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V. N. Pichkov, N. M. Sinitsyn, O. E. Zvyagintsev

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Abstract

Full Text

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On the nitrosoruthenium compound $[RuNO(NO_2)_2(NH_3)_2OH]$

(Presented by Academician I. I. Chernyaev, 12 II 1964)

Up to the present time, in the series of ammine complexes of nitrosoruthenium of the general formula $[RuNO(NH_3)_nA_{(5-n)}]^{n-2}$, where A is an acido ligand and n varies from 0 to 5, only the tetra- and pentammines were known ([1–3]), whereas the remaining members of this series had not been described. In the literature there is likewise no information on mixed complexes of nitrosoruthenium containing both nitro groups and ammonia in the inner sphere.

We succeeded in synthesizing and studying some properties of diammine-dinitrohydroxonitrosoruthenium $[RuNO(NO_2)_2(NH_3)_2OH]$. As the starting substance we used the sodium salt of tetranitrohydroxonitrosoruthenium, $Na_2[RuNO(NO_2)_4OH] \cdot 2H_2O$. It was dissolved in concentrated ammonia, and the solution was heated almost to boiling for several minutes. The color of the solution changed from orange to red. From the resulting solution, left to crystallize at room temperature, yellow crystals in the form of octahedral prisms precipitated very slowly. The crystals were filtered off from the mother liquor, washed on the filter with water, acetone, and ether, and analyzed.

Fig. 1. Absorption spectrum of aqueous solutions:
I –$[RuNO(NO_2)(H_2O)_2OH]$; II –freshly prepared solution of $[RuNO(NO_2)(NH_3)_2OH]$; III –solution II after 7 days; IV –solution II after 2-hour boiling.

$$[RuNO(NO_2)_2(NH_3)_2OH].$$

Found, %: Ru 36.6; N_{total} 25.45; NH_3 12.4

Fig. 2

Figure 2: Fig. 2

Calculated, %: Ru 36.9; N_{total} 25.5; NH_3 12.4

Crystallo-optical analysis confirmed the homogeneity of the substance and gave the following refractive indices: $N_p = 1.681$; $N_m = 1.755$; $N_g = 1.780$.

The substance obtained is poorly soluble in water and in ordinary organic solvents. In air the crystals undergo no changes. However, in aqueous solutions the complex $[RuNO(NO_2)_2(NH_3)_2OH]$ slowly undergoes hydrolysis. Thus, the value of the molecular electrical conductivity, equal to 4.9 $\Omega^{-1} \cdot cm^{-1}$, indicating that the complex is not an electrolyte in aqueous solution at a dilution of $1 : 500$, slowly changes over 50 days to 34.0 $\Omega^{-1} \cdot cm^{-1}$. Heating increases the rate of hydrolysis; for example, after 2 hours of boiling the solution, its electrical conductivity rises to 73.5 $\Omega^{-1} \cdot cm^{-1}$. It should be noted that the observed processes proceed both in the light and in the dark.

A spectrophotometric study of aqueous solutions of $[RuNO(NO_2)_2(NH_3)_2OH]$ in the visible and ultraviolet regions of the spectrum also confirms the presence of hydrolysis.

Figure 1 shows the change with time in the spectrum of an aqueous solution of $[RuNO \cdot (NO_2)_2(NH_3)_2OH]$ (curve *II*) in comparison with the spectrum of a solution of $[RuNO(NO_2)_2(H_2O)_2OH]$ ([5]) (curve *I*).

It seemed reasonable to assume that if ammonia is washed out from the inner sphere, then curve *II* (the spectrum of a freshly prepared solution) should gradually coincide with curve *I*. However, as is seen from the data obtained, after the solution is kept for 7 days at room temperature, curve *III* is obtained, and after the solution is boiled for 2 hours—curve *IV*. Thus, apparently, the NO_2 groups, and not ammonia, are removed first from the inner sphere.

Fig. 2. Thermograviogram of $[RuNO(NO_2)_2 \cdot (NH_3)_2OH]$: *I*, *II*—heating curves; *III*—weight-loss curve.

