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Abstract

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On the Mutual Influence of Atoms and Groups in Complex Nitroso Compounds of Ruthenium

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The mutual influence of atoms and groups in the inner sphere of complex compounds is one of the fundamental problems of modern coordination chemistry, widely discussed in the world literature ([1–5]).

The effects of the trans- and cis-influence of atoms and groups have been found in complex compounds of Pt, Rh, Pd, Ir, Co ([6–11]), but have not yet been observed in octahedral complex compounds of ruthenium. In the presence in ruthenium complexes of a nitroso group, which forms a covalent, donor–acceptor, and dative bond with the central atom, a redistribution of electron density should occur throughout the molecule and, above all, a change in the properties of substituents situated in the trans-position to the nitroso group. It also seemed probable that different ligands situated in the trans-position to NO should in turn change the electronic configuration of the latter, causing a change in the frequency of the valence vibrations ν NO in the infrared absorption spectrum.

Indeed, when the properties of ruthenium nitrosopentaammine trichloride $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ ([12]) were studied both in solution and in the solid state, increased mobility was observed for only one ammine group, situated in the trans-position to NO on the coordinate NH_3—Ru—NO. If $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ is treated with an ammonia solution, $[RuNO(NH_3)_4OH]Cl_2$ is formed, which in composition and properties corresponds to trans-$[RuNO(NH_3)_4OH]Cl_2$, obtained from $(NH_4)_2[RuNOCl_5]$.

$$[RuNO(NH_3)_5]Cl_3 \cdot H_2O \longrightarrow \text{trans-}[RuNO(NH_3)_4OH]Cl_2 \longleftarrow (NH_4)_2[RuNOCl_5]$$

$$\downarrow 210^\circ \qquad\qquad \downarrow +HCl$$

$$\longrightarrow \text{trans-}[RuNO(NH_3)_4Cl]Cl_2$$

The trans-configuration was proved by X-ray structural investigations of G. B. Bokii and N. A. Parliev ([13]). The strong trans-influence of the nitroso group was demonstrated by the thermogravimetric method. On heating $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$, $[RuNO(NH_3)_4Cl]Cl_2$ is formed, which in composition

Fig. 1. Heating curves (I and II) and loss in weight (III) of [RuNO(NH3)5]Cl3 · H2O

Figure 1: Fig. 1. Heating curves (I and II) and loss in weight (III) of [RuNO(NH3)5]Cl3 · H2O

and properties corresponds completely to trans-$[RuNO(NH_3)_4Cl]Cl_2$, obtained by the exchange reaction of OH for Cl from trans-$[RuNO(NH_3)_4OH]Cl_2$. As is seen from the heating curves (I and II) and the weight loss (III) for ruthenium nitrosopentaammine $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ (see Fig. 1), a 1.6% loss in weight corresponds to removal of adsorbed water. The first endothermic effect at 115—135° is associated with removal of one molecule of water (weight loss 5.2%, calculated for one H_2O molecule 5.26%).* The second endothermic effect at 210—240° corresponds to removal of one ammonia molecule (weight loss 5.2%, calculated for one ammonia molecule 5.25%). Further removal of ammonia begins at a temperature of 270°. The nitroso group is removed from the inner sphere of the complex at 395—410°, with simultaneous decomposition of the entire complex.

* The interpretation of the effects from the weight loss is confirmed by elemental analysis.

Consequently, the nitroso group, very firmly bound to the central atom of the complex and possessing a strong trans influence, directs the decomposition reactions of ruthenium nitrosopentammine toward the elimination of the opposite ammonia with the formation of tetrammines of trans configuration.

We followed the change in the electronic structure of the nitroso group by the change in the frequencies of the stretching vibrations νNO in the infrared absorption spectrum (IR spectrum), depending on the nature of the ligand situated in the trans position to the NO group on the coordinate

A—Ru—NO*,

where $A = Cl, Br, OH, NH_3$, etc.

Fig. 1. Heating curves (I and II) and loss in weight (III) of $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$

As is seen from the data of Table 1, the frequency of the stretching vibrations νNO on going from OH to NH_3 increases, which corresponds to a decrease in the distance between nitrogen and oxygen r_{NO} (15). At the same time there occurs a decrease in the distance between ruthenium and the nitrosyl nitrogen r_{RuN}, which is confirmed by X-ray structural data: for OH—Ru—NO the distance $r_{RuN} = 2.04$ Å (13, 16), and for Cl—Ru—NO, $r_{RuN} = 1.70$ Å (17, 18).

The accuracy of determination of r_{RuN} is ± 0.05 Å. An increase is observed in the force constant f of the NO bond and in the bond order N of NO. The quantities f and N were estimated approximately from the equations of Johnathan (15).

