Crystal and Molecular Structures of Two Isomers for Chlorobis(2-methyl-8-quinolinolato)nitrosylruthenium(III)

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Two isomers of [RuCl(2mqn)$_2$(NO)] (2mqn=2-methyl-8-quinolinolate ion) were isolated and their crystal structures were determined by X-ray diffraction. In both the isomers, the Cl atom lies cis to the NO group and the O atom of one of the quinolinolato ligands lies trans to the NO group. One of the two isomers, (1), is in cis(O,O) and trans(N,N) configuration for the two quinolinolato ligands, another, (2), being in cis(O,O) and cis(N,N). Crystal data: 1, space group $P2_1/c$ (monoclinic), a=7.412(1), b=27.241(6), c=9.752(1) Å, β=105.49(1)°; 2, space group $P2_1/c$ (monoclinic), a=7.157(2), b=20.205(4), c=13.359(3) Å, β=107.70(2)°. The final R values for 1 and 2 are 0.044 for non-hydrogen atoms and 0.037 for all the atoms, respectively. The coordination geometries of 1 and 2 are distorted octahedron. The interatomic distances are qualitatively discussed on the basis of π- and σ-bonding abilities of the NO group, the Cl, and the coordinating atoms, N and O, of the quinolinolato ligands.

There has been a report for the solvent extraction of nitrosylruthenium(III) with 8-quinolinol.[1] However, there has been no report on the isolation of nitrosylruthenium(III) complexes with 8-quinolinol or its derivatives. In the reactions of nitrosylruthenium(III) species with 2-methyl-8-quinolinol in ethanol, we isolated two geometrical isomers of [RuCl(2mqn)$_2$(NO)] (2mqn=2-methyl-8-quinolinolate ion). The crystal structures of the isomers were determined by X-ray diffraction. Further, the isomers were characterized by NMR and IR.

Experimental

Materials. Hydrated trichloronitrosylruthenium(III) (Ru=30.8%) was prepared by nitrosylation of commercial $RuCl_3 \cdot 3H_2O$ in a hydrochloric acid solution and evaporation of the solution.[2] The other reagents used were of special grade.

Preparation and Separation of the Isomers of Chlorobis(2-methyl-8-quinolinolato)nitrosylruthenium(III). An ethanol solution of 2-methyl-8-quinolinol (5.4 mmol in 80 cm^3) was added to an ethanol solution of the hydrated trichloronitrosylruthenium(III) (0.90 mmol in 10 cm^3). After the mixture solution had been refluxed for 5 h, it was allowed to stand overnight at room temperature, and evaporated with a rotary evaporator. The dried residue was dissolved in 50 cm^3 of dichloromethane. The dark red solution was added on the silica-gel column (Wakogel C-200, ϕ 3 cm×15 cm). Two red adsorption bands were eluted with dichloromethane. The species in the front and back bands were named **1** and **2**, respectively. The eluates containing **1** and **2** were separately concentrated with a rotary evaporator to a small volume and dried in the open air to obtain reddish brown **1** and dark reddish brown **2**. Yield: 42% for **1** (based on the ruthenium compound); and 9% for **2**. Found: Ru, 21.3; Cl, 7.6; C, 49.6; H, 3.3; N, 8.8% for **1**; Ru, 20.9; Cl, 7.7; C, 49.8; H, 3.2; N, 8.7% for **2**. Calcd for [RuCl(C$_{10}$H$_8$NO)$_2$(NO)]: Ru, 20.9; Cl, 7.3; C, 49.7; H, 3.4; N, 8.7%. The ruthenium was determined by the ruthenate method.[3] The C, H, N, and Cl were analyzed by the Organic Analysis Center of the Institute of Physical and Chemical Research.

