# Reaction of $[CoL_2]\cdot 2H_2O$, $[Co(NO)L_2]$, or $[Co(NO)L_2(py)]$ (L=8-Quinolinolate Ion; py=Pyridine) with Nitrogen Monoxide: Disproportionation of Nitrogen Monoxide Induced by Cobalt Complexes

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$[Co(qn)_2]\cdot 2H_2O$ (**1**) (qn=8-quinolinolate ion) and $[Co(NO)(qn)_2]$ (**2**) reacted with NO in 10 vol% pyridine-DMF or pyridine to give the nitrato complex, $[Co(NO_3)(qn)_2L]$ (L=pyridine or DMF), with liberation of $N_2O$. $[Co(NO)(qn)_2(py)]$ (py=pyridine) having $NO^-$ group (**3**) reacted with NO in $CH_2Cl_2$, the py-DMF, or pyridine to give $[Co(qn)_2(NO_3)(py)]$ with liberation of $N_2O$. The mass analyses of the residual NO for the reaction of **2** or **3** with NO in the pyridine medium and for the reaction of **3** with NO in $CH_2Cl_2$, using the nitrogen-15 labelled compounds showed that a perfect nitrogen scramble occurred between the NO gas and the NO group of **2** or **3**. In the reaction of **2** with NO in $CH_2Cl_2$, ca. 80% of the coordinating NO reacted with NO gas accompanying a rupture of the original Co-NO bond. The present results were compared with those obtained in the cases that 2-methyl-, 4-methyl-, 5-chloro-, and 5-nitro-8-quinolinolate ions were used as ligands. The electronic effects caused by the substituent of the quinoline ring and by the solvents on the reactions were discussed.

It is well-known that the coordinating $NO^+$ (NO stretching vibration more than ca. 1880 $cm^{-1}$) for nitrosyl complexes of the Group 8 metals is attacked at the nitrogen atom by nucleophile such as $OH^-$, $OR^-$ (R=alkyl), $NH_3$, $N_2H_4$, $NH_2OH$, or $N_3^-$, and the nitrosyl ligand (NO stretching vibration in the 1600—1760 $cm^{-1}$ region) reacts with electrophile such as HX (X=Cl, Br), $O_2$, NO, or $PhCH_2Br$.[1] For nitrosylcobalt complexes having $NO^+$ or $NO^-$ group, the nitrosyl group reacts with NO to cause the homogeneous disproportionation of the NO, and the reaction mechanisms have been discussed.[2-6]

We have investigated the reactions of NO gas with $[CoL_2]\cdot nH_2O$ (L=2-methyl-, 4-methyl-, 5-chloro-, or 5-nitro-8-quinolinolate ion) and $[Co(NO)L_2]$ having $NO^-$ group in some organic solvents, found new disproportionation reactions of the NO, and discussed the reaction mechanisms.[7-10]

In this paper, we wish to report the reactions of $[Co(NO)(qn)_2(py)]$, $[Co(NO)(qn)_2]$, and $[Co(qn)_2]\cdot 2H_2O$ (qn=8-quinolinolate ion) with NO in $CH_2Cl_2$, DMF, 10 vol% pyridine-DMF, or pyridine, and to compare the present results with those which have been reported on our previous papers (Refs. 6—10). The reactions were characterized by $^{13}C$ and $^{15}N$ NMR, IR (including $^{15}N$-isotopic shifts), and MS (the gaseous and the solid products) measurements.

