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Photoinduced Preparation of Geometrical Isomers of $[RuX(2mqn)_2(NO)]$ (X = Cl or Br; 2mqn = 2-Methyl-8-quinolinolate Ion) from Two Kinds of the Cis Isomers

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trans-$[RuX(2mqn)_2(NO)]$ (X = Cl or Br; 2mqn = 2-methyl-8-quinolinolate ion) was prepared photochemically from two kinds of the cis isomers, *cis(O,O),cis(N,N)*- and *cis(O,O),trans(N,N)*-$[RuX(2mqn)_2(NO)]$, in deoxygenated dichloromethane or dibromomethane. From the former cis isomer, the latter cis isomer was also prepared.

Cis - trans isomerizations induced by photochemical, thermal, or electrochemical reactions have been extensively studied for ruthenium(II) complexes with 2,2'-bipyridine,[1-3] triphenylphosphine and its derivatives.[4,5] For Ru^{II}-NO^+ type of nitrosylruthenium(3+) complexes, only a few cis to trans isomerizations induced by thermal reactions have been reported.[6-8] However, there has been no report on photoinduced cis to trans isomerization for nitrosylruthenium(3+) complexes although the photoinduced denitrosylation,[9,10] and the photoinduced hydroxide addition to the NO group of $[RuCl(bpy)_2(NO)]^{2+}$ [11] have been reported.

Recently, in the reaction of hydrous nitrosylruthenium(3+) chloride with 2-methyl-8-quinolinol in ethanol, we have isolated two kinds of *cis*-$[RuCl(2mqn)_2(NO)]$ (2mqn = 2-methyl-8-quinolinolate ion),[12] but the trans isomer could not be isolated under the conditions. We have now photochemically prepared *trans*-$[RuX(2mqn)_2(NO)]$ (X = Cl or Br) by the irradiation of the cis isomers, *cis(O,O),*-

trans(N,N)- and *cis(O,O),cis(N,N)*-[RuX(2mqn)$_2$(NO)][13] in deoxygenated dichloromethane or dibromomethane with a Xe-lamp. *cis(O,O),trans(N,N)*-[RuX(2mqn)$_2$(NO)] has been also prepared from *cis(O,O),cis(N,N)*-[RuX(2mqn)$_2$(NO)].

After *cis(O,O),trans(N,N)*-[RuCl(2mqn)$_2$(NO)] (chloro cis isomer-1) (0.11 mmol) had been dissolved in dichloromethane (20 cm^3) and then deaerated with nitrogen for 30 min, the solution in a Pyrex vessel was exposed to a Xe-lamp (300 W) for ca. 4 h. The reddish brown solution was darkened. After the solvent had been evaporated off, the residue was dissolved in dichloromethane. The solution was charged on a silica-gel column (Wakogel C-200, ϕ 1.5 cm x 15 cm), and the product was eluted with dichloromethane. The effluent of the first adsorption band was evaporated off to obtain a dark red product. This was found to be *trans*-[RuCl(2mqn)$_2$(NO)] (**A**) as shown later. Under the irradiation of another cis isomer, *cis(O,O),cis(N,N)*-[RuCl(2mqn)$_2$(NO)] (chloro cis isomer-2), in dichloromethane, the trans isomer was also obtained from the first adsorption band. The yield of **A** was ca. 25% based on the cis isomers. **A**: Anal. ($RuClC_{20}H_{16}N_3O_3$) C, H, N. IR(Nujol mull): 1830(vs) and 1806(w) cm^{-1} (νNO of the NO group); 314 cm^{-1} (νRu-Cl). UV(CH_2Cl_2): 24600 cm^{-1} (log ε 3.73).

trans-[RuBr(2mqn)$_2$(NO)] (**B**) was prepared from the corresponding cis-bromo complexes by a method similar to **A**. Dibromomethane was used as the solvent in irradiation and the product was eluted with dichloromethane. In column chromatography the trans isomer was obtained from the first adsorption band (yield: ca. 30%). **B**: Anal. ($RuBrC_{20}H_{16}N_3O_3$) C, H, N, Br. IR(Nujol mull): 1827(vs) and 1801(w) cm^{-1} (νNO of the NO group); 249 cm^{-1} (νRu-Br). UV(CH_2Cl_2): 24500 cm^{-1} (log ε 3.75).

