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Reversible Thermal Isomerization of Three Geometrical Isomers for Chlorobis(2-methyl-8-quinolinolato)nitrosylruthenium(III)

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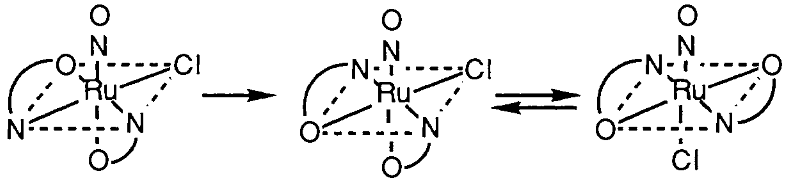
The reversible thermal isomerization among the trans and two kinds of cis geometrical isomers of [RuCl(2mqn)$_2$(NO)] (2mqn=2-methyl-8-quinolinolate ion) was observed in degassed DMSO (dimethyl sulfoxide) at higher than 363 K. The mole ratio of the cis-1, the cis-2, and the trans isomers was 20:9:1 after the equilibrium was reached at 413 K, and it did not depend on the starting species.

For Ru(II)-NO$^+$ type of nitrosylruthenium(3+) complexes, several irreversible thermal isomerizations have been reported: cis to trans isomerization for [Ru(OH)(NH$_3$)$_4$(NO)]$^{2+}$ in alkaline medium,$^{1,2)}$ cis to trans isomerization for [RuIL$_2$(NO)] (L=1,2-diphenylethanedione dioximate or 2,3-butanedione dioximate ion) in EtOH/CH$_2$Cl$_2$,$^{3)}$ cis to another cis isomerization for [RuX(bpy)$_2$L(NO)](BF$_4$)$_2$ (X=Cl, Br, or I; L=1,2-bis(diphenylphosphino)-ethane or 1,2-bis(diphenylphosphino)ethylene) in the solid state,$^{4)}$ and cis to trans isomerization for [RuXL$_2$(NO)](BF$_4$)$_2$ (X=Cl or Br; L=bis(diphenylphosphino)methane) in halocarbon medium and in the solid state.$^{5)}$ However, there has been no report on reversible thermal isomerization for nitrosylruthenium(III) complexes.

We have reported the synthesis and the X-ray structure analysis of two kinds of cis isomers of [RuCl(2mqn)$_2$(NO)],$^{6)}$ and photochemical synthesis of the trans isomer from the cis isomers.$^{7)}$ Among the three isomers, photoisomerization reactions were observed: the cis-1 isomer isomerized to the trans isomer reversibly, and the cis-2 isomer isomerized to the cis-1 and the trans isomers irreversibly. The schematic structures and their photochemical behavior are shown below:



cis-2 cis-1 trans

where 2-methyl-8-quinolinolate ion is represented by N O.

We have now found the reversible thermal isomerization among the three isomers in degassed DMSO at 373-413 K.

The cis-1 and the cis-2, and the trans complexes were prepared according to Refs. 6 and 7, respectively. The products of the isomerization were identified by the ^{1}H NMR spectra. Each of the isomers (5 mg, 0.01 mmol) was dissolved in 1 cm^3 of dimethyl-d$_6$ sulfoxide and transferred into an NMR tube. After the solution had been degassed by the freeze-pump-thaw method, the tube was sealed in a flame. The ^{1}H NMR spectra were measured at the temperature range from 303 to 403 K every 20 K, after keeping the desired temperature for 30 min. Using the cis-1 isomer as a starting species, the resonances due to the cis-2 isomer were observed at higher than 363 K. When the cis-2 isomer was used, the resonances due to the cis-1 isomer were also observed. In both cases, the resonances due to the trans isomer were too small to confirm the formation. Mole ratio of the trans isomer was very small in the equilibrium state as mentioned later. When the trans isomer was used, the resonances due to the cis-1 and cis-2 isomers were observed at higher than 363 K, and the resonances due to the trans isomer disappeared after keeping the temperature above 403 K for 30 min. The intensity ratio of the resonances due to the two cis isomers at 403 K was the same as that after cooling to 303 K. Figure 1 shows the ^{1}H NMR spectra of the cis-1 isomer at 303 K before heating (a) and after heating at 403 K (b), and that of the cis-2 isomer before heating (c).

