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Preparation and Characterization of Tow kinds of *cis*-[RuCl(qn)$_2$NO] (Hqn= 4-Methyl-, 2,4-dimetyl-, 2-ethly-, or 5-chloro-8-quinolinol), and the Photoinduced Preparation of the *trans*-[RuCl(qn)$_2$NO] from the *cis*-Complex

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A mixture of hydrous trichloronitrosylruthenium(III) and 8-qulinolinol derivative (4-methyl-, 2,4-dimethyl-, 2-ethyl-, or 5-chloro-8-quinolinol) (mole ratio 1 : 4—5) was refluxed in ethyl alcohol in the dark to prepare two kinds of cis-type complexes, [RuCl(qn)$_2$NO] (Hqn=8-quinolinol derivative), cis-1 and cis-2, as major products. Using 2,4-dimethyl- or 2-ethyl-8-quinolinol, the trans complex was prepared in low yield with the cis-type complexes. The trans complex could be photochemically generated from the cis-1 complex in dichloromethane in good yield. The introduction of an alkyl group with an electrondonating nature to the 2-position in the quinolinol ring could induce the formation of the trans complex. The complexes were characterized by NMR, IR UV-vis, and field desorption mass spectrometries. From the cis-1-trans photoisomerization reaction in the presence of ^{15}NO (^{15}N atom %=99), a bond rupture between Ru and NO was found to be involved in the reaction.

The coordinating NO$^+$ group behaves as a weak σ-donor and a strong π-acceptor; its peculiarity affects the synthesis, reactivity, and structure of the {Ru(II)-NO$^+$} type of nitrosylruthenium(III) complexes.[1—5]

Geometrically isomeric pairs of [RuCl(qn)$_2$NO] (Hqn=8-quinolinol) and [RuCl(2mqn)$_2$NO] (H2mqn= 2-methyl-8-quinolinol), cis-1 and cis-2, were prepared from the reaction of hydrous trichloronitrosylruthenium(III) with the quinolinol (mole ratio 1 : 5) in ethanol in the dark, and the structures of the cis-1-(qn, 2mqn) and cis-2(2mqn) complexes were determined by X-ray analysis by us.[6,7] In the isomers, the Cl atom is cis to NO, and the O atom of one of the quinolinolato ligands is trans to NO. The cis-1 isomer is in a cis(O, O) and trans(N,N) configuration for the ligating atoms, N and O, of the quinolinolato ligands; the cis-2 isomer is in a cis(O,O) and cis(N,N) configuration, as shown in Fig. 1. Other neutral complexes containing the 8-quinolinolato ligands could not be prepared.

For the {Ru(II)-NO$^+$} type of nitrosylruthenium(III) complexes, some geometrical isomerizations induced by thermal reaction have been reported.[8—12] However, there has been no report concerning photoinduced geometrical isomerization for the nitrosylruthenium(III) complexes. Since the halide ion may behave as σ- and π-donors, there is a possibility for the preparation of trans type of isomers in which the halide ion is trans to the NO. Recently, we have reported that *trans*-[RuX-(2mqn)$_2$NO] (X=Cl or Br) can be photochemically prepared from the corresponding cis-1 and cis-2 isomers using a xenon lamp, and that the trans isomers have a trans(O,O) and trans(N,N) configuration for the ligating atoms in 2mqn, as shown in Fig. 1.[13] However, *trans*-[RuCl(qn)$_2$NO] could not be photochemically prepared from two kinds of cis isomers.

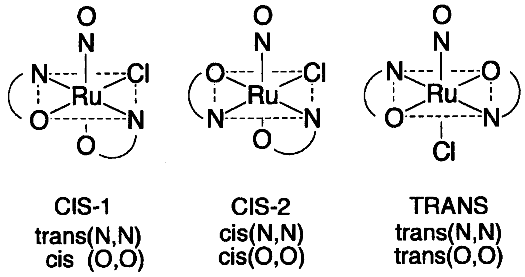


Fig. 1. Schematic structures of the *trans*-, *cis*-1, and *cis*-2 types of [RuCl(2mqn)$_2$NO] (H2mqn=2-methyl-8-quinolinol), Where the quinolinolato ions is represented by NO.

In this paper we report on the products produced from the reaction of hydrous trichloronitrosylruthenium(III) with 4-methyl-, 2,4-dimethyl-, 2-ethyl- or 5-chloro-8-quinolinol in a hot ethanol solution in the dark, as well as those from photochemical reactions using a xenon lamp in order to further examine the effect of introducing methyl, an ethyl group, or chlorine to the quinoline ring in the thermal and photochemical preparation reactions. The products have been characterized by NMR (^{1}H COSY), IR, UV-vis, as well as field desorption mass spectrometries.

Experimental

Measurements. The electronic spectra in dichloromethane were recorded on a Hitachi U-3410 spectrometer. The IR spectra in Nujol mull were measured with JASCO A-202 and JASCO IR-F spectrometers. The NMR spectra were recorded on a JEOL JNM GSX-400 spectrometer. CDCl$_3$ was used as a solvent and the chemical shifts were referred to an internal TMS. The FD mass spectra in the m/z range 0—1500 were measured by a combined FD unit on a Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi M-003 data-processing system. The complex was dissolved in dichloromethane and placed on a carbon emitter (an emitter current of 15—20 mA; a cathode potential of −4 kV; and an ion accelerating potential of 3 kV).

Materials. Hydrous trichloronitrosylruthenium(III) was prepared by the nitrosylation of $RuCl_3\cdot 3H_2O$ in a hydrochloric acid solution and evaporation of the solution to dryness.

4-Methyl-8-quinolinol (H4mqn),[14] 2,4-dimethyl-8-quinolinol (H24mqn),[14] and 2-ethyl-8-quinolinol (H2eqn)[15] were prepared according to the methods described in the literature. The formation of 8-quinolinols was confirmed with the elemental analyses, melting points, and NMR spectra. Commercial 5-chloro-8-quinolinol (H5cqn) was recrystallized from ethanol before use. The other reagents used were of special grade.

