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Synthesis and Structure of *cis*(*O*,*O*),*trans*(*N*,*N*)-Chlorobis(8-quinolinolato-N^1, O^8)nitrosylruthenium

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Synopsis. Molecular structure of the title compound has been determined by the X-ray diffraction. The Cl atom is in cis to the NO group, the O atom of one of the two quinolinolato ligands is in trans to the NO group, and the coordinating N and O atoms of two quinolinolato ligands are in cis(O,O) and trans(N,N) configuration.

It is well-known that a coordinating NO^+ possesses weak σ-donor and strong π-acceptor abilities and its property affects synthesis and reactivity of transition metal nitrosyl complexes.[1,2] Recently, we prepared two geometrical isomers of $[RuCl(2mqn)_2(NO)]$ (2mqn=2-methyl-8-quinolinolate ion), determined their structures by the X-ray diffraction, and discussed the trans shortening effect of the NO^+ group.[3] In this paper, we have examined the reaction of hydrous nitrosylruthenium(3+) chloride with 8-quinolinol which can coordinate to metal ion by deprotonation without steric hindrance compared with 2-methyl-8-quinolinol, determined the molecular structure of one of two geometrical isomers of $[RuCl(qn)_2(NO)]$ (qn=8-quinolinolate ion) chromatographically separated from the reaction products, and compared the structure of the $[RuCl(qn)_2(NO)]$ with that of $[RuCl(2mqn)_2(NO)]$ having the same geometrical configuration.

Experimental

Preparation. A mixture (270 cm^3) of ethyl alcohol solutions of hydrous nitrosylruthenium(3+) chloride (Ru=30.8%) (3.1 mmol) and 8-quinolinol (30 mmol) was refluxed for 6.5 h. After the solution had been left overnight at room temperature, it was evaporated up. The dried residue was dissolved in dichloromethane and the red filtrate was added on a silica-gel column (Wakogel C-200, ϕ 4 cm×14 cm). Major bands, the first and second red bands, were eluted with dichloromethane. The effluents were separately dried on a rotary evaporator. Terra rosa (**1**) and maroon (**2**) compounds were obtained from the first and second bands, respectively. Yield: 67%, 0.95 g (based on the starting ruthenium compound) for **1**; and 10%, 0.14 g for **2**. Found for **1**: Ru, 22.5; Cl, 8.2; C, 47.5; H, 2.6; N, 9.2%. Found for **2**: Ru, 22.1; Cl, 7.5; C, 47.8; H, 2.9; N, 9.1%. Calcd for $[RuCl(qn)_2(NO)]$ ($RuC_{18}ClH_{12}N_3O_3$): Ru, 22.2; Cl, 7.8; C, 47.5; H, 2.6; N, 9.2%. The UV, IR, and conductivity data of **1** and **2** are as follows; **1**: UV (CH_2Cl_2) 31300 cm^{-1} (sh) (log ε 3.7) and 24880 cm^{-1} (log ε 3.85); IR (Nujol) 1838 cm^{-1} (N-O stretching of the NO group) and 338 cm^{-1} (Ru-Cl stretching); Λ_m(CH_2Cl_2, 5.21×10^{-4} mol dm^{-3}, 25 °C) 5.74×10^{-7} S m^2 mol^{-1}.[4] **2**: UV(CH_2Cl_2) 31300 cm^{-1} (sh) (log ε 3.6) and 24750 cm^{-1} (log ε 3.81); IR (Nujol) 1843 cm^{-1} (N-O stretching of the NO group) and 333 cm^{-1} (Ru-Cl stretching).