Table 1. Crystallographic Data for the Complexes **1** and **2**

Complex	1	2
Formula	$RuClO_3N_3C_{20}H_{16}$	$RuClO_3N_3C_{20}H_{16}$
M_w	482.9	482.9
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	7.412(1)	7.157(2)
b/Å	27.241(6)	20.205(4)
c/Å	9.752(1)	13.359(3)
β/°	105.49(1)	107.70(2)
V/Å^3	1897.5(5)	1840.3(7)
Z	4	4
D_m/g cm^{-3}	1.68	1.72
D_c/g cm^{-3}	1.691	1.743
R	0.044	0.037

X-Ray Crystallographic Analysis. The crystalline samples were prepared by concentrating a dilute CH_2Cl_2-$CH_3COOC_2H_5$ solution of **1**, and a dilute CH_2Cl_2-CH_3CN solution of **2** in the open air. The crystals of **1** with dimensions 0.1×0.15×0.25 mm and **2** with 0.1×0.2×0.55 mm were used for intensity measurements. X-Ray diffraction data were collected on a Rigaku AFC-4 automated four-circle diffractometer at the X-Ray Analysis Center of the Institute of Physical and Chemical Research with graphite-monochromatized Mo$K\alpha$ radiation (λ=0.71073 Å). The space groups were determined with the observed systematic absences, and the lattice parameters were determined by the least-squares refinement using ten high-angle reflections for **1**, and twenty for **2**. The crystal data are shown in Table 1. Intensities were measured by ω—2θ scanning techniques at a ω-scanning speed of 4°/min. The diffraction intensities were monitored by three standard reflections for every 100 reflections recorded. No signs of decomposition of the crystals were observed. The ordinary Lorenz and polarization corrections were applied, but no absorption correction was applied. Independent reflections with $|F_o|>3\sigma(|F_o|)$, 2268 ($2\theta<50°$) and 4702 ($2\theta<70°$) reflections for **1** and **2**, respectively, were used for the structure determinations. Calculations were performed on a FACOM 230-75 computer for **1** and a FACOM M-200 computer for **2** using the UNICS-III Program System.[4] The structures were solved by the heavy atom method,