Preparation. **[RuCl(24mqn)$_2$NO]:** An ethanol solution of H24mqn (2.5 mmol in 20 cm^3) was added to an ethanol solution of hydrous trichloronitrosylruthenium(III) (0.5 mmol in 20 cm^3) dissolved perfectly upon heating. After the mixture had been refluxed for 2—5 h in the dark, the solvent was removed by a rotary evaporator. The dried residue was dissolved in dichloromethane (ca. 10 cm^3) and the insoluble solid was filtered off. The filtrate was charged on a silica gel column (Wakogel C-300, ϕ 2.5×10—15 cm). Three reddishbrown adsorption bands were eluted with dichloromethane. The eluates were collected and evaporated to dryness. The yields of the first, second, and third reddish-brown compounds (24mqn-a, 24mqn-b, and 24mqn-c) were 0.4, 50, and 10%, respectively. For 24mqn-b. Found: C, 51.9; H, 4.0; N, 8.1%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol): 1840 (ν NO), and 318 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25800 (log ε 3.83), 37700 (4.63), and 42000 cm^{-1} (4.59). ^{13}C NMR ($CDCl_3$) δ=167.84, 167.56, 162.83, 158.04, 149.49, 148.83, 143.39, 142.68, 129.26, 128.96, 128.93, 128.87, 125.24, 124.97, 115.19, 114.58, 111.22, 110.64, 27.34, 26.97, 19.07, and 18.82. For 24mqn-c. Found: C, 51.3; H, 3.8; N, 7.7%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol) 1840 (ν NO), and 322 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25800 (log ε 3.83), 37700 (4.61), and 41500 cm^{-1} (4.50). ^{13}C NMR ($CDCl_3$) δ=168.70, 164.31, 158.46, 156.91, 149.81, 149.01, 143.02, 142.82, 129.62, 129.57, 129.10, 128.73, 125.42, 123.91, 116.59, 115.54, 110.95, 110.23, 27.19, 23.90, 19.06, and 18.81.

[RuCl(2eqn)$_2$NO]: Preparation and chromatographic separation were carried out on the same scale and by a similar procedure as that for [RuCl(24mqn)$_2$NO]. The yields of the first, second, and third reddish-brown compounds (2eqn-a, 2eqn-b, and 2eqn-c) were 0.5, 42, and 7%, respectively. Upon refluxing under a dinitrogen atmosphere, the yields of the 2eqn-b and -c increased by about twice as much. For 2eqn-b. Found: C,50.9; H, 3.9; N, 8.2%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol) 1824 (ν NO) and 316 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25000 (log ε 3.74), 37300 (4.65), and 41800 cm^{-1} (4.53). ^{13}C NMR ($CDCl_3$) δ=168.93, 167.71, 164.21, 163.23, 143.61, 143.06, 140.35, 139.47, 129.59, 129.20, 129.08, 129.01, 123.23, 122.20, 115.32, 114.74 (2C), 114.26, 33.58, 32.62, 15.49, and 14.16. For 2eqn-c. Found: C, 52.0; H, 3.7; N, 7.9%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol) 1830 (ν NO) and 322 cm^{-1} (ν RuCl). UV (CH_2Cl_2): 25000 (log ε 3.76) 37200 (4.65) and 40800 cm^{-1} (4.53). ^{13}C NMR-($CDCl_3$) δ=168.62, 163.93, 163.58, 163.22, 143.51, 143.09, 140.38, 139.43, 129.93 (2C), 129.29, 128.69, 122.25, 121.09, 116.73, 115.73 114.54, 113.91, 33.56, 30.97, 13.87, and 13.60.

[RuCl(4mqn)$_2$NO]: An ethanol solution (100 cm^3) of 1.5 mmol of hydrous trichloronitrosylruthenium(III) and 6 mmol of H4mqn was refluxed in the dark; a similar chromatographic procedure to that for [RuCl(24mqn)$_2$NO] or [RuCl(2eqn)$_2$NO] was carried out using dichloromethane as an eluent. A PLC plate (20×20×0.2 cm, Merck) was used for further purification. The yields from the major first and second adsorption bands (4mqn-b and 4mqn-c) were 26 and 11%, respectively. For 4mqn-b. Found: C, 48.8; H, 3.3; N, 8.4%. Calcd for $RuClC_{20}H_{16}N_3O_3$: C, 49.7; H, 3.3; N, 8.7%. IR (Nujol) 1840 (ν NO) and 314 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25400 (log ε 3.90), 29900 (3.53), 38800 (4.61), and 41900 cm^{-1} (4.56). ^{13}C NMR ($CDCl_3$) δ=168.00, 165.00, 150.52, 149.12, 147.57, 145.92, 143.12, 142.23, 130.71, 130.67, 130.64, 130.39, 122.97, 122.43, 115.01, 114.87, 111.42, 110.53, 19.50, and 19.03. For 4mqn-c. Found: C, 49.5; H, 3.7; N, 8.8%. Calcd for $RuClC_{20}H_{16}N_3O_3$: C, 49.8; H, 3.3; N, 8.7%. IR (Nujol) 1840 (ν NO) and 310 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25400 (log ε 3.91), 29800 (3.59), and 39100 cm^{-1} (4.64). ^{13}C NMR ($CDCl_3$) δ=169.25, 164.03, 150.44, 149.38, 144.50, 144.19, 142.72, 142.36, 131.22, 131.19, 130.73, 130.47, 123.35, 121.90, 116.62, 115.50, 111.11, 110.28, 19.36, and 19.10.

[RuCl(5cqn)$_2$NO]: A similar procedure to that for [RuCl(4mqn)$_2$NO] was used for the synthesis. One mmol of hydrous trichloronitrosylruthenium(III) and 4 mmol of H5cqn were used. Two elution bands were obtained by chromatographic separation (Wakogel C-300 ϕ 2.5×15 cm) using dichloromethane as an eluent. The yields of the first and second adsorption bands (5cqn-b and 5cqn-c) were 24 and 20%, respectively. For 5cqn-b. Found: C, 41.1; H, 2.1; N, 7.9%. Calcd for $RuCl_3C_{18}H_{10}N_3O_3$: C, 41.3; H, 1.9; N, 8.1%. IR (Nujol) 1840 (ν NO) and 332 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 23800 (log ε 3.91), 29100 (3.56), 32100 (3.64), 37700 (4.55), and 42700 cm^{-1} (4.60). ^{13}C NMR ($CDCl_3$) δ=166.83, 163.71, 148.80, 147.21, 144.23, 143.24, 137.92, 136.66, 130.76, 130.47, 128.09, 128.04, 122.97, 122.52, 117.44, 116.54, 114.93, and 114.69. For 5cqn-c. Found: C, 40.6; H, 1.9; N, 7.9%. Calcd for $RuCl_3C_{18}H_{10}N_3O_3$: C, 41.3; H, 1.9; N, 8.1%. IR (Nujol) 1840 (ν NO) and 330 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 23700 (log ε 3.83), 29000 (3.54), 31700 (3.61), 37800 (4.53), and 40600 cm^{-1} (4.49). ^{13}C NMR ($CDCl_3$) δ=168.11, 162.70, 145.92, 145.54, 143.78, 143.33, 137.84, 136.88, 131.33, 131.30, 128.15, 127.90, 123.37, 122.10, 117.21, 116.44, 116.35, and 115.57.

