Journal of Structural Chemistry. Vol. 47, No. 2, pp. 380-382, 2006
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SYNTHESIS AND CRYSTAL STRUCTURE OF NITROSORUTHENIUM AQUADIAMMINE COMPLEX, $[Ru(NO)(NH_3)_2Cl_2(H_2O)]Cl\cdot H_2O$

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UDC 546.96:548.737

The reaction between $[RuNO(NH_3)_2(NO_2)_2OH]$ and an excess of 3 M HCl leads to denitration of the starting complex and precipitation of $[Ru(NO)(NH_3)_2Cl_3]$. Crystals of the tittle complex have been obtained by evaporation of the mother liquor at ambient temperature. The crystal structure of the product has been determined. The linear nitroso group and a water molecule are coordinated in the *trans* positions, three nitrogen atoms from NO and NH_3 ligands occupy the coordination octahedron face.

Keywords: Nitroso complex; Ammine complex; Chloride complex; Ruthenium(II); Crystal structure.

The discovery of the nitric oxide (NO) participation in a wide range of physiological processes gave rise to a new wave of interest in understanding the fundamental chemistry of NO and of metal nitrosyl complexes [1]. The most convenient objects for this task are stable nitrosoammine ruthenium complexes which allow to preserve some coordinates with the strong Ru–N bond and to substitute the other ligands rather easily. In general, nitrosotetraammine complexes $[RuNO(NH_3)_4L]X_n$ are widely used for this purpose [2]. Structural data are available for only three ruthenium nitrosocomplexes with less than four NH_3 groups in the coordination sphere: $[RuNO(NH_3)_2(NO_2)_2OH]$ [3], $[Ru(NO)(NH_3)_2Cl_3]$ [4] and $[RuNO(NH_3)_3Cl(H_2O)]Cl_2$ [5].

In the present work, we report a new example of the cationic ruthenium nitrosocomplex which contains two NH_3 molecules in the coordination sphere — nitrosodichlorodiammineaquaruthenium chloride.

Experimental. The complex $[RuNO(NH_3)_2(NO_2)_2OH]$ was synthesised by V.N. Pichkov's procedure [6]. Denitration of this complex by heating with an excess of 3 M HCl leads to precipitation of $[Ru(NO)(NH_3)_2Cl_3]$. Orange-red crystals of 1-nitroso-2,3-dichloro-4,5-diammine-6-aquaruthenium(II) chloride monohydrate, $[Ru(NO)(NH_3)_2Cl_2(H_2O)]Cl\cdot H_2O$ (**1**), were obtained by evaporation of the mother liquor at ambient temperature.

The crystal structure of **1** was determined by single-crystal X-ray diffraction analysis. The crystals, unstable in air, were protected by a thin glue film. Diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer (MoK_α radiation, graphite monochromator, standard technique) at room temperature. Absorption correction was applied using azimuthal scan curves. The structure was solved by direct methods and refined in anisotropic approximation for all non-hydrogen atoms on F^2 using the SHELX-97 program set [7]. Hydrogen atoms were partially located from the difference electron density map, the other being set to the idealised positions.

Crystallographic data for **1**: chemical formula $H_{10}Cl_3N_3O_3Ru$, F.W. 307.53, monoclinic, $a = 6.304(1)$ Å, $b = 13.601(2)$ Å, $c = 11.020(2)$ Å, $\beta = 96.57°$, $V = 938.6(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_x = 2.176$ g·cm^{-3}, $D_{exp} = 2.174$ g·cm^{-3},