Table 2. Atomic and Thermal Parameters with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
[RuCl(2mqn)$_2$(NO)] (**1**)$^{a)}$					[RuCl(2mqn)$_2$(NO)] (**2**)$^{a)}$				
Ru	3417(1)	1240(1)	1948(1)	3.0	Ru	1704(0)	2037(0)	1516(0)	2.3
Cl	5717(4)	1126(1)	4149(3)	5.9	Cl	3313(1)	1131(0)	2559(1)	3.4
O(1)	589(11)	1101(3)	3380(8)	8.1	O(1)	−299(5)	2470(2)	2977(3)	5.6
O(2)	1790(7)	1426(2)	24(5)	3.4	O(2)	4050(3)	2618(1)	2113(2)	3.0
O(3)	5494(6)	1256(2)	1040(5)	3.5	O(3)	3015(3)	1857(1)	434(2)	2.8
N(1)	1604(10)	1168(3)	2803(7)	4.8	N(1)	528(4)	2271(1)	2420(2)	3.1
N(2)	2960(8)	527(2)	1072(6)	3.3	N(2)	621(3)	2896(1)	630(2)	2.5
N(3)	4062(8)	1991(2)	2207(6)	3.3	N(3)	−231(3)	1316(1)	616(2)	2.4
C(1)	3471(11)	80(3)	1602(9)	3.7	C(1)	−1149(4)	3059(2)	−8(2)	2.8
C(2)	3194(12)	−340(3)	708(10)	4.3	C(2)	−1461(5)	3674(2)	−531(3)	3.5
C(3)	2344(11)	−301(3)	−698(9)	4.1	C(3)	40(6)	4113(2)	−399(3)	3.8
C(4)	711(12)	238(3)	−2740(9)	4.7	C(4)	3513(6)	4407(2)	522(3)	4.4
C(5)	90(12)	695(4)	−3220(9)	4.8	C(5)	5243(6)	4228(2)	1250(3)	4.4
C(6)	438(11)	1108(3)	−2295(8)	3.9	C(6)	5479(5)	3623(2)	1778(3)	3.5
C(7)	1419(10)	1048(3)	−880(8)	3.2	C(7)	3926(4)	3178(2)	1585(2)	2.8
C(8)	2037(9)	573(3)	−367(8)	3.1	C(8)	2139(4)	3351(2)	812(2)	2.6
C(9)	1691(10)	165(3)	−1299(8)	3.6	C(9)	1905(5)	3966(2)	291(3)	3.3
C(10)	4337(13)	17(3)	3192(9)	4.8	C(10)	−2845(5)	2595(2)	−194(3)	3.7
C(11)	3323(11)	2356(3)	2796(8)	4.4	C(11)	−1775(4)	1015(2)	777(3)	2.9
C(12)	3893(13)	2853(3)	2661(9)	4.8	C(12)	−2872(5)	558(2)	34(3)	3.5
C(13)	5205(14)	2962(3)	1990(10)	5.2	C(13)	−2370(5)	382(2)	−822(3)	3.7
C(14)	7524(12)	2659(4)	717(10)	5.0	C(14)	65(6)	506(2)	−1832(3)	3.5
C(15)	8297(12)	2264(4)	247(10)	5.3	C(15)	1731(6)	810(2)	−1901(3)	3.7
C(16)	7678(11)	1777(3)	370(8)	4.1	C(16)	2750(5)	1276(2)	−1161(3)	3.1
C(17)	6209(10)	1697(2)	978(8)	3.2	C(17)	2088(4)	1438(2)	−319(2)	2.5
C(18)	5442(10)	2102(3)	1533(8)	3.2	C(18)	355(4)	1135(1)	−242(2)	2.4
C(19)	6062(12)	2589(3)	1403(9)	4.3	C(19)	−675(5)	668(2)	−991(2)	2.9
C(20)	1901(13)	2238(4)	3604(10)	5.6	C(20)	−2358(6)	1164(2)	1731(3)	4.0

a) Atomic parameters are multiplied by 10^4.

and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques. The final R values were 0.044 for **1** with anisotropic temperature factors for non-hydrogen atoms, and 0.037 for **2** with anisotropic temperature factors for non-hydrogen atoms and isotropic for hydrogen atoms. The atomic parameters of **1** and **2** are given in Table 2.

The complete F_o—F_c data are deposited as Document No. 8727 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Other Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM FX-90Q spectrometer. CD_2Cl_2 was used as solvent and the chemical shifts were referred to internal TMS. IR spectra were measured by the Nujol mull method with JASCO A-202 spectrometer. Electronic spectra in dichloromethane were recorded on a HITACHI 340 spectrometer. Conductivities of the dichloromethane solutions were measured at 25.0 °C using a conventional bridge (Model 4225A of Yokogawa-Hewlett-Packard Ltd.).