[RuCl(2mqn)$_2$NO] and [RuCl(qn)$_2$NO]: cis-1 and cis-2, and *trans*-[RuCl(2mqn)$_2$NO] were prepared according to Refs. 6 and 13, respectively. cis-1 and cis-2 [RuCl(qn)$_2$NO] were prepared according to Ref. 7.

Photochemical Preparation. **24mqn-a:** After 24mqn-b (0.1 mmol) had been dissolved in dichloromethane (20 cm^3) and then degassed by the freeze-pump-thaw method, nitrogen monoxide (1 mmol) derived from potassium nitrate was trapped into a Pyrex vessel containing the solution. The solution was irradiated with a xenon lamp (300 W) through a combination of a UV cut filter (UV36, Hoya) and a water filter for about 4 h at room temperature. The solution was darkened. After the solvent and residual gas had been removed, the solid residue was dissolved in dichloromethane again. The solution was charged on a silica-gel column (Wakogel C-300, ϕ 1.5×10—20 cm), and then eluted with dichloromethane. From the first adsorption band 24mqn-a was obtained (yield 30%), and 24mqn-b was recovered from the second adsorption band (60%). In the absence of nitrogen monoxide, the yield of 24mqn-a was 5% and the recovery of 24mqn-b 30%. Found: C, 51.9; H, 3.8; N, 8.0%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol) 1828, 1805 (sh) (ν NO) and 315 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 25100 (log ε 3.87), 37300 (4.66), and 41500 cm^{-1} (4.58). ^{13}C NMR ($CDCl_3$) δ=168.10, 161.22, 149.01, 142.85, 129.10, 128.67, 125.28, 115.06, 109.74, 24.53, and 18.97.

2eqn-a: The starting compound was 2eqn-b. The preparation and chromatographic separation procedure were the same as for those for 24mqn-a. 2eqn-a was obtained from the first adsorption band (yield 25%) and 2eqn-b was recovered from the second adsorption band (70%). In the absence of nitrogen monoxide, the yield of 2eqn-a and the recovery of 2eqn-b were comparable to those in the presence of nitrogen monoxide. Found: C, 52.6; H, 3.4; N, 7.8%. Calcd for $RuClC_{22}H_{20}N_3O_3$: C, 51.7; H, 4.0; N, 8.2%. IR (Nujol) 1825, 1838 (sh), 1810 (sh) (ν NO), and 315 cm^{-1} (ν RuCl). UV (CH_2Cl_2) 24700 (log ε 3.73), 37000 (4.66), and 40700 cm^{-1} (4.52). ^{13}C NMR ($CDCl_3$) δ=168.09, 167.24, 143.14, 139.87, 129.48, 128.81, 123.49, 115.13, 113.14, 30.62, and 15.54.

Photochemical Reaction in the Presence of Nitrogen Monoxide. 4mqn and 5cqn Complexes: 4mqn-b, -c, 5cqn-b, or -c dissolved in dichloromethane was irradiated in the presence of ten equivalents of nitrogen monoxide, and the products were separated chromatographically by the procedure described in the previous section. Only the original complex was recovered and a portion of it was decomposed to form unidentified denitrosyleted green species. In the absence of nitrogen monoxide, both 4mqn-b and 5cqn-b were mostly decomposed with evolving nitrogen monoxide to form the green species.

24mqn and 2eqn Complexes: The same irradiation to 2eqn-c or 24mqn-c resulted in the decomposition of almost all of the starting complex, although 24mqn-a (2%) and 24mqn-b (4%), as well as 2eqn-a (2%) and 2eqn-b (10%) were generated. On the same irradiating to 24mqn-a or 2eqn-a, 24mqn-b or 2eqn-b was obtained (ca. 60%), and 30% of 24mqn-a or 2eqn-a was recovered.

Photochemical Isomerization in the Presence of Nitrogen [^{15}N] Monoxide. The same experiments for 2eqn-a and 2eqn-b were carried out in the presence of ^{15}NO (^{15}N atom %=99). The dichloromethane solution of 2eqn-a (0.05 mmol in 10 cm^3) or of 2eqn-b (0.1 mmol in 20 cm^3) was degassed and ten equivalents of ^{15}NO was added. Then, the solution was separately irradiated for 0.5, 1, 3, 5, or 10 h. During irradiation, the solution was stirred vigorously and the rather wide surface of the solution was contacted with gaseous NO. After irradiation, the solvent and residual gas were removed. The residue was dissolved in dichloromethane, and the starting complex and product were separated by a silica-gel column (Wakogel C-300, ϕ 2.5×8 cm) using dichloromethane as the eluent. For the eluates of each complex, the band strengths in the absorbance of the ^{14}NO and ^{15}NO stretching vibrations were measured in a CaF_2 liquid cell (0.5 mm length) by using a Perkin Elmer 1600 FT-IR spectrometer. The amounts of the starting complex and the product were determined spectrophotometrically.

Results and Discussion

The products of the preparations in the dark, as well as the photochemical preparation and reaction schemes are summarized in Table 1.