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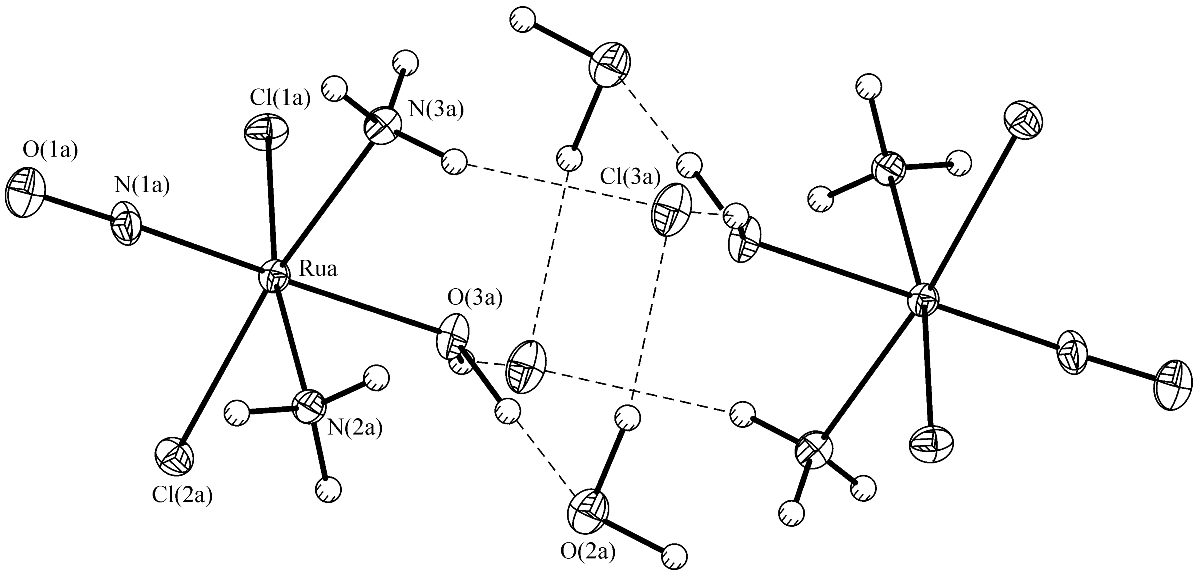

Fig. 1. Fragment of crystal structure of compound **1**. Hydrogen bonds are shown by dashed lines. The main bond distances (Å): Ru–N(1) 1.710(6), Ru–O(3) 2.037(4), Ru–N(2) 2.065(5), Ru–N(3) 2.079(5), N(1)–O(1) 1.137(6), Ru–Cl(1) 2.371(2), Ru–Cl(2) 2.365(2). Bond angles (deg): N(1)–Ru–O(3) 179.0(2), N(1)–Ru–N(2) 94.1(3), N(1)–Ru–N(3) 95.2(2), O(3)–Ru–N(2) 85.5(2), O(3)–Ru–N(3) 83.9(2), N(2)–Ru–N(3) 90.9(2), N(1)–Ru–Cl(2) 91.5(2), O(3)–Ru–Cl(2) 89.4(1), N(2)–Ru–Cl(2) 88.4(2), N(3)–Ru–Cl(2) 173.3(2), N(1)–Ru–Cl(1) 94.2(2), O(3)–Ru–Cl(1) 86.2(1), N(2)–Ru–Cl(1) 171.6(2), N(3)–Ru–Cl(1) 87.2(1), Cl(2)–Ru–Cl(1) 92.5(1), O(1)–N(1)–Ru 177.2(6). Some hydrogen bonds: O(3)–H…O(2) 2.62 (1.64) Å, 163.7°, O(3)–H…Cl(3) 3.04 (2.22) Å, 162.2°, N(3)–H…Cl(3) 3.28 (2.41) Å, 164.9°, O(2)–H…Cl(3) 3.43 (2.29) Å, 156.0°.

$\mu = 2.487\ \mathrm{mm}^{-1}$, crystal size 0.20×0.15×0.05 mm (plate). Total 1399 unique reflections were measured up to $2\theta_{\max} = 50°$. Final residuals are: $R1 = 0.0271$, $wR2 = 0.0516$ for 969 $F_{hkl} \geq 4\sigma(F)$, $R1 = 0.0452$, $wR2 = 0.0550$, $GOOF = 0.652$ for all reflections used in the refinement.

The X-ray investigation of the compound was carried out using a DRON-UM1 diffractometer ($R = 192$ mm, CuK_α radiation, Ni filter). The crystals were ground with heptane to crystallite dimensions ~50 μm. A specimen was deposited in a thin layer on the smooth side of a standard quartz sample holder. The X-ray diffraction pattern was indexed completely using single crystal data indicating the single-phase nature of the synthesised product.