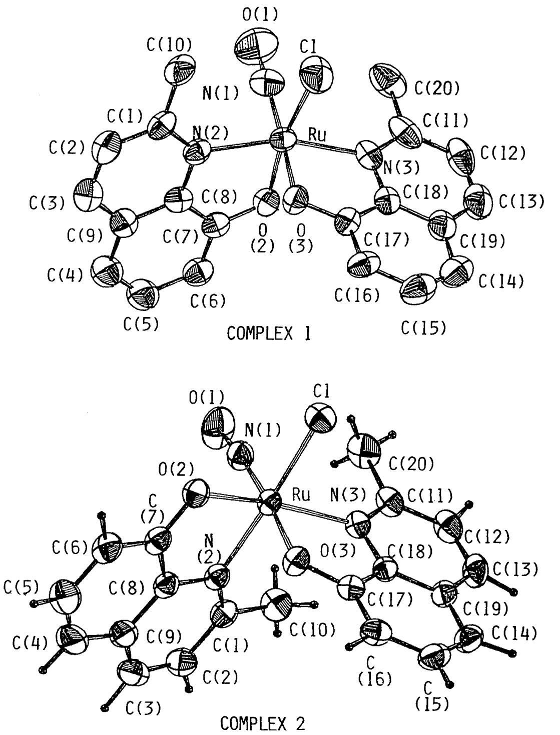

Fig. 1. ORTEP drawing of [RuCl(2mqn)$_2$(NO)] (**1** and **2**) (thermal ellipsoids are drawn at 50% probability).

The UV, IR, conductivity, and NMR data of **1** and **2** are as follows; **1**: UV (CH_2Cl_2) 31300 (log ϵ 3.49) and 25000 cm^{-1} (log ϵ 3.75); IR (Nujol) 1835 cm^{-1} (N-O stretching of the nitrosyl group); Λ_m (CH_2Cl_2, 4.86×10^{-4} mol dm^{-3}, 25 °C) 3.48×10^{-7} S m^{2}mol^{-1}; ^{1}H NMR (CD_2Cl_2) δ=3.06 (3H, s, CH_3), 3.27 (3H, s, CH_3), 6.80—7.48 (8H, m, the hydrogen atoms of the two quinoline rings except the H(3) and the H(13)),[5] 8.18 (1H, d, the H(3) or the H(13)), 8.22 (1H, d, the H(13) or the H(3)); ^{13}C NMR (CD_2Cl_2) δ=27.30 (s, CH_3), 27.63 (s, CH_3), 115—140 (m, the two quinoline rings except the quaternary carbons). **2**: UV(CH_2Cl_2) 31300 (log ε 3.45) and 25300 cm^{-1} (log ε 3.77); IR (Nujol) 1840 cm^{-1} (N-O stretching of the nitrosyl group); Λ_m (CH_2Cl_2, 5.29×10^{-4} mol dm^{-3}, 25 °C) 11.7×10^{-7} S m^2 mol^{-1}); ^{1}H NMR (CD_2Cl_2) δ=1.83 (3H, s, CH_3), 3.14 (3H, s, CH_3), 6.77—7.55 (8H, m, the

Table 3. Relevant Interatomic Distances (l/Å) and Bond Angles (ϕ/°) within a Molecule of the Complexes **1** and **2** (Their estimated standard deviations in parentheses)

Complex Distances	1	2	Complex Angle	1	2
Ru-Cl	2.378(2)	2.376(1)	Ru-N(1)-O(1)	174.9(7)	174.8(3)
Ru-N(1)	1.772(8)	1.735(3)	N(2)-Ru-O(2)	82.1(2)	82.1(1)
N(1)-O(1)	1.068(12)	1.155(5)	N(3)-Ru-O(3)	81.5(2)	80.4(1)
Ru-N(2)	2.112(6)	2.111(3)	Cl-Ru-N(1)	90.6(2)	93.0(1)
Ru-N(3)	2.100(6)	2.116(2)	Cl-Ru-N(2)	104.1(2)	172.9(1)
Ru-O(2)	2.005(5)	2.005(2)	Cl-Ru-N(3)	86.2(2)	85.4(1)
Ru-O(3)	1.971(6)	1.981(3)	Cl-Ru-O(2)	169.9(2)	91.1(1)
Cl-C(10)	3.245(9)	—	Cl-Ru-O(3)	87.2(2)	92.0(1)
N(1)-C(20)	3.011(13)	2.994(5)	N(3)-Ru-O(2)	85.8(2)	162.6(1)
O(3)-C(10)	—	3.635(5)	N(1)-Ru-N(3)	103.2(3)	102.2(1)
C(10)-C(20)	—	3.814(6)	N(2)-Ru-N(3)	162.0(3)	100.5(1)
			N(2)-Ru-O(3)	84.2(2)	85.2(1)
			O(2)-Ru-O(3)	85.5(2)	82.7(1)