Identification of the Complexes. FD Mass Spectra: The FD mass spectra of 24mqn-a, -b, -c; 2eqn-a, -b, -c; 4mqn-b, -c, and 5cqn-b, -c showed the molecular ions as well as its isotopic peaks in the range *m*/*z* 505—517, 505—517, 477—488, and 517—530, respectively. Although no other peaks were observed in the *m*/*z* 0—1500 range, dipositive-charged molecular ions were observed for 24mqn-a and 24mqn-b. The observed relative intensities of the isotopic patterns agreed with those calculated in consideration of the isotopic abundance for all elements of the complexes. S.D.=0.011 for 24mqn-a, 0.013 for -b, 0.018 for -c; 0.030 for 2eqn-a, 0.022 for -b, 0.032 for -c; 0.018 for 4mqn-b, 0.037 for -c; and 0.054 for 5cqn-b, 0.030 for -c. The FD mass spectrum in the region of *m*/*z* 505—517 for 24mqn-b is shown in Fig. 2. The elemental analyses were also consistent with the chemical formulae proposed for the complexes. These suggest that the obtained complexes are the monomer and geometrical isomers of each other.

UV-vis Spectra: It has been reported that the $d\pi(Ru)\longrightarrow\pi^*(NO)$ charge-transfer band for the {Ru(II)-NO$^+$} type of nitrosylruthenium(III) complexes is observed in the 21000—23800 cm^{-1} range with $\varepsilon<50$ mol^{-1} dm^3 cm^{-1}.[8,16,17] The $d\pi(Ru)\longrightarrow\pi^*(qn)$ (Hqn= 8-quinolinol derivative) bands for the complexes were observed at about 24000—26000 cm^{-1} with log ε= 3.7—3.9. The $d\pi(Ru)\longrightarrow\pi^*(NO)$ bands were obscured by the more intense $d\pi(Ru)\longrightarrow\pi^*(qu)$ bands. The charge-transfer bands in the qn ligands were observed at ca. 37000—38000 cm^{-1} with log ε=4—5 and ca. 41000—42000 cm^{-1} with log ε=4.5, as observed for other nitrosylruthenium(III) complexes with the 8-quinolinolato ligand.[6,7]

IR Spectra: The NO stretching vibrations were observed in the 1800—1840 cm^{-1} region, indicating that the studied complexes were of the {Ru(II)-NO$^+$} type.[1—7] The Ru–Cl stretching bands were observed at 310—330 cm^{-1}.

^{13}C NMR Spectra: The spectra for 24mqn-a and 2eqn-a showed that two of the 8-quinolinolato ligands are geometrically equivalent, as observed for *trans*-[RuX(2mqn)$_2$NO] (X=Cl or Br; H2mqn=2-methyl-8-quinolinol).[13] Considering the steric hindrance due to the methyl or ethyl groups in the 2-position of the quinolinolato ligands, the a type of complexes are trans isomer with a trans(O,O) and trans(N,N) configuration, as shown in Fig. 1. On the other hand, the b and c types of complexes were shown to have geometrically

Table 1. Products of Preparations in the Dark,[a] and Photochemical Preparation and Reaction Schemes[b]

Ligand	Products of preparation in the dark (yield/%[c])			Ref.	Photochemical preparation and reaction schemes	Ref.
24mqn	a (0.4)	b (50)	c (10)	This work	c→b⇄a ↘decomposition	This work
2eqn	a (0.5)	b (42)	c (7)	This work	c→b⇄a ↘decomposition	This work
4mqn		b (26)	c (11)	This work	No isomerization	This work
5cqn		b (24)	c (20)	This work	No isomerization	This work
2mqn		cis-1 (42)	cis-2 (9)	6	cis-2→cis-1⇄trans[d]	13
qn		cis-1 (67)	cis-2 (10)	7	No isomerization[d]	7

a) In boiling ethyl alcohol. b) In dichloromethane in the presence of NO gas at room temperature: Light source, a xenon lamp (300 W). c) Based on hydrous trichloronitorosylruthenium(III). d) In dichloromethane in the absence of NO gas at room temperature: Light source, a xenon lamp (300 W).

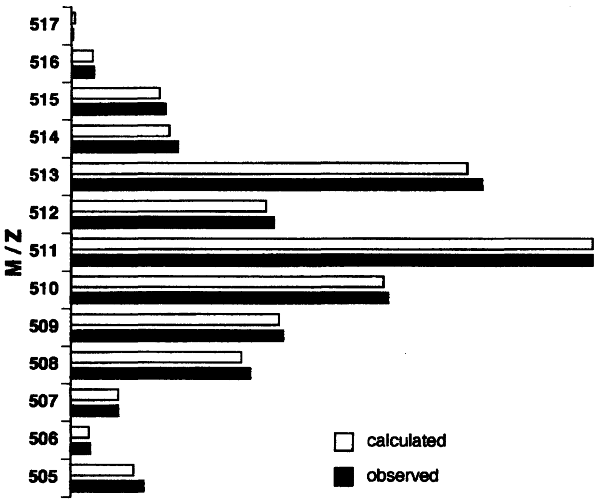


Fig. 2. FD mass spectra of *cis*-1 [RuCl(24mqn)$_2$NO] (24mqn-b) (H24mqn=2,4-dimethyl-8-quinolinol).

unequivalent 8-quinolinolato ligands. Thus, the b and c are cis isomers.

^{1}H NMR Spectra: The structures of two kinds of *cis*-[RuCl(2mqn)$_2$NO], cis-1 and cis-2 isomers, have been determined by the present authors.[6] However, no detailed measurments or discussion for the ^{1}H NMR spectra have yet been performed. On the basis of the ^{1}H COSY spectra for the cis-1 and cis-2 isomers, an attempt was made determine the structures of the b and c types of complexes. The observed resonances and their assignments are summarized in Table 2.

1) 2mqn Complexes. The signals due to the quinolinolato rings and the methyl groups were observed in the ranges of δ=6.8 to 8.5 and δ=1.8 to 3.4, respectively. The ^{1}H COSY spectrum of the ring proton region for the cis-1 isomer is shown in Fig. 3.