Results and discussion. The infrared spectrum (SPECORD IR-75, 3800-400 cm^{-1}, Nujol) of **1** has the following bands (cm^{-1}) for which assignments are given in parentheses: 3540 m, 3365 m (νH_2O) 3280 sh, 3260 s, 3200 sh, 3140 s (νNH), 1915 s, 1875 s (νNO), 1630 sh (δH_2O), 1550 br m, 1335 m, 1315 m (δNH), 820 br w, 780 sh, 720 w (ρ_rNH), 650 w, 580 w ($\rho_r H_2O$), 620 w (νRu–NO), 610 w (δRu–NO), 510 w, 460 sh ($\delta_w H_2O$), 480 w ($\nu Ru–NH_3$) (s = strong; br = broad; m = medium; w = weak; sh = shoulder). This spectrum agrees well with that reported for the $[RuNO(NH_3)_2Cl_3]$, provided inclusion of H_2O modes [8].

The structure of the complex cation $[RuNO(NH_3)_2Cl_2(H_2O)]^+$ is shown in Fig. 1. The linear nitroso group and the water molecule are coordinated in the *trans* positions, three nitrogen atoms from NO and NH_3 ligands occupy the coordination octahedron face. The ruthenium atom deviates from the rms equatorial plane N_2Cl_2 to the nitroso group by 0.14 Å. The geometry of the complex is usual for the coordination compounds with a trans H_2O–Ru–NO fragment [9].

The complex cations, chloride anions and solvate water molecules are joint together by a system of hydrogen bonds O–H…O (2.62 Å), O–H…Cl (3.04-3.43 Å) and N–H…Cl (3.14-3.58 Å) shown in Fig. 1. The distances from a chloride anion to five ruthenium atoms are 4.45-5.20 Å, to the solvate water molecule 3.16 Å. The packing of complex cations along the *y* axis is pseudohexagonal (Fig. 2), the shortest eight separations Ru…Ru vary within 6.028-7.00 Å. The nitroso oxygen atoms of two neighbouring cations of the complex are separated by 3.23 Å.

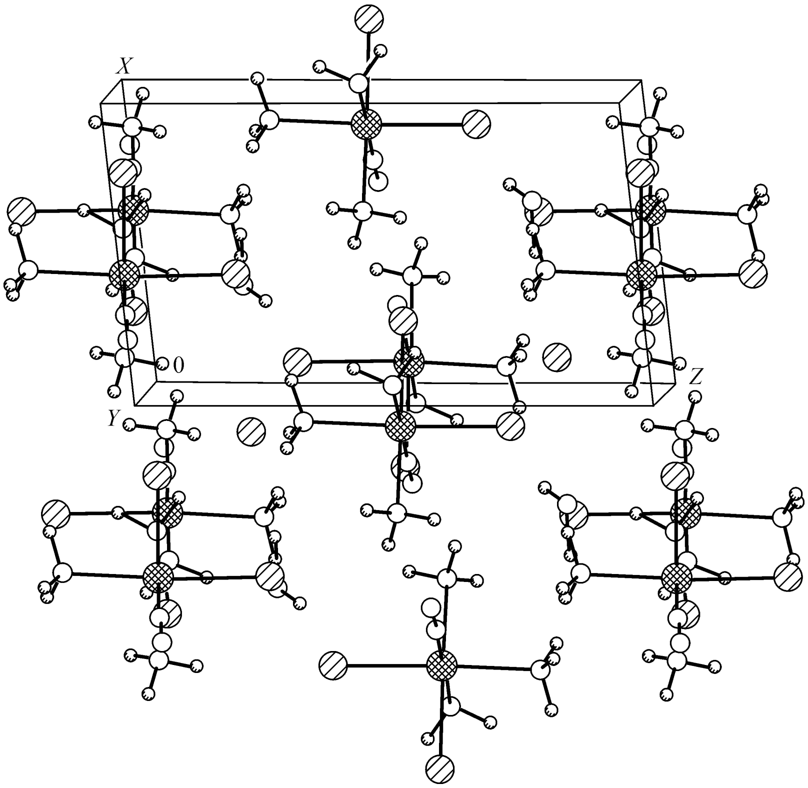

Fig. 2. Crystal packing in compound **1** (view along y axis).

Crystallographic data for compound **1** have been deposited at Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen and can be obtained under the depository number CSD-411982.

We thank Dr N. V. Pervukhina for assistance in obtaining single-crystal XRD data and Mrs T. S. Yudanova for help in preparing this paper. This work was partially supported by INTAS (grant No. 00-0651).

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