FD mass spectra of **A** and **B** showed the molecular ions and its isotopic peaks in the regions of *m/z* 477 - 488 and 521 - 533, respectively. The observed relative intensities of the isotopic patterns agreed with the relative ones which were calculated in consideration of the isotopic abundances for all of the constituent elements.

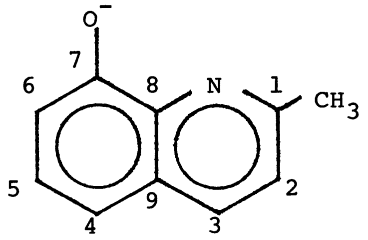
The ^1H and ^{13}C NMR spectra of **A** and **B** were measured in CD_2Cl_2. A signal attributable to the methyl hydrogens for **A** was observed at δ = 3.30 and for **B** at δ = 3.28, indicating that the two methyl groups in each complex are equivalent. Table 1 shows the chemical shifts and the assignments for ^{13}C NMR spectra of **A** and **B**. The assignments were made on the basis of those for 2-methyl-8-quinolinol by Howie et al.14) The ^{1}H and ^{13}C NMR data indicate that both A and B are the trans isomers. Considering the steric hindrance due to the methyl groups, both A and B are in a trans(O,O) and trans(N,N) configuration with respect to the two quinolinolato ligands.15)

The wave number of the NO stretching vibration for the trans isomers hardly changed upon the substitution of the halogeno ligand although the wave number of the NO stretching band for the $Ru^{II}-NO^+$ type complexes where the NO^+ is trans to the halogeno ligand generally decreases by ca. 10 - 30 cm^{-1} in the order of Cl > Br > I,16) because the NO^+ ligand is a π-acceptor while the π-donor ability of the halogeno ligand decreases in the order of I > Br > Cl.17) The NO stretching frequencies of A and B suggest that not only the σ and π effects to the Ru-Cl bonding but also those to the bonding of the Ru with 2-methyl-8-quinolinolato ligands cis to the NO group influence the bonding state of the NO of the trans isomers.6)

Table 1. ^{13}C NMR Chemical Shifts(δ) and Assignments of A and B

	Aa)	Bb)
C1 c)	162.8	163.1
C2	125.2	125.3
C3	140.0	139.9
C4	115.2	115.1
C5	129.7	129.6
C6	113.5	113.5
C7	168.3	168.4
C8	143.8	144.0
C9	129.1	128.9
Methyl	24.8	24.9

a) A: *trans*-[RuCl(2mqn)$_2$(NO)] (2mqn=2-methyl-8-quinolinolate ion).
b) B: *trans*-[RuBr(2mqn)$_2$(NO)].
c) Numbering of the carbons is



From the second adsorption band of the irradiated chloro or bromo cis isomer-1 solution, the original cis isomer was recovered. On the other hand, the product obtained from the second adsorption band of the irradiated chloro or bromo cis isomer-2 solution was found to be the chloro or bromo cis isomer-1 (yield: ca. 20%). From the third adsorption band, the original cis isomer was recovered. In conclusion, the cis isomer-1 and the trans isomer were prepared from the cis isomer-2 under the photoirradiation although from the cis isomer-1 only the trans isomer was formed.

These photoinduced preparations are the first example for a nitrosylruthenium(3+) complex. The investigation of the formation mechanism is in progress.

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15) The formal name of the trans isomer is *a*-halogeno-*bc,de*-bis(2-methyl-8-quinolinolato-*O,N*)-*f*-nitrosylruthenium.
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