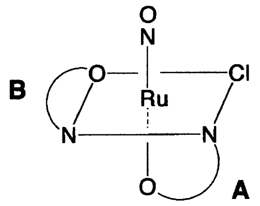
Five pairs of the signals were observed, and those pairs could be divided into two groups. One (δ=7.38, 7.39, 8.17, 8.23) was assigned to the 3- and 4-H protons, and another (δ=6.87, 6.92, 7.10, 7.14, 7.37, 7.39) to the 5-, 6-, and 7-H protons. The 24mqn complexes showed 3-H to be singlet; the signals were distinguishable from the others, and these 3-H protons were observed at δ=6.9—7.3 (see Table 2) and shifted to −0.23—+0.12 ppm from the 3-H proton of H24mqn. The 3-H protons of the 2mqn complexes are also expected to show the same tendency as do the 24mqn complexes. Two 3-H protons are in a similar environment, since *cis*-1 [RuCl(2mqn)$_2$NO] has a trans(N,N) configuration. Thus, the signals at δ=7.38 and 7.39 were assigned to the 3-H protons, and those at δ=8.17 and 8.23 to the 4-protons. The 6-H protons were assigned to δ=7.37 and 7.39 according to the splitting pattern. The 5-H protons are the most distant from the ligating atoms, similarly to the 4-H protons, and directed toward the outside of the complex. Hence, the δ values are nearly equal to those of the 5-H proton in H2mqn. Contrary, the 7-H protons are largely influenced by coordination. Thus, the 5-H protons were assigned to δ=7.10 and 7.14, and the 7-H protons to δ=6.87 and 6.92.

The ^{1}H COSY spectrum in the ring proton region for the cis-2 isomer is shown in Fig. 4. The assignments were performed in the same manner as that for the cis-1 isomer. The signals were classified to groups A and B, as shown in the Table 2. The δ values in group A were nearly equal to those observed for the cis-1 isomer. In group B, although the δ=8.15 due to 4-H and 7.12 due to the 5-H protons were nearly equal to those for the cis-1 isomer, the δ=7.04 (3-H), 7.54 (6-H), and 7.50 (7-H) were largely shifted from those for the cis-1 isomer. In addition, the δ=1.83 due to the CH$_3$ group in group B shifted largely to upfield, as compared with δ=3.16, due to another CH$_3$ group. These shifts were caused

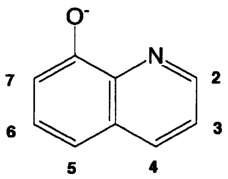
Table 2. ^{1}H NMR Data of Nitrosylruthenium Complexes

Complex	Group[a)]	2-H	3-H	4-H	5-H	6-H	7-H[b)]	CH_3	CH_3	CH_2
H2mqn			7.27	8.00	7.26	7.36	7.14	2.70		
trans(2mqn)			7.38	8.43	7.23	7.45	7.08	3.32		
cis-1(2mqn)			7.39	8.23	7.14	7.39	6.87	3.33		
			7.38	8.17	7.10	7.37	6.92	3.09		
cis-2(2mqn)	A		7.42	8.18	7.10	7.36	6.85	3.16		
	B		7.04	8.15	7.12	7.54	7.50	1.83		
	Δ		−0.38	−0.03	+0.02	+0.18	+0.65	−1.33		
H24mqn			7.13		7.39	7.38	7.12	2.66	2.63	
24mqn-a			7.24		7.22	7.46	7.15	3.27	2.71	
24mqn-b			7.25		7.21	7.39	6.85	3.27	2.72	
			7.25		7.18	7.37	6.91	3.03	2.72	
24mqn-c	A		7.27		7.16	7.35	6.83	3.09	2.73	
	B		6.90		7.18	7.53	7.48	1.79	2.64	
	Δ		−0.37		+0.02	+0.18	+0.65	−1.30	−0.09	
H2eqn			7.31	8.04	7.28	7.37	7.14	1.40		2.99
2eqn-a			7.42	8.23	7.21	7.46	7.07	1.53		3.73
2eqn-b			7.45	8.27	7.14	7.40	6.94	1.61		3.89 3.72
			7.44	8.22	7.11	7.38	6.90	1.47		3.33
2eqn-c	A		7.49	8.22	7.09	7.35	6.86	1.65		3.47 3.35
	B		7.09	8.17	7.11	7.53	7.50	0.55		2.37 2.00
	Δ		−0.40	−0.05	+0.02	+0.18	+0.64	−1.10		
H4mqn		8.71	7.41		7.49	7.47	7.10	2.66		
4mqn-b		9.23	7.47		7.30	7.52	7.08	2.83		
		8.51	7.41		7.29	7.51	6.96	2.81		
4mqn-c	A	8.55	7.48		7.28	7.50	6.94	2.84		
	B	7.19	7.00		7.25	7.64	7.51	2.69		
	Δ	−1.36	−0.48		+0.03	+0.14	+0.57	−0.15		
H5cqn		8.83	7.57	8.53		7.52	7.11			
5cqn-b		9.41	7.76	8.81		7.58	7.01			
		8.69	7.71	8.71		7.57	6.89			
5cqn-c	A	8.75	7.80	8.76		7.57	6.89			
	B	7.40	7.34	8.67		7.71	7.44			
	Δ	−1.35	−0.46	−0.09		+0.14	+0.55			
Hqn		8.77	7.40	8.12	7.31	7.44	7.58			
qn-b(cis-1)		9.37	7.63	8.45	7.24	7.52	7.10			
		8.65	7.57	8.35	7.23	7.51	6.98			
qn-c	A	8.70	7.65	8.40	7.23	7.51	6.97			
	B	7.31	7.18	8.30	7.19	7.64	7.53			
	Δ	−1.32	−0.47	−0.10	+0.04	+0.13	+0.56			

a) A and B for cis-2.