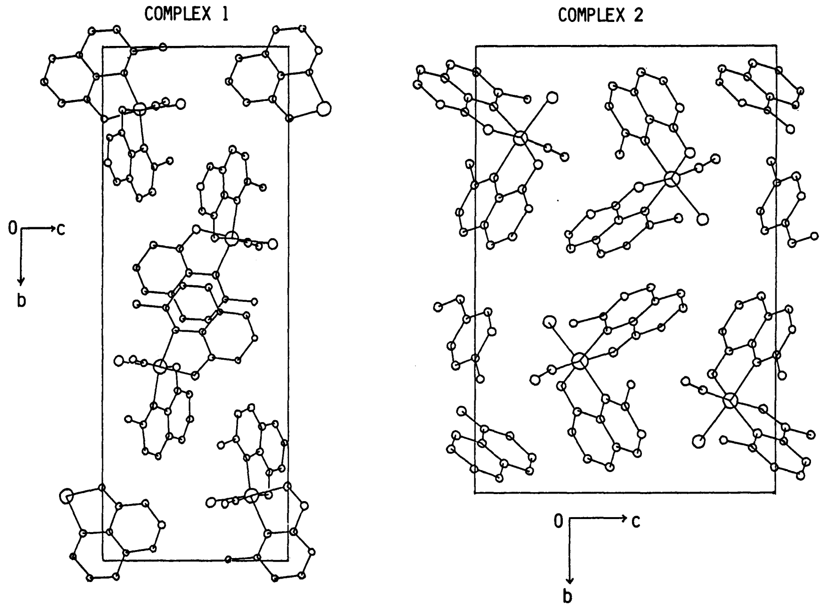

Fig. 2. Crystal structures of [RuCl(2mqn)$_2$(NO)] (**1** and **2**) projected along the a axis.

hydrogen atoms of the two quinoline rings except the H(3) and the H(13)), 8.17 (1H, d, the H(3) or the H(13)), 8.22 (1H, d, the H(13) or the H(3)); ^{13}CNMR (CD_2Cl_2) δ=24.38 (s, CH_3), 27.70 (s, CH_3), 114—141 (m, the two quinoline rings except the quaternary carbons).

Results and Discussion

The wave numbers of the N-O stretching bands[6] and the molar conductivities (Λ_m)[7] of **1** and **2** were consistent with the molecular structures determined as will be mentioned later.

Molecular Structures. The molecular and crystal structures of the two isomers of [RuCl(2mqn)$_2$(NO)], **1** and **2**, are shown in Figs. 1 and 2, respectively. In both isomers, the Cl atom is in cis position to the NO group, the O atom of one of the quinolinolato ligands being in trans to the NO group. On the other hand, the geometry of the N and O atoms of the two quinolinolato ligands is in trans (N,N) and cis (O,O) for **1**, and in cis (N,N) and cis (O,O) for **2**. Hence, in **2**, the methyl group of the C(10) lies under the other quinoline ring.

The bond distances and the angles are shown in Table 3. In **1**, the Cl-C(10) distance is shorter than the sum of the van der Waals radii of methyl group (2.0 Å) and Cl (1.8 Å), and the Cl-Ru-N(2) angle is larger than 100° due to the repulsion between the Cl atom and the methyl group. In **2**, the N(2)-Ru-N(3) angle is about 100° due to the repulsion of the methyl group of the C(10) by the other quinoline ring. The N(1)-Ru-N(3) angle is larger than 100° in both **1** and **2** due to the repulsion between the methyl and the NO groups.