## Experimental

**Materials.** The starting materials, $[Co(qn)_2]\cdot 2H_2O$ (**1**) and $[Co(NO)(qn)_2]$ (**2**) were prepared according to Refs. 6 and 11. $[Co(NO)(qn)_2(py)]$ (py=pyridine) (**3**) was prepared by dissolving **2** in a small excess of pyridine at ca. 253 K and removing the pyridine immediately on evacuation ($\nu_{NO}$, 1616 $cm^{-1}$. Found: C, 59.4; H, 3.8; N, 12.2%. Calcd: C, 60.5; H, 3.8; N, 12.3%), or was prepared by reacting **1** dissolved in pyridine with a small excess of NO at ca. 253 K and removing the pyridine and residual NO immediately on evacuation ($\nu_{NO}$, 1616 $cm^{-1}$. Found: C, 61.4; H, 3.9; N, 11.8%). $^{14}NO$ or $^{15}NO$ ($^{15}N$ atom%=99 or 99.7) gas was quantitatively derived from the corresponding potassium nitrate, and was purified by fractional distillation at ca. 147 K (methylcyclohexane slush bath). The MS analysis showed a small amount of contamination of $N_2O$ (0.8%). $CH_2Cl_2$ and DMF were distilled and stored under argon over moleculer sieves 4A. Special grade pyridine and diethyl ether were used without further purification.

**Reactions.** All the reactions were carried out using a vacuum line. The organic solvents were degassed by three cycles of freeze-pump-thaw or deaerated with argon before use. The NO gas (5.0 mmol) was trapped into a reaction vessel containing the starting cobalt complex (0.25—0.50 mmol), **1**, **2**, or **3**, suspended or dissolved in 10 $cm^3$ of $CH_2Cl_2$, 10 vol% pyridine-DMF, pyridine, or DMF. The contents were stirred for 1—7 d at room temperature to give the solid product or clear brown solution. The liberated and residual gases were transferred to a sample tube for the mass or IR spectrometric analysis. $CH_2Cl_2$ was freezed and removed from the gaseous substances by cooling at ca. 147 K because $N_2O$ region ($m/z$=44, 45, and 46) was disturbed by the fragment ions produced from $CH_2Cl_2$ in measuring the mass spectra. In the case that the solid product was obtained, the product was collected by filtration, washed with diethyl ether, and then dried under vacuum. In the case that the clear solution was prepared, the product was precipitated by dropping deoxygenated diethyl ether (ca. 150 $cm^3$) to the solution.

**Measurements.** The C, H, and N contents of the products were analyzed by the Institute of Physical and Chemical Research (Wako, Saitama). The cobalt was photometrically determined by the method of sodium 1-nitroso-2-naphthol-3,6-disulfonate.[12] The magnetic susceptibilities were measured at room temperature by the Gouy method. The molar conductance was measured by a Toa Electronics CM-40S conductivity meter. The IR spectra of the solid products were measured as Nujol or poly(chlorotrifluoroethylene) oil mull in the 200—4000 cm$^{-1}$ region. In many cases, the isotopic shifts upon the $^{15}$N-substitution were carefully measured at 80 K using a Liquid Nitrogen Cooling Unit-DN 70 (Oxford Instruments) in the 400—4000 cm$^{-1}$ region. The IR spectrum in $CH_2Cl_2$ or pyridine solution was measured in an NaCl liquid cell.

The gaseous products were identified by a Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi M-003 data processor and by the IR bands in the 1000—4000 cm$^{-1}$ region.[7—10]

The positive SIMS (Secondary-Ion Mass Spectrometry) spectra of the solid compounds were measured up to $m/z$ =1500 by the mass spectrometer with the SIMS unit. The products were dissolved or suspended in a glycerol/3-mercapto-1,2-propanediol, and placed on a platinum plate probe tip. Xenon was used to produce the primary ion (the ionization method: electron impact; the primary ion accelerating potential: 8 kV).

Carbon-13 NMR spectra of the solid products and nitrogen-15 NMR spectra of the nitrogen-15 labelled solid products ($^{15}$N atom%=99 or 99.7) were measured in chloroform-*d* or DMSO-$d_6$ using a JEOL FX-90Q spectrometer and were referenced to internal TMS and to external liquid ammonia, respectively. The spectral conditions were same as those in Ref. 8.