b) Numbering of the hydrogens is



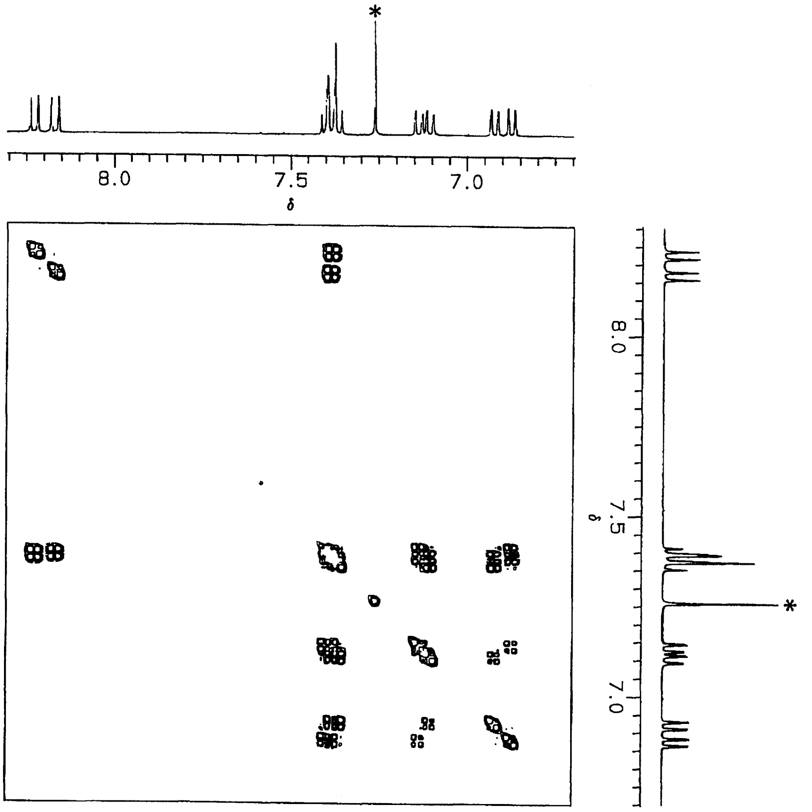


Fig. 3. ^{1}H COSY spectrum of *cis*-1 [RuCl(2mqn)$_2$NO] (H2mqn=2-methyl-8-quinolinol). *: solvent.

by a paramagnetic ring-current effect of the quinolinolato ring, as expected form the cis(N,N) and cis(O,O) configuration of the cis-2 isomer. Thus, group A could be assigned to quinolinolato ring A, whose O atom coordinates in trans to the NO, and group B to another quinolinolato ring B (see Table 2). The signal due to the 3-H proton in ring B shifted to upfield by 0.38 ppm, as compared with that in ring A. The 6-H and 7-H protons in ring B shifted downfield by 0.18 and 0.65 ppm, respectively. Because the 4-H and 5-H protons exist far away from the ligating atoms, and are directed to the outside of the complex, their δ values hardly changed with the structure change from the cis-1 to the cis-2 isomer.

These results show that the ^{1}H NMR spectra of the cis-1 and cis-2 isomers reflect the structure of the complexes. The resonances due to two kinds of the quinolinolato ligands of the cis-1 complex could not be distinctively assigned because the two quinolinolato protons are in a similar environment.

2) 24mqn and 2eqn Complexes. The data show that 24mpn-b and 2eqn-b contain two kinds of the quinolinolato ligands. The two-quinolinolato protons were resonated near to each other. The tendency was the same as that of *cis*-1[RuCl(2mqn)$_2$NO]. The 24mqn-c and 2eqn-c spectra were also classified to groups A and B. The difference (Δ) between the signals of group A and those of group B have a strong resemblance to the difference in *cis*-2[RuCl(2mqn)$_2$NO]. It is thus concluded that 24mqn-b and 2eqn-b have a trans(N,N) and cis(O,O), and that 24mqn-c and 2eqn-c have a cis(N,N) and cis(O,O) configuration.

The ethyl region spectra of the 2eqn complexes are shown in Fig. 5. The CH$_2$ protons of one of the ethyl groups for 2eqn-b and those of the two ethyl groups for 2eqn-c were observed as multiplets. Each of the CH$_2$ protons in 2eqn-b resonated at different frequencies, and the geminal-type coupling ($J=15$ Hz) was observed, since the CH$_2$ group of ring A trans to the NO can not rotate freely. For 2eqn-c, the CH$_2$ group of ring B, in addition to the CH$_2$ group of ring A, also can not rotate because of a steric hindrance of ring A. The ring-current effect of ring A also caused upfield shifts of the resonances due to the CH$_2$ and the CH$_3$ groups in ring B.

The spectra of 24mqn-a and 2eqn-a showed that two of the quinolinolato ligands coordinated equivalently to the ruthenium, indicating that 24mqn-a and 2eqn-a have trans(N,N) and trans(O,O) configurations. The CH$_2$ protons of 2eqn-a also split into a multiplet, which shows the presence of a steric hindrance between the ethyl group and the other quinolinolato ring.

3) 4mqn and 5cqn Complexes. 4mqn-b and 5cqn-b as well as 4mqn-c and 5cqn-c showed spectral

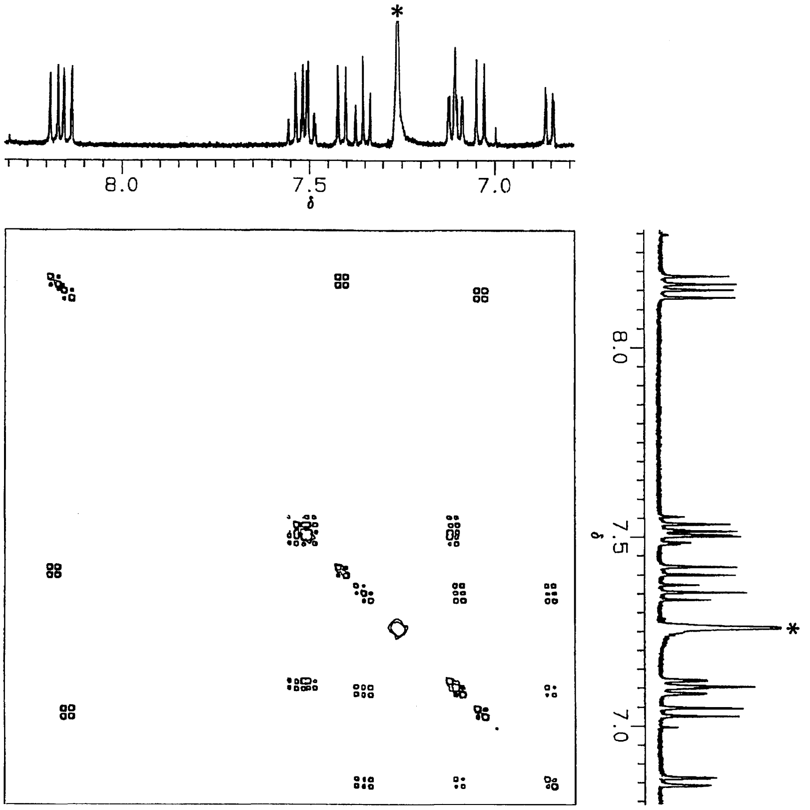


Fig. 4. ^{1}H COSY spectrum of *cis*-2 [RuCl(2mqn)$_2$NO] (H2mqn=2-methyl-8-quinolinol). *: solvent.

