperature. The samples were applied as a thin layer on a polished side of the standard quartz cell. The diffraction patterns of the compounds were fully indexed by the XRD data, which confirms the single-phase character of the products obtained.

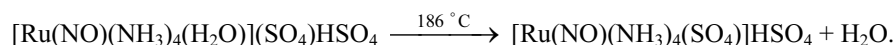
Unit cells parameters and experimental intensities for the solution of the crystal structures were measured at 150 K on a Bruker X8 Apex CCD diffractometer (MoK_α radiation). The structures are solved by the heavy atom method and refined by full-matrix least-squares methods in the anisotropic approximation; hydrogen atoms were refined isotropically and placed in geometrically idealized positions. All the calculations were carried out using the SHELX-97 software package [8]. The CIF-files containing the complete information on the investigated structures have been deposited with the Cambridge Crystallographic Data Centre under nos. 1416860 and 854835 (http://www.ccdc.cam.ac.uk/data_request/cif). The crystallographic data and the main parameters are listed in Table 1.

RESULTS AND DISCUSSION

It is possible to obtain compound **I** with a high yield by the exchange reaction because the solubility of initial *trans*-[Ru(NO)(NH₃)₄(SO₄)]HSO₄·H₂O in water is notably higher than that of the forming perchlorate salt.

The IR spectrum of compound **I** shows the following bands (cm⁻¹): 3264 s, 3125 sh ν(NH₃); 2926 w ν(H₃O⁺); 1892 vs ν(NO); 1618 m δ(H₂O); 1341 m, 1307 m δ(NH₃); 1219, 1189, 1133, 1053, 1024 s ν(SO₄^{coord.}, HSO₄^{coord.}); 1100 s, br ν(ClO₄^{outer}); 959 s ν(SO₄^{outer}); 836 m ρ(NH₃); 660 w, 602 m, ν(Ru–NO), δ(Ru–NO); 640 m δ(SO₄^{coord.}); 622 s δ(ClO₄^{outer}); 581 m δ(SO₄^{outer}); 488 w ν(Ru–NH₃).

We have previously described in detail [9] the thermal decomposition of *trans*-[Ru(NO)(NH₃)₄(H₂O)](SO₄)HSO₄. It was noted that on heating up to 186 °C, the loss of the coordinated water molecule is observed



Further heating leads to the removal of coordinated ammonia molecules, at the same time, due to the presence of the hydrosulfate ion in the outer sphere, the removal of the first ammonia molecule occurs at a relatively low temperature (220 °C), which makes it possible to isolate the triammino complex [Ru(NO)(NH₃)₃Cl(SO₄)]·2H₂O [9].

TABLE 1. Crystallographic Data and Basic Refinement Parameters

Parameter	I	II
Compound	<i>trans</i> -[Ru(NO)(NH ₃) ₄ SO ₄]ClO ₄	[Ru(NO)(NH ₃) ₄ SO ₄][Ru(NO)(NH ₃) ₃ Cl(SO ₄)]×HSO ₄ ·H ₂ O
Temperature, K	150(2)	150(2)
Cell parameters: <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg	6.6949(9), 13.7049(19), 12.8641(17); 101.028(4)	14.1304(4), 12.4908(3), 11.6264(3); 94.1980(10)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> ; <i>V</i> , Å ³	4; 1158.5(3)	4; 2046.55(9)
ρ _{calc} , g/cm ³	2.263	2.350
μ, mm ⁻¹	1.812	2.000
<i>F</i> (000)	784	1440
θ range, deg.	from 2.97 to 33.33	from 2.40 to 30.05
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	-10 ≤ <i>h</i> ≤ 7, -18 ≤ <i>k</i> ≤ 21, -19 ≤ <i>l</i> ≤ 19	-19 ≤ <i>h</i> ≤ 18, -17 ≤ <i>k</i> ≤ 16, -15 ≤ <i>l</i> ≤ 16
Measured/ independ. reflections	14533 / 4456	14529 / 5977
[<i>R</i> (int)]	0.0340	0.0263
θ range for data collection, deg.	25.25	25.00
Completeness of data collection, %	99.9	99.5
Refinement method	Full-matrix OLS on <i>F</i> ²	Full-matrix OLS on <i>F</i> ²
Number of parameters refined	202	368
<i>S</i> -factor on <i>F</i> ²	1.017	1.040
<i>R</i> 1 / <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0253 / 0.0508	0.0268 / 0.0698
<i>R</i> 1 / <i>wR</i> 2 (all data)	0.0355 / 0.0529	0.0307 / 0.0717

When the thermolysis experiment was repeated, we managed to crystallize earlier unknown compound **II** containing both tetra- and triammino complexes.