The Ru-N(1) distance in **1** is longer than that in **2**. On the other hand, the N(1)-O(1) distance in **1** is shorter than that in **2** which is about the same with those in other six-coordinate mononitrosylruthenium complexes with the linear $\{RuNO\}^6$ group, 1.11—1.17 Å.[6,8]

For nitrosyl complexes, the trans-influence of the NO group has been examined on the basis of the accurate X-ray crystal structure analyses[9] and the molecular orbital theory treatment.[10] Relative bond strengths between the metal ion and the donor atoms of the ligands trans to each other depend on the σ- or π-bonding ability of the donor atoms.[10,11] Since the Ru-N(1)-O(1) angles for **1** and **2** are close to 180°, the NO group is formally bound as NO^+.[6] The NO^+ is a strong π-acceptor and weak σ-donor. Chloride ion and the ligating atoms, the N and O atoms, of the quinolinolato ligands seem to be moderate σ-donor, hence are better σ-donor than the NO^+, while these are poor π-acceptor than the NO^+. When the ligand (L) trans to the NO is a good σ-donor and poor π-acceptor, the Ru-NO and Ru-L bond distances are shortened by the mutual reinforcement of the σ- and π-bonding.[10] Thus, in both **1** and **2**, both the σ- and π-electron densities of the O(3) flow into the NO^+ by way of the Ru; the Ru-O(3) bond distances are expected to be shorter than the Ru-O(2). The differences is 0.034 Å for **1** and 0.024 Å for **2** as shown in Table 3. The Ru-Cl bond distances in **1** and **2** are the same as those of the Ru-Cl (cis to NO) in $[RuCl_5(NO)]^{2-}$, av 2.374 Å, but are longer than those of the Ru-Cl (trans to NO), av 2.358 Å,[9] because the ligand trans to the Cl in **1** and **2** does not possess the trans shortening effect. No effects of the methyl group in the quinoline rings on the Ru-Cl bond distance were found.

In addition to the bond angles, the following torsion angles were calculated. Table 4 gives the clockwise torsion of the bond 3—4 with reference to the bond 1—2 when looking the atom-3 from the atom-2. In **2**, the Ru, the N(2), the C(1), and the C(10) are arranged in a plane as well as the Ru, the N(3), the C(11), and the C(20) are. On the other hand, in **1**, the methyl groups undergo considerable torsion; the C(10) and the C(20) are repulsed by the Cl and the NO group, respectively. The two quinoline rings are practically flat in both **1** and **2**.

Table 4. The Torsion Angles (ϕ/°)

Atoms 1 2 3 4	Complex **1**	Complex **1**
Ru-N(2)-C(1)-C(10)	10.0(11)[a]	1.1(5)
Ru-N(3)-C(11)-C(20)	8.5(12)	−1.2(5)

a) Parentheses indicate the estimated standard deviations.

The NMR spectral data were consistent with the determined molecular structures. The ^1H resonance peaks of the two methyl groups were observed at δ=3.06 and 3.27 for **1**, while at δ=1.83 and 3.14 for **2**. The methyl carbons resonated at δ=27.30 and 27.63 for **1**, while at δ= 24.38 and 27.70 for **2**. According to the molecular structural analysis, the methyl carbon, the C(10), in **2** lies just under the plane of the other quinoline ring. Evidently it causes high field shifts of the methyl carbon, the C(10), and the methyl protons owing to ring-current effect of the quinoline ring. Thus, the resonance peaks at δ=24.38 and 1.83 of **2** can be assigned to the C(10) and the protons attached to it, respectively.

A few six-coordinate metal complexes containing two 2-methyl-8-quinolinolato ligands have been characterized by X-ray structure analysis and NMR measurement. The geometrical arrangement of **1** for the quinolinolato ligands was the same as found for $[Co(2mqn)_2en]$,[12] that of **2** being the same as found for $[TcCl(2mqn)_2O]$.[13] Recently, Bottomley et al. have reported the similar geometrical isomers of *cis*-$[RuCl(pyca)_2(NO)]$ (pyca=2-pyridinecarboxylate ion) as found for the present isomers.[14]

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