patterns that are characteristic of the cis-1 and cis-2 isomers, respectively. The 2-H protons were observed at δ=8.51 and 9.23 for 4mqn-b and at δ=7.19 and 8.55 for 4mqn-c. Since the 2-H protons exist in the nearest position from the ligating atom, these signals are very sensitive to the effect of the neighboring ligand, as observed for the 6-H protons of the Ru-bpy complexes.[18] The upfield (δ=7.19, −1.36 from the δ=8.55) shift was caused by a paramagnetic ring-current effect of ring A in 4mqn-c. The downfield (δ=9.23, +0.72 from the δ=8.51) shift may be caused by an interaction with the Cl$^-$ ligand in 4mqn-b. Thus, the resonances at δ=7.19 for 4mqn-c and δ=9.23 for 4mqn-b were assigned to the 2-H proton in ring B. The same phenomena were also observed for 5cqn-b and -c.

The spectra of qn-b and qn-c were also shown to be of the cis-1 and cis-2 types, respectively. The NMR data of *cis*-1[RuCl(qn)$_2$NO] (qn-b) support the structure determined by an X-ray crystal analysis.[7]

Thus, the b type of complexes was assigned to the cis-1 type and the c type of complexes to the cis-2 type from detailed analyses of the NMR spectra.

Preparation in the Dark. As shown in Table 1, by using 8-quinolinol or 2-methyl-8-quinolinol, the cis-1 and cis-2 type of complexes were prepared through a thermal reaction; the trans isomer, however, could not be prepared.[6,7] The same result was obtained using 4-methyl- or 5-chloro-8-quinolinol. On the other hand, the trans isomer was prepared in low yield (ca. 0.5%) using 2,4-dimethyl- or 2-ethyl-8-quinolinol. The cis complexes of 24mqn or 2eqn did not isomerize upon boiling in CH$_2$Cl$_2$. When the cis-1 isomer of 2eqn was refluxed in ethyl alcohol in the dark, the trans isomer was prepared in ca. 0.4% yield. In the presence of H2eqn, the trans and cis-2 isomers were confirmed to be prepared in the refluxed solution by HPLC analysis. These facts suggest that a further addition of the CH$_3$ group or an introduction of the C$_2$H$_5$ group with its electron-donating nature to the 2-position in the quinolinol ring, or an increase of the reaction temperature, prompts the formation of a trans isomer.

Photochemical Preparation and Reaction. 24mqn and 2eqn Complexes: An attempt was made to prepare the trans isomers photochemically in CH$_2$Cl$_2$. The trans isomer, 24mqn-a or 2eqn-a, could be prepared in good yield (ca. 30%), and the starting cis-1 isomer, 24mqn-b or 2eqn-b, was recovered (ca. 60%) under reaction in the presence of NO. Upon irradiating to the trans isomer (24mqn-a or 2eqn-a) the cis-1 isomer (24mqn-b or 2eqn-b) was obtained in ca. 60% yield, and 30% of 24mqn-a or 2eqn-a was recovered. This trans-cis-1 reversible isomerizations of 24mqn and 2eqn were similar to those of [RuX(2mqn)$_2$NO] (X=Cl or Br),[13] and the yields of the trans isomer from the cis-1 isomer and of the cis-1 isomer from the trans isomer were comparable to those for the corresponding 2mqn complexes.

From the cis-2 isomers of 24mqn and 2eqn, small amounts of the trans isomer of 24mqn (2%) and the cis-

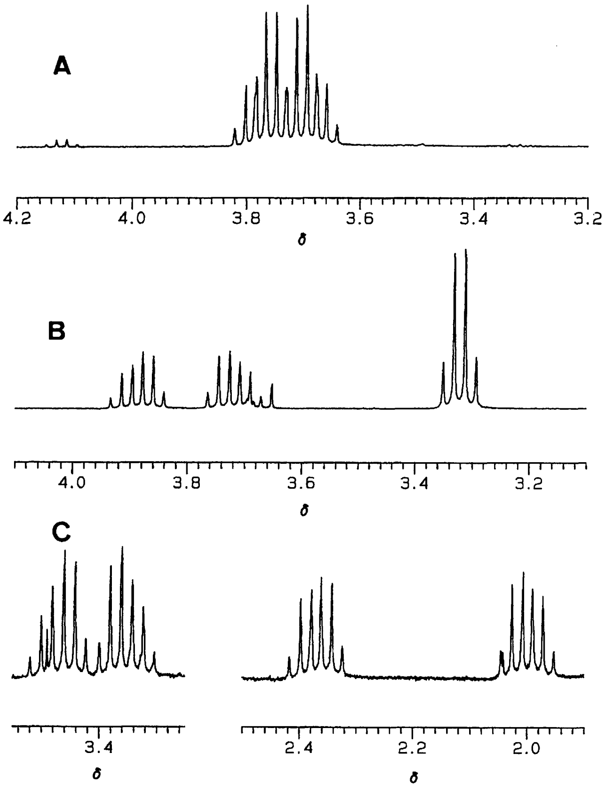


Fig. 5. ^1H NMR spectra in the CH_2 group region of 2eqn complexes. A: 2eqn-a, B: 2eqn-b, C: 2eqn-c.

Table 3. Isomerization Yield and Area Ratio in Absorbance of ^{15}NO-stretching band to ^{14}NO-one for cis–trans Isomerization of *cis*- and *trans*-[RuCl(2eqn)$_2$NO] (H2eqn=2-ethyl-8-quinolinol) [a]

cis to trans Isomerization

Irradiation time/h	Yield/% (trans)	Recovery/% (cis-1)	Area ratio (trans)	($^{15}NO/^{14}NO$) (cis-1)
0.5	12	78	23	0.5
1	13	84	23	0.5
3	23	66	18	4.3
5	25	64	9.3	7.6
10	24	54	8.7	8.4

trans to cis Isomerization

Irradiation time/h	Yield/% (cis-1)	Recovery/% (trans)	Area ratio (cis-1)	($^{15}NO/^{14}NO$) (trans)
0.5	39	45	14	0.7
1	50	33	12	1.8
3	61	25	11	8.1
5	62	25	8.1	8.0

[a] Mole ratio of the complex to ^{15}NO (^{15}N atom %=99)=1:10.