The IR spectrum of **II** shows the following bands (cm⁻¹): 3536 s, 3447 s ν(H₂O); 3264 s, 3125 sh ν(NH₃); 2926 w ν(OH^{hyd. bond}); 1911, 1890 vs ν(NO); 1632, 1618, 1576 m δ(H₂O); 1340, 1316, 1307, 1295 m δ(NH₃); 1219, 1189, 1053, 1043, 1133, 1024 s ν(SO₄^{coord.}, HSO₄^{coord.}); 959, 955 s ν(SO₄^{outer}); 880, 836 m ρ(NH₃); 660, 620 w ν(Ru–NO), δ(Ru–NO); 640 m δ(SO₄^{coord.}); 602 m, 581 m δ(SO₄^{outer}); 480, 488 w ν(Ru–NH₃). The band positions in the spectrum are in good agreement with those for the majority of the known ruthenium nitroso ammino complexes [10-12].

Compounds **I** and **II** were characterized by the single crystal XRD analysis. The structure of the complex particles and their outer sphere environment with atomic numbering and thermal ellipsoids is shown in Fig. 1.

The crystal structure of **I** consists of complex [Ru(NO)(NH₃)₄(SO₄)]⁺ cations and ClO₄⁻ anions. The structure of **II** contains both complex [Ru(NO)(NH₃)₄(SO₄)]⁺ cations and neutral complex particles [Ru(NO)(NH₃)₃Cl(SO₄)], as well as outer sphere hydrosulfate ions and crystallization water molecules.

Since the structures of the complex [Ru(NO)(NH₃)₄(SO₄)]⁺ cations in the structures of **I** and **II** are practically the same, let us compare the geometry of the complex particles [Ru(NO)(NH₃)₄(SO₄)]⁺ (**a**) and [Ru(NO)(NH₃)₃Cl(SO₄)] (**b**). The main interatomic distances and bond angles in these particles are listed in Tables 2 and 3 respectively.

The central Ru atom in the complex particles (**a**) and (**b**) has a slightly distorted octahedral environment formed by the oxygen atom of the sulfate ion, the nitrogen atom of the nitroso group, and four nitrogen atoms of the ammonia molecule (for **a**), either by three nitrogen atoms of the ammonia molecules and the chlorine atom (for **b**) lying in the equatorial plane. In both particles the sulfate ion is in the *trans*-position to the nitroso group.

The Ru–N_(NH₃) distances in the complex particles (**a**) and (**b**) are within 2.09-2.11 Å; the ruthenium atom is out of the mean-square equatorial plane by ~0.1 Å relative to the nitroso group. The Ru(1)–N and N–O distances in the structures are