Thermogravimetric study of $[RuNO(NO_2)_2(NH_3)_2OH]$ shows that the simultaneous presence of NO_2- and NH_3-groups in the inner sphere leads to a lowering of the temperature at which decomposition of the complex begins, in comparison with the tetrammine and tetranitro complexes of nitrosoruthenium. On heating curves *I* and *II* in Fig. 2,* decomposition of the complex is accompanied by an endothermic effect at 200–230°, which immediately changes into a very strong exothermic effect at 240–260°, accompanied by complete destruction of the complex to ruthenium dioxide.

In the IR spectrum of $[RuNO(NO_2)_2(NH_3)_2OH]$, the presence of a very intense split band with absorption maxima at 1869 cm^{-1} (principal) and 1900 cm^{-1} indicates the presence of a nitroso group bonded to ruthenium by a multiple

bond ([6,7]).

The close value of the frequencies of the stretching vibrations ν_{NO} in the complex under investigation and in $[RuNO(NO_2)_2(H_2O)_2OH]$ ([8]) shows that the displacement of electron density from NH_3 and from H_2O to ruthenium is approximately the same. The IR spectral data also give grounds for assuming that the distance r_{RuN} (from NO) in the complex under investigation lies in the interval from 1.85 ± 0.05 Å to 2.07 ± 0.05 Å.

The presence of a band at ~ 3610 cm^{-1} (ν_{OH}) and 956 cm^{-1} (δ_{OH}), which occurs only in hydroxo compounds of nitrosoruthenium and was assigned by Scargill ([9]) to deformation vibrations of the OH group, attests to the presence in the complex of a coordinated OH group. Since in the starting complex δ_{OH} is equal to 995 cm^{-1} (in the dihydrate) and 923 cm^{-1} (in the anhydrous salt) ([4,9]), the absence of these bands in the spectrum of $[RuNO(NO_2)_2 \cdot (NH_3)_2OH]$ means that the 1900 cm^{-1} band is not due to an impurity of the starting product, in which ν_{NO} is equal to 1900 cm^{-1}. The relatively low value of the frequency of the rocking vibrations of ammonia, 800 cm^{-1}, in our diammine, in comparison with tetrammine, for example 850 cm^{-1} in $[RuNO(NH_3)_4Cl]Cl_2$, indicates that the strength of the ammonia bond in $[RuNO(NO_2)_2(NH_3)_2OH]$ is less than in nitrosoruthenium tetrammines ([10]).

The frequencies of the NO_2-group in the spectrum of the diammine indicate that the bond of Ru with the NO_2-group, as in $Na_2[RuNO(NO_2)_4OH]$ ([4,11]), is through nitrogen.

On the basis of I. I. Chernyaev' s trans-influence regularity, which is also manifested in nitrosoruthenium complexes ([6]), and of X-ray structural

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* The heating and weight-loss curves were obtained on a Kurnakov vertical pyrometer with a Pt–Pt/Rh thermocouple in air.

data for $K_2[RuNO(NO_2)_4OH]$ [(11)], the structure of the complex obtained can be represented as follows. It is evident that, upon interaction of the O_2N—Ru—NO_2 coordinate with ammonia, owing to the greater trans influence of the NO_2 group as compared with NH_3, formation of the O_2N—Ru—NH_3 coordinate occurs. Thus, the trans-hydroxonitroso-cis-dinitro-diammine complex of ruthenium is formed:

$$\begin{array}{lcl} & NO & \\ O_2N & / & NO_2 \\ & Ru & \\ O_2N & \backslash & NO_2 \\ & OH & \end{array} + NH_4OH \longrightarrow \begin{array}{lcl} & NO & \\ O_2N & / & NH_3 \\ & Ru & \\ O_2N & \backslash & NH_3 \\ & OH & \end{array}$$

and upon hydrolysis the O_2N—Ru—NH_3 coordinate probably converts into

H_2O—Ru—NH_3.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.