1 isomer of 24mqn (2%), as well as the trans isomer of 2eqn (4%) and the cis-1 isomer of 2eqn (10%), were prepared; however, almost all of the cis-2 isomers decomposed, even in the presence of NO. In both cases of *cis*-2 [RuCl(2mqn)$_2$NO] and *cis*-2 [RuBr(2mqn)$_2$NO], the trans and cis-1 isomers were prepared in ca. 25% yields and 30% of the cis-2 isomer was recovered.[13] The cis-2 isomers of the 24mqn and 2eqn complexes seem to be more unstable than the cis-2 isomer of 2mqn complex.

4mqn and 5cqn Complexes: From the cis isomers, 4mqn-b, -c, and 5cqn-b, -c, the corresponding trans isomer could not be prepared and the original complex was recovered, even in the presence of NO.

Photochemical trans-cis-1 Isomerization in the Presence of Nitrogen[^{15}N] Monoxide. As shown in the previous section, reversible isomerization reactions between the trans and the cis-1 complexes of 24mqn and 2eqn were observed. The mechanism of the cis-1-trans isomerization for the 2eqn complexes was preliminarily explored. Table 3 shows the results of the photochemical reaction in the presence of ^{15}NO. In spite of the strict experimental procedure, increases in the irradiation time caused a decomposition of the complex during the cis-to-trans isomerization; during the trans-to-cis isomerization the decomposition of the complex was observed from the initial irradiation. The ^{14}NO and ^{15}NO stretching vibrations of the trans isomer in dichloromethane were observed at 1843 and 1806 cm^{-1}, and those of the cis-1 isomer were also observed at 1843 and 1806 cm^{-1}, respectively.

The longer was the irradiation time, the greater was the degree of isomerization increased, to reach a photostationary state. When the irradiation took place for only a short time, the ratio of ^{15}NO to ^{14}NO for the isomerization product was larger than 10, and that for the starting materials was smaller than 10. The ratio of ^{15}NO to ^{14}NO for the product became almost equal to that for the starting materials, and the photostationary state was achieved after the 5—10 h-irradiation.

The cis-1-to-trans isomerization reaction for the 24mqn complex was carried out on the same scale (the cis-1 isomer, 0.100 mmol in 20 cm^3 of CH_2Cl_2; the mole ratio of the cis-1 isomer to ^{15}NO was 1 : 10). The yield of the trans isomer was 27%, and 67% of the cis-1 isomer was recovered after the 4.5 h-irradiation, at which point the photostationary state was thought to have been established. The ^{15}NO and ^{14}NO stretching bands were observed for both the trans and the cis-1; the ratio ($^{15}NO/^{14}NO$) was 6 for both of the isomers.

These results suggest that the photostationary state is present and a Ru–NO bond rupture takes part in both the cis-to-trans and the trans-to-cis isomerizations; a further investigation, however, is necessary to elucidate the reaction mechanism.

Conclusion

Concerning the reaction of hydrous trichloronitrosylruthenium(III) with 2,4-dimetyl- or 2-ethyl-8-quinolinol in hot ethyl alcohol in the dark, a small amount of the trans isomer was prepared along with the cis isomers. A further introduction of the methyl group to the 4-position in 2-methyl-8-quinolinol and an introduction of the ethyl group with a better electron-donating nature than that of the methyl group to the 2-position in 8-quinolinol seem to be involved in the preparation of the trans isomer upon a thermal reaction. The introduction of an electron-donating group, such as a methyl or ethyl group, to the 2-position in the 8-quinolinolato ligand seems to cause a photoinduced cis-trans isomerization.

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References

1) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

2) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975).

3) F. Bottomley, *Coord. Chem. Rev.*, **26**, 7 (1978).

4) F. Bottomley, "Reactions of Nitrosyls," in "Reactions of Coordinating Ligands," ed by P. S. Braterman, Plenum Press, New York (1989), Vol. 2, pp. 115—222.

5) D. M. P. Mingos and D. J. Sherman, "Transition Metal Nitrosyl Complexes," in "Advances in Inorganic Chemistry," ed by A. G. Sykes, Academic Press, New York (1989), Vol. 34, pp. 293—377.

6) Y. Kamata, T. Kimura, R. Hirota, E. Miki, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **60**, 1343 (1987).

7) Y. Kamata, E. Miki, R. Hirota, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **61**, 594 (1988).

8) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).

9) F. Bottomley, E. M. R. Kiremine, and S.G. Clarkson, *J. Chem. Soc., Dalton Trans.*, **1975**, 1909.

10) T. Fukuchi, E. Miki, K. Mizumachi, and T. Ishimori, *Chem. Lett.*, **1987**, 1133.

11) A. B. Nikol'skii, A. M. Popov, T. S. Repinskaya, Yu. N. Kukushkin, and M. B. Egorova, *Sov. J. Coord. Chem.* (*Engl. Transl.*), **13**, 529 (1987).

12) A. B. Nikol'skii, A. M. Popov, M. B. Egorova, and V. V. Khorunzhii, *Sov. J. Coord. Chem.* (*Engl. Transl.*), **15**, 800 (1989).

13) H. Kamata, Y. Konishi, Y. Kamata, E. Miki, K. Mizumachi, T. Ishimori, T. Nagai, and M. Tanaka, *Chem. Lett.*, **1988**, 159.

14) J. P. Phillips, R. L. Elbinger, and L. L. Merritt, Jr., *J. Am. Chem. Soc.*, **71**, 3986 (1949).

15) W. Buchowiecki and J. Zjawiony, *J. Prakt. Chem.*, **327**, 1015 (1985).

16) A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, **11**, 880 (1977).

17) R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **16**, 574 (1977).

18) B. E. Buchanan, P. Degn, J. M. P. Velasco, H. Hughes, B. S. Creaven, C. Long, J. G. Vos, R. A. Howie, R. Hage, J. H. Diemen, J. G. Haasnoot, and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, **1992**, 1177.