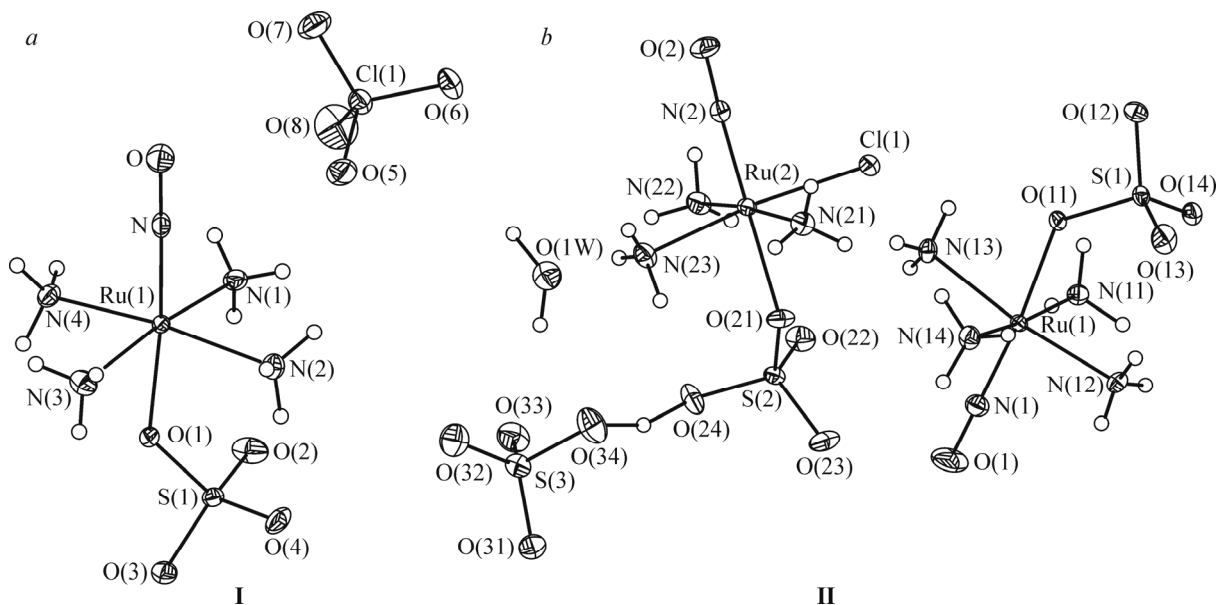


Fig. 1. Structure of complex particles and the outer sphere environment in **I** (*a*) and **II** (*b*).

~ 1.73 Å and ~ 1.15 Å respectively. These values are typical of the known ruthenium nitroso ammino complexes [13, 14]. The Ru(1)–O(1) distances between the central atom and the coordinated sulfate ion is 2.028 Å (for *a*) and 2.033 Å (for *b*), being slightly shorter than those in [Ru(NO)(PPh₃)₂Cl(SO₄)] (Ru–O 2.079 Å), in which the sulfate ion is bidentately coordinated [15]. In the sulfate ion, the length of the bond with the coordinated oxygen atom is ~ 1.52 Å, the other three bonds are similar, their average value is ~ 1.47 Å. The scatter in the bond angle values is within 106.3–111.5°.

The Ru(1)–Cl(1) bond length in the complex (*a*) is 2.378 Å, which is close to the similar values for the known nitrosoruthenium ammino complexes with the chloride ion in the equatorial plane [14, 16].

The O–N–Ru(1) angle in the structures is $\sim 178^\circ$, and the N–Ru(1)–O(1) angle is 174° (for *a*) and 178° (for *b*). These values are typical of ruthenium nitroso complexes [13–17]. The bond angles formed by the atoms in the equatorial plane of the coordination sphere of the N(1)–Ru(1)–N(2) type are close to 90° (deviate by $\pm 1.2^\circ$), at the same time, the O(1)–Ru(1)–N(1) and O(1)–Ru(1)–N(2) angles in the complex (*a*) are noticeably less than 90° (81.5° and 83.1° respectively). In the complex particle (*b*), the deviation of the angles is not so pronounced, but, nevertheless, there is a trend to a decrease in the O(1)–Ru(1)–N(2) (86.6°) and O(1)–Ru(1)–N(2) (87.2°) angles.

TABLE 2. Main Interatomic Distances (*d*, Å) and Angles (ω , deg) in the Complex [Ru(NO)(NH₃)₄(SO₄)⁺ Cation (*a*)