An X-Ray Crystallographic Analysis of 1. Although the crystals of **2** suitable for an X-ray structural analysis could not be obtained, the crystals of **1** were prepared by concentrating a dilute dichloromethane-acetonitrile solution. Crystallographic data: $[RuCl(C_9H_6NO)_2(NO)]$, $RuC_{18}ClH_{12}N_3O_3$, F. W.=454.9, monoclinic, space group $P2_1/c$, $a=14.386(5)$, $b=7.123(1)$, $c=16.315(5)$ Å, $\beta=95.31(3)°$, $V=1664.5(8)$ Å^3, graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å), $D_x=1.815$ Mg m^{-3}, $D_m=1.81$ Mg m^{-3}, $Z=4$, μ(Mo $K\alpha$)=11.08 cm^{-1}, crystal dimensions 0.25×0.05×0.48 mm. The diffraction data were measured on a Rigaku AFC-4 automated four-circle diffractometer (the X-Ray Analysis Center of the Institute of Physical and Chemical Research). The intensities were collected by the (ω, ω-2θ) scanning technique in $2\theta\leqq70°$ at a ω scanning speed, 4° min^{-1}. Independent 2614 reflections with $|F_o|>3\sigma(|F_o|)$ were used for determining the structure. Three standard reflections were measured after every 100 reflections and no decomposition of the crystal was confirmed during the data collection. The ordinary Lorentz and polarization corrections were applied, but no absorption correction was made. The space group was determined with the observed systematic absences, and the lattice parameters were determined by the least-squares refinement using 18 strong reflections. The structure was solved by the heavy atom method and refined by standard Patterson, Fourier, and block-diagonal least-squares procedures. The final refinements were performed using anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. The final R value was

Table 1. Atomic and Thermal Parameters of $[RuCl(qn)_2(NO)]$ (**1**) (qn=8-Quinolinolate Ion) with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/Å^{2\,a)}$
Ru	2360(0)	2551(1)	3919(0)	2.6(0.0)
Cl	1139(1)	3903(3)	4601(1)	4.3(0.0)
O1	1685(3)	−1104(8)	4347(3)	5.3(0.2)
O2	3473(3)	1708(6)	3335(2)	3.2(0.1)
O3	2741(3)	5131(6)	3621(3)	3.3(0.1)
N1	1978(3)	286(7)	4180(3)	2.9(0.1)
N2	3354(3)	2725(8)	4909(3)	3.0(0.1)
N3	1533(3)	2849(7)	2810(3)	3.0(0.1)
C1	3242(5)	3121(10)	5680(4)	3.7(0.2)
C2	4015(5)	3323(10)	6264(4)	4.2(0.2)
C3	4891(5)	3100(9)	6034(4)	4.0(0.2)
C4	5909(4)	2311(11)	4912(4)	4.0(0.2)
C5	5949(4)	1794(10)	4111(4)	4.1(0.2)
C6	5139(4)	1571(10)	3566(4)	3.6(0.2)
C7	4269(4)	1909(8)	3822(3)	2.7(0.1)
C8	4228(3)	2444(10)	4654(3)	2.8(0.1)
C9	5039(4)	2624(10)	5207(3)	3.1(0.1)
C11	912(4)	1680(10)	2449(4)	3.7(0.2)
C12	420(4)	2120(11)	1685(4)	4.3(0.2)
C13	571(5)	3807(12)	1323(4)	4.4(0.2)
C14	1395(5)	6907(11)	1399(4)	4.3(0.2)
C15	2034(5)	8026(10)	1830(4)	4.6(0.2)
C16	2503(4)	7492(11)	2590(4)	3.9(0.1)
C17	2329(4)	5757(9)	2908(3)	2.9(0.1)
C18	1687(4)	4566(8)	2465(3)	2.8(0.1)
C19	1197(4)	5117(10)	1699(3)	3.5(0.2)

Atomic parameters are multiplied by 10^4. a) $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$.

0.0408. The calculations were performed on a FACOM M-200 computer using the UNICS-III Program System.[5] The atomic and thermal parameters are given in Table 1. Tables of anisotropic thermal parameters, coordinates of hydrogen atoms, and the complete F_o-F_c data are deposited as Document No. 8780 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The molecular structure of **1** is shown in Fig. 1. The coordination geometry was similar to that of **1** of $[RuCl(2mqn)_2(NO)]$ (2mqn=2-methyl-8-quinolinolate ion) (named hereafter **A**) reported previously;[3] the Cl is in cis to the NO, the O atom of one of the two quinolinolato ligands is in trans to the NO, and the N and O atoms of the two quinolinolato ligands are in trans (N,N) and cis (O,O) configuration.

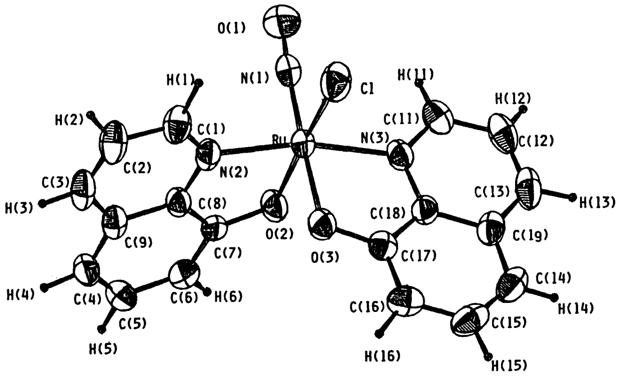

Fig. 1. ORTEP drawing of $[RuCl(qn)_2(NO)]$ (**1**) (qn=8-quinolinolate ion) (Thermal ellipsoids are drawn at 50% probability).