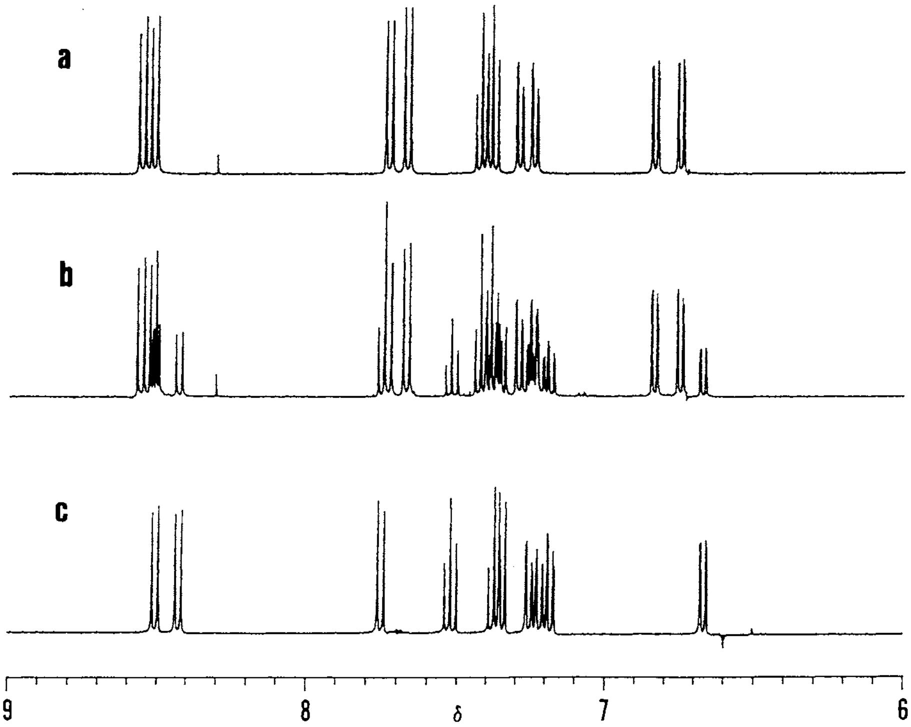


Fig. 1. ^{1}H NMR spectra of the cis-1 and cis-2 isomer at 303 K:
a) the cis-1 isomer before heating,
b) the cis-1 isomer after heating,
c) the cis-2 isomer before heating.

The mole ratio of the isomer was analyzed quantitatively by the use of HPLC (JASCO Trirotar-V, UVIDEC-100-IV, Finpak SIL C_{18} silica gel reversed phase column, detection wave length was 400 nm, eluent was 75 vol% MeOH-H_2O). The sample solution (0.3 cm^3, 2.1×10^{-3} mol dm^{-3}) was transferred into a glass tube. After the contents were bubbled by argon gas for 3 min, the tube was sealed in a flame. The tube was heated in an oil bath at 373, 393, or 413 K in the dark. The heated tube was removed from the oil bath, cooled in an ice-bath immediately to stop the isomerization and cut open, and the isomers were analyzed by HPLC. Three peaks were detected, and their retention times agreed with the authentic cis-2, cis-1, and trans isomers. The residual sample was chromatographically separated (Wakogel C-300, $\phi = 2.5 \times 15$ cm; eluent CH_2Cl_2). The ^1H NMR spectra for the three eluates also agreed with those for the authentic complexes. The time-course of the isomerization is shown in Fig.2 in which the trans isomer was heated at 393 K. The trans isomer was rapidly decreased with almost comparable increase of the cis-1 isomer, and the cis-2 isomer was gradually produced with increase of the cis-1 isomer. The reaction attained the equilibrium state after heating at 393 K for 24 h.

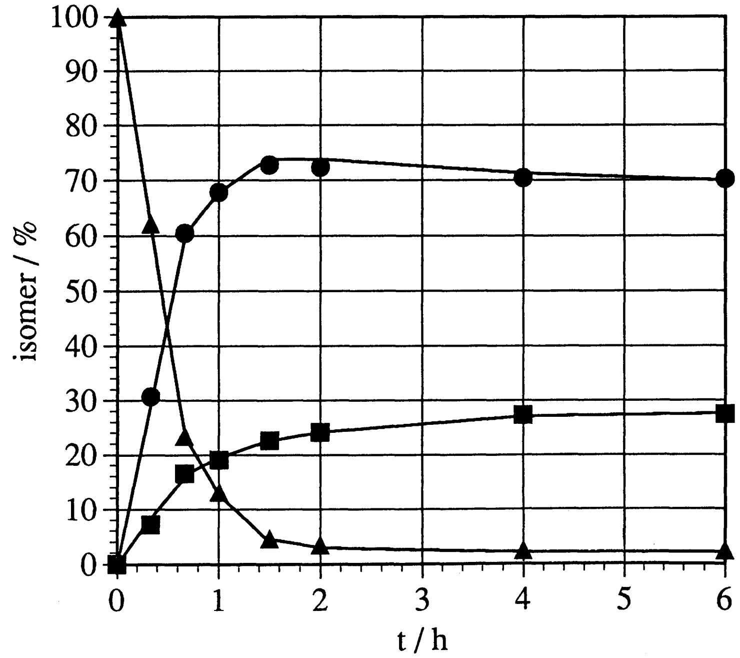


Fig.2. The time-course of the isomerization at 393 K.
(▲:trans, ●:cis-1, ■:cis-2; starting species was trans isomer)

The mole ratios of the three isomers, when each of the complexes was heated until no further change was detected (3 h-8 d), are shown in Table 1. The mole ratios did not depend on the starting species at the same temperature. The higher the temperature, the more rapidly the equilibrium state was reached. The mole ratio of the trans isomer increased and that of the cis-2 isomer decreased with the increase in temperature. At all of the examined temperatures, the side reaction (maximal 12 %) was observed, but the equilibrium mole ratio did not depend on the amount of the side reaction products.

Table 1. Equilibrium Mole Fractions of the Isomers

T/K	Starting species	Time/h[a)]	cis-1	cis-2	trans
413	cis-1	3	0.683(2)	0.284(1)	0.033(1)
	cis-2	3	0.687(4)	0.282(4)	0.031(1)
	trans	3	0.688(1)	0.280(2)	0.032(1)
393	cis-1	24	0.686(1)	0.290(1)	0.026(1)
	cis-2	48	0.683(3)	0.294(3)	0.024(1)
	trans	24	0.684(2)	0.291(3)	0.025(1)
373	cis-1	48	0.681(1)	0.301(1)	0.018(1)
	cis-2	192	0.677(3)	0.305(3)	0.017(1)
	trans	48	0.681(2)	0.302(3)	0.017(1)

a) Necessary time to attain the equilibrium state.

The reversible isomerization and the resultant equilibrium among the isomers for nitrosylruthenium(III) complexes were first observed at the present work. The investigation of the mechanism is in progress.

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