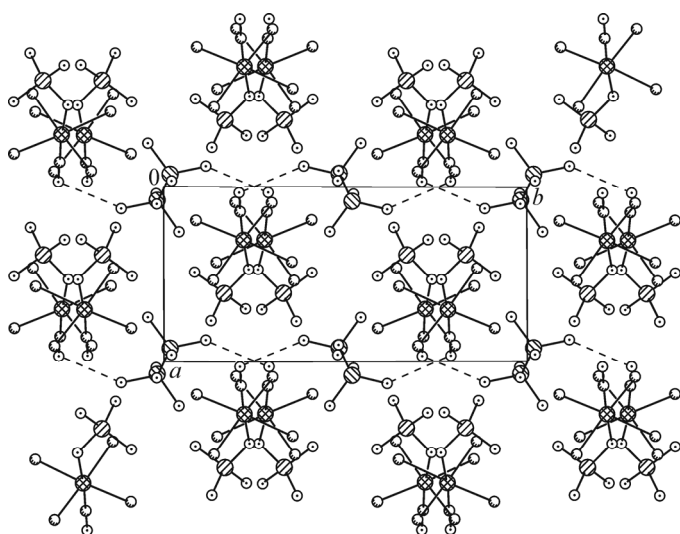
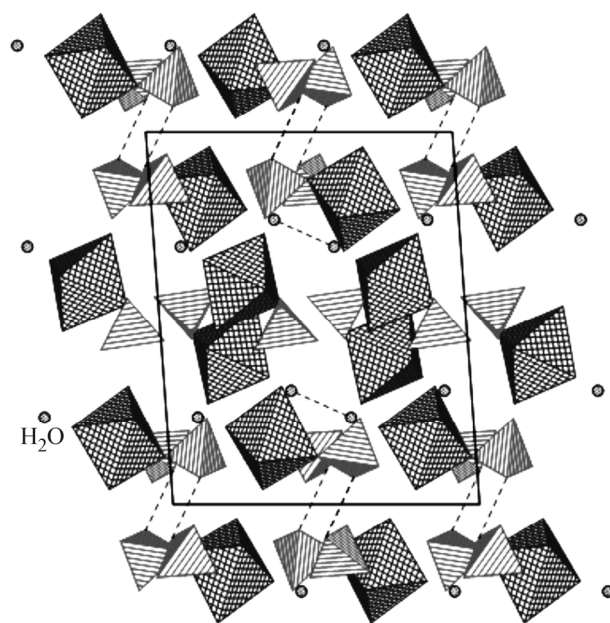
Distance	<i>d</i>	Angle	ω	Angle	ω
Ru(1)–N	1.724(2)	N–Ru(1)–O(1)	174.9(1)	O(1)–Ru(1)–N(2)	90.8(1)
Ru(1)–O(1)	2.015(1)	N–Ru(1)–N(4)	92.6(1)	N(4)–Ru(1)–N(2)	173.5(1)
Ru(1)–N(4)	2.097(2)	O(1)–Ru(1)–N(4)	82.7(1)	N(3)–Ru(1)–N(2)	92.1(1)
Ru(1)–N(3)	2.109(2)	N–Ru(1)–N(3)	94.2(1)	N(1)–Ru(1)–N(2)	88.8(1)
Ru(1)–N(1)	2.087(2)	O(1)–Ru(1)–N(3)	83.58(1)	O–N–Ru(1)	178.2(2)
Ru(1)–N(2)	2.114(2)	N(4)–Ru(1)–N(3)	87.1(1)	O(3)–S(1)–O(2)	111.8(1)
N–O	1.150(2)	N–Ru(1)–N(1)	93.4(1)	O(3)–S(1)–O(4)	111.3(1)
S(1)–O(1)	1.532(1)	O(1)–Ru(1)–N(1)	88.7(1)	O(2)–S(1)–O(4)	111.4(1)
S(1)–O(2)	1.463(1)	N(4)–Ru(1)–N(1)	91.2(1)	O(3)–S(1)–O(1)	105.9(1)
S(1)–O(3)	1.459(1)	N(3)–Ru(1)–N(1)	172.2(1)	O(2)–S(1)–O(1)	108.5(1)
S(1)–O(4)	1.465(1)	N–Ru(1)–N(2)	93.9(1)	O(4)–S(1)–O(1)	107.7(1)

TABLE 3. Main Interatomic Distances (d , Å) and Angles (ω , deg) in the Complex $[\text{Ru}(\text{NO})(\text{NH}_3)_3\text{Cl}(\text{SO}_4)]$ Particle (**b**)