Table 2. Interatomic Distances (*l*/Å) and Bond Angles (*ϕ*/°) of the Coordination Sphere for $[RuCl(qn)_2(NO)]$ (**1**) (qn=8-Quinolinolate Ion) (Their Estimated Standard Deviations in Parentheses)

Distance (*l*/Å)	
Ru-Cl	2.369(2)
Ru-N(1)	1.769(5)
N(1)-O(1)	1.120(8)
Ru-N(2)	2.059(4)
Ru-N(3)	2.082(4)
Ru-O(2)	2.029(4)
Ru-O(3)	1.991(4)
Angle (*ϕ*/°)	
Ru-N(1)-O(1)	175.9(5)
N(2)-Ru-O(2)	82.2(2)
N(3)-Ru-O(3)	80.9(2)
Cl-Ru-N(1)	89.9(2)
Cl-Ru-N(2)	95.7(1)
Cl-Ru-N(3)	88.7(1)
Cl-Ru-O(2)	173.1(1)
Cl-Ru-O(3)	88.4(1)
N(3)-Ru-O(2)	92.0(2)
N(1)-Ru-N(3)	97.9(2)
N(2)-Ru-N(3)	167.1(2)
N(2)-Ru-O(3)	87.1(2)
O(2)-Ru-O(3)	84.9(2)

The bond distances and angles in the coordination sphere are given in Table 2. The RuNO angle, ca. 176°, shows that the NO is formally bound as NO^+.[6] The Ru-N(1) and the N(1)-O(1) bond distances were comparable to those in other six-coordinate nitrosylruthenium(3+) complexes.[3,6] The Ru-O(3) bond distance trans to the NO was shorter than the Ru-O(2) bond distance trans to the Cl by 0.038 Å due to the trans shortening effect of the NO^+ as was discussed in Refs. 2 and 3. Furthermore, the Ru-O(2) and the Ru-O(3) bond distances of **1** were longer than those of **A** by 0.024 and 0.020 Å, respectively.[3] The phenolic oxygen atom of 2-methyl-8-quinolinolate ion seems to be slightly stronger as a π-donor than that of 8-quinolinolate ion due to electron-donating power of the methyl group. As the NO^+ group is a strong π-acceptor, the π-electron densities of the O(3) of **A** more favorably flow into the NO^+ through the Ru as compared with those of the O(3) of **1**; the Ru-O(3) bond distance of **1** is expected to be longer than that of **A**. As a chloride ion is considered to be weaker as a π-donor than the phenolic oxygen of the quinolinolate ion, the Ru-O(2) bond distance of **1** is also expected to be longer than that of **A**. The Ru-N(2) and Ru-N(3) bond distances of **1** were shorter than those of **A** by 0.053 and 0.018 Å, respectively because of exclusion of the steric hindrance of the methyl groups. This influence was also found to the bond angles; the Cl-Ru-N(2) and N(1)-Ru-N(3) bond angles of **1** were smaller than those of **A** by ca. 8° and 5°, respectively, while the N(3)-Ru-O(2), N(2)-Ru-N(3), and N(2)-Ru-O(3) bond angles of **1** being larger than those of **A** by 3—6°. The coordination geometry of **1** is close to regular octahedral compared with that of **A**.

The chemical composition of **2** was equal to that of **1**. The IR, visible spectra, and the chromatographic behavior suggest that **2** is geometrically isomeric with **1** as observed for two of the 2-methyl-8-quinolinolato complexes;[3] **2** is in cis(O,O) and cis(N,N) configuration with respect to the two quinolinolato ligands.

The more geometrical isomers of the formula $[RuCl(qn)_2(NO)]$ were expected to be isolated because 8-quinolinolate ion can coordinate as bidentate ligand to nitrosylruthenium(3+) group without steric hindrance compared with 2-methyl-8-quinolinolate ion. However, the two geometrical isomers were isolated similarly to the 2-methyl-8-quinolinolato complexes.

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