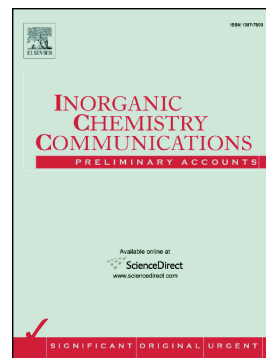


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Nitrosyl cis-dichlorodiammine ruthenium complex with bridging H_3O_2^- ligand

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Abstract. The ruthenium complex with bridging H_3O_2^- ligand was obtained and the crystal structure was determined. The compound *cis*-[$\{\text{RuNO}(\text{NH}_3)_2\text{Cl}_2\}_2(\mu_2\text{-H}_3\text{O}_2)\text{Cl}$] crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ with cell parameters $a = 15.0651(5)$, $b = 6.3624(2)$, $c = 15.3813(6)$ Å, $\beta = 94.9690(10)^\circ$, $Z = 4$ and $R = 0.0185$. The hydroxide hydrate anion is coordinated to the ruthenium atoms of the identical *cis*- $\{\text{RuNO}(\text{NH}_3)_2\text{Cl}_2\}$ fragments. The protonation of the starting *cis*- $[\text{RuNO}(\text{NH}_3)_2(\text{NO}_2)_2\text{OH}]$ complex leads to the required coordinated aqua/hydroxide ratio if the specific amount of hydrochloric acid is used. The DFT calculations confirm the formation of the dimer structure in the gas phase. However, the presence of water molecules dramatically reduces the dimerization efficiency.

Water molecules due to amphoteric properties can form anionic and cationic aggregates. Despite the great variety of studies based on the H_3O^+ , H_3O_2^+ and other cations, the H_3O_2^- anions are less presented. The free anion was detected in $\text{Ca}_2[\text{Be}_2(\text{OH})_7][\text{H}_3\text{O}_2] \cdot 2\text{H}_2\text{O}$ compound.¹ Also, the H_3O_2^- anion can play a bridging role. The complexes with this ligand are presented for various metals. The dinuclear zinc² or nickel³ complexes were designed by choosing the right scaffold to form H_3O_2^- anion. In the case of copper complexes, the encapsulation in a cryptate was used to form squeezed bihydroxide anion which bridges two copper centers.⁴ The formation of a hydrogen bond between coordinated water molecules and hydroxide has some use in the assembling of the metal-organic framework.⁵

Moreover, the additional connection of two metal centers is not required to form complexes with the H_3O_2^- ligand. The hydrothermal reaction between metal oxide and the appropriate salt results these complexes.⁶ Also, the bihydroxide complexes can be obtained from an aqueous solution of hydroxo pentaammine rhodium(III) and aqua pentaammine rhodium(III) dithionates.⁷ If the hydroxo complex is not available, it can be prepared *in situ* by the deprotonation of the coordinated water molecule.⁸ Even recrystallization from aqueous media can lead to the formation of the H_3O_2^- complexes from aquacomplexes.⁹

On the other hand, required ratio of hydroxyl/aqua complexes can be reached by partial protonation of the starting hydroxo complex. The aqua complex $[\text{RuCO}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ is a weak acid with pKa about 7.7.¹⁰ The nitrosyl group occurrence in the complex $[\text{RuNO}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$ efficiently enhances the coordinated water molecule acidity up to 1.4.¹¹ As a result, the addition of strong acid is required to convert coordinated hydroxyl to water molecule in case of the nitrosyl ruthenium compounds.¹² Thus, the reaction of *cis*- $[\text{RuNO}(\text{NH}_3)_2(\text{NO}_2)_2\text{OH}]$ ¹³ complex with hydrochloric acid was used to prepare the *cis*- $[\{\text{RuNO}(\text{NH}_3)_2\text{Cl}_2\}_2(\mu_2\text{-H}_3\text{O}_2)]\text{Cl}$ complex (**1**). As shown, the elimination of the coordinated nitro groups occurs in the strongly acidic media.¹⁴ In this paper, we present the investigation of the complex **1** with H_3O_2^- bridging ligand by IR, density functional theory (DFT) and single-crystal X-ray studies.

The starting compound (0.50 g, 1.8 mmol) was mixed with 2.5 equivalents of 1 M HCl. The suspension was stirred at room temperature until the solution became clear. The resulting red solution was set aside and the product **1** precipitated in three days with 70-80% yield. To obtain single-crystals, the nitrate complex *fac*- $[\text{RuNO}(\text{NH}_3)_2(\text{NO}_3)_3]$ ¹⁵ (0.20 g, 0.57 mmol) was dissolved in three equivalents of 0.1 M HCl and gently heated. The resulting solution was slowly evaporated at r.t. The product was recrystallized two times from water at room temperature. As a result, the orange prisms of **1** suitable for X-ray crystallography studies were obtained. Diffraction data were measured at 296(2) K on a BRUKER X8APEX (MoK α radiation, graphite monochromator, standard technique). All used chemicals and **1** are air stable. For formulae $\text{H}_{15}\text{Cl}_5\text{N}_6\text{O}_4\text{Ru}_2$, calculated Cl 32.67, N 15.49, H 2.79; found Cl 32.5(2), N 15.5(2), H 2.9(3). The X-ray diffraction pattern was indexed completely using the data for a selected single crystal, which indicated the single-phase nature of the synthesized product (Fig. S1).

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