Distance	d	Angle	ω	Angle	ω
Ru(2)–N(2)	1.729(2)	N(2)–Ru(2)–O(21)	176.7(1)	N(21)–Ru(2)–Cl(1)	88.2(1)
Ru(2)–O(21)	2.020(2)	N(2)–Ru(2)–N(23)	94.6(1)	N(22)–Ru(2)–Cl(1)	89.6(1)
Ru(2)–N(21)	2.102(2)	O(21)–Ru(2)–N(23)	85.3(1)	N(23)–Ru(2)–Cl(1)	173.9(1)
Ru(2)–N(22)	2.097(2)	N(2)–Ru(2)–N(22)	93.0(1)	O(24)–S(2)–O(23)	111.6(1)
Ru(2)–N(23)	2.083(2)	O(21)–Ru(2)–N(22)	90.4(1)	O(24)–S(2)–O(22)	110.3(1)
Ru(2)–Cl(1)	2.398(1)	N(23)–Ru(2)–N(22)	91.0(1)	O(23)–S(2)–O(22)	112.1(1)
S(2)–O(24)	1.469(2)	N(2)–Ru(2)–N(21)	94.2(1)	O(24)–S(2)–O(21)	108.2(1)
S(2)–O(23)	1.461(21)	O(21)–Ru(2)–N(21)	82.4(1)	O(23)–S(2)–O(21)	105.1(1)
S(2)–O(22)	1.453(2)	N(23)–Ru(2)–N(21)	90.4(1)	O(22)–S(2)–O(21)	109.4(1)
S(2)–O(21)	1.523(1)	N(22)–Ru(2)–N(21)	172.5(1)	S(2)–O(21)–Ru(2)	134.7(1)
N(2)–O(2)	1.141(3)	N(2)–Ru(2)–Cl(1)	91.5(1)	O(2)–N(2)–Ru(2)	177.2(2)
				O(21)–Ru(2)–Cl(1)	88.6(1)

The structure of **II** is of the island type, and consists of complex $[\text{RuNO}(\text{NH}_3)_4(\text{SO}_4)]^+$ cations and ClO_4^- anions in the general positions. The general packing of the structure along the Z direction is shown in Fig. 2. In the crystal, the structural fragments are linked by numerous $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds that involve the oxygen atoms of the sulfate ions and perchlorate ions, and all the molecules of the coordinated ammonia. The $\text{N}\cdots\text{O}$ distances of these bonds are estimated to be within 2.89–3.21 Å. There are intermolecular contacts of 2.80 Å and 2.93 Å between the oxygen atoms of the nitroso group and the perchlorate ion. The shortest distances between the central Ru atoms in the structure are within 6.486–7.383 Å. In the ClO_4^- anion, the maximum difference between the $\text{Cl}\text{--}\text{O}$ bond lengths (1.430–1.446 Å) does not exceed 0.016 Å; the average bond angle value is 109.5°.

In the crystal structure of **II** (Fig. 3), the complex particles are packed in layers perpendicular to the Z direction. Between the layers there are outer-sphere hydrosulfate ions and water molecules linked to coordinated sulfate ions by a net of hydrogen bonds. The $\text{O}\cdots\text{O}$ distances between the water molecule and the hydrosulfate ion is estimated to be

**Fig. 2.** Packing of particles in the crystal of **I** (projection along the z axis).**Fig. 3.** Packing of particles in the crystal of **II** (projection along the y axis).

~2.92 Å, and the length of hydrogen bonds between the coordinated sulfate ion in the $[\text{Ru}(\text{NO})(\text{NH}_3)_3\text{Cl}(\text{SO}_4)]^+$ complex and the outer sphere hydrosulfate ion is estimated to be ~2.52 Å. Between the complex particles there are also hydrogen bonds formed by the coordinated sulfate ions and the coordinated ammonia molecules of the neighboring complex particles. The O...N distances are estimated to be 2.8-2.9 Å.

Thus, we have obtained and structurally characterized new nitroso ammino complexes of ruthenium containing coordinated sulfate ions in the *trans*-position to the nitroso group. The isolation of compound **II** containing both tetra- and triammino complexes has proved the previously proposed schemes of reactions occurring in the thermal decomposition of *trans*- $[\text{Ru}(\text{NO})(\text{NH}_3)_4(\text{H}_2\text{O})](\text{SO}_4)\text{HSO}_4$.

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