This can be explained by the appearance of additional donor-acceptor bonds at the expense of the free electron pair of the nitrosyl oxygen:

$$\mathrm{Ru} \rightleftarrows \mathrm{N} \leftarrow \mathrm{O}^{(+\delta)}.$$

Table 1

Coordinate in trans-tetrammine	νNO, cm^{-1}	f, mdyn/Å	r_{NO}, Å	N
NH_3–Ru–NO	1922; 1935	17.2	1.13_8	2.3
Cl–Ru–NO	1893	17.0		
Br–Ru–NO	1885(14)	16.9		
OH–Ru–NO	1845(14)	16.2	1.14_3	2.2

If the frequencies of the stretching vibrations of NO are compared with $K_2[RuNOJ_5]$ 1850 cm^{-1}, $K_2[RuNOCl_5]$ 1905 cm^{-1}, and $K_2[RuNO(CN)_5]$ 1930 cm^{-1} (14), then ultimately the following series can be compiled for increasing ligand-field strength in ruthenium nitroso complexes:

$$\mathrm{OH} > \mathrm{J} > \mathrm{Br} > \mathrm{Cl} > \mathrm{CN},\ \mathrm{NH_3}.$$

On proceeding along the series from OH to NH_3, one should observe an increase in the strength of the bond of ruthenium with the nitroso group, which corresponds to a decrease in the distances r_{NO}, r_{RuN} and to an increase in νNO, f_{NO}, apparently $\angle$RuNO, and the effective positive charge $(+\delta)$ on the nitroso group.

An additional influence on the redistribution of electron density in the molecule is exerted by the ligands situated in the cis position to the nitroso group. The greater the donor properties of the cis substituent, the more strongly its electrons are shifted onto the central atom, and the stronger the observed effect of the trans influence of the substituent situated on the coordinate *A—Ru—NO*. Thus, in trans-$(NH_4)_2(RuNOCl_4OH)$, where Cl is in the cis position to NO,

* IR absorption spectra were recorded jointly with O. N. Evstaf' eva.

r_{RuN} = 2.04 Å, while in trans-$K_2[RuNO(NO_2)_4OH]$, where NO_2 is in the cis-position to NO, r_{RuN} = 1.80 Å (19).

Extrasphere ions also exert a noticeable influence on the redistribution of electron density in the molecule of ruthenium nitroso complexes. With an increase

in the ability of cations to shift their electrons toward ruthenium (i.e., with an increase in electron-donor properties), there is an increase in the covalency of the bond in the molecule, associated with a decrease in its solubility and a decrease in the vibration frequency νNO in the series $Na^+ < K^+$, $NH_4^+ < Rb^+ < Cs^+$ (see Table 2).

Table 2

Compound	ν NO, cm^{-1}	Solubility, g/l	Compound	ν NO, cm^{-1}	Solubility, g/l
$K_2(RuNOCl_5)$	1919(20); 1905(14)	12	$Cs_2(RuNOCl_5)$	1880(14)	0.2
$(NH_4)_2[RuNOCl_5]$	1916; 1907	5	$Na_2(RuNO(NO_2)_4OH)$	1907(20)	
$Rb_2[RuNOCl_5]$	—	0.57	$K_2(RuNO(NO_2)_4OH)$	1900(14)	

In the multicomplex compound we synthesized, $[RuNO(NH_3)_5]_2 \cdot [RuNOCl_5]_3 \cdot 4H_2O$, there are four bands of the nitroso group νNO—1945, 1935, 1924, 1896 cm^{-1}—which differ from the νNO vibration frequencies in the starting compounds: $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$, 1935, 1922 cm^{-1}, and $(NH_4)_2[RuNOCl_5]$, 1916, 1907 cm^{-1}. This fact indicates that the nitroso groups located in the anionic and cationic parts of one molecule retain their electronic individuality. This is also confirmed by the presence of two exothermic effects of decomposition of the nitroso group on the thermogram of the substance obtained. The observed splitting of the nitroso-group bands can apparently be explained by an additional interaction of the nitroso group with neighboring atoms in the crystal.

The examination carried out of the frequencies of the valence vibrations of the nitroso group and their comparison with the chemical properties of the complexes allow one to conclude that there is a mutual influence of atoms and groups in ruthenium nitroso complexes, which is manifested most clearly in the trans-influence on the coordinate A—Ru—NO upon substitution of ligands located in the trans-position to the nitroso group. The electronic structure of the nitroso group is characteristic of each individual ruthenium compound and changes depending on changes in the electron-donor properties of both intrasphere substituents and extrasphere ions.

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