## Results and Discussion

**Starting Materials.** For **3**, the pure compound could not be isolated in spite of the preparation at low temperature. The IR spectra showed the weak bands (ca. 1410 cm$^{-1}$ for the $^{14}$NO-complex and ca. 1300 cm$^{-1}$ for the $^{15}$NO-complex) characteristic of the coordinating nitrate ion in addition to the NO stretching vibration because **3** reacts further with NO in pyridine. Thus **3** was used without purification. The wavenumber of the NO stretching vibration shifted from 1646 of **2** to 1616 cm$^{-1}$. The wavenumber of the NO stretching band indicates that **2** and **3** are formally $NO^-$ complex.[6]

**Gaseous Products.** The IR and MS measurements showed that the gaseous product was only $N_2O$ in the reactions except for the reaction of **1** or **2** in $CH_2Cl_2$. On the other hand, the gaseous products for the reaction of **1** or **2** in $CH_2Cl_2$ were $N_2$ and $CO_2$ in addition to $N_2O$.

**Solid Products. Reactions in 10 vol% Pyridine-DMF:** **1** or **2** dissolved in the solvent reacted with NO to precipitate $[Co(NO_3)(qn)_2(DMF)]\cdot py$ (**4**). From the filtrate, $[Co(NO_3)(qn)_2(py)]\cdot py\cdot 3H_2O$ (**5**) was obtained. By the addition of diethyl ether to a clear brown solution obtained from the reaction of suspending **3** with NO, **5** was precipitated.

**Reactions in Pyridine:** By the addition of diethyl ether to a clear brown solution obtained from the reaction of soluble **1** or **2**, or suspending **3** with NO, $[Co(NO_3)(qn)_2(py)]\cdot py\cdot H_2O$ (**6**) was precipitated.

**Reactions in Dichloromethane:** Soluble **2** reacted with NO to gradually precipitate a dark violet compound containing nitrosyl cation, $[NO]^+[Co^{III}(NO_3)(NO_2)(qn)_2]^-$, (yield: 70—90%).[6] **1** suspended in $CH_2Cl_2$ reacted with NO to give a soluble dark green **2** immediately and then gradually precipitate the dark violet compound. The IR spectrum of the dark green solution showed the strong band at 1674 cm$^{-1}$ due to the NO stretching vibration characteristic of **2**. When $^{15}$NO gas was used, the NO stretching band of **2** shifted to 1645 cm$^{-1}$. The violet compound in the solid state was stable in dry air, and was also stable in fully deaerated dry DMF or DMSO at least for 2—4 d at room temperature in the dark. The molar conductance in the DMF was $26.9\times10^{-4}$ S m$^2$ mol$^{-1}$ at $5.14\times10^{-4}$ mol dm$^{-3}$ at 18 °C, suggesting that this compound is a 1 : 1 electrolyte.[13] By the addition of a deoxygenated diethyl ether to the DMF or the DMSO solution, the adduct of the solvent was precipitated: $[NO][Co(NO_3)(NO_2)(qn)_2]\cdot 0.5\,DMF$ (Found: Co, 11.2; C, 44.1; H, 3.1; N, 14.6%. Calcd: Co, 11.3; C, 44.9; H, 3.0; N, 14.8%. $\nu_{CO}$ of DMF, 1650 cm$^{-1}$[14]); and $[NO][Co(NO_3)(NO_3)(qn)_2]\cdot 0.25\,DMSO$ (Found: C, 44.9; H, 2.6; N, 13.8%. Calcd: C, 44.0; H, 2.7; N, 13.9%. $\nu_{SO}$ of DMSO, 1025 cm$^{-1}$; $\delta r(CH_3)$, 952 cm$^{-1}$[15]).

**3** dissolved in $CH_2Cl_2$ reacted with NO to precipitate $[Co(NO_3)(qn)_2(py)]\cdot 2H_2O$ (**7**). By the addition of deoxygenated diethyl ether to the filtrate, **6** was precipitated.

**Reactions in DMF:** After **1** or **2** had been dissolved in DMF, NO was trapped in the DMF solution and stirred at room temperature to give a dull red solution. By the addition of diethyl ether to the solution, the brick-red precipitate was obtained. The IR spectrum was seemingly the same as that of $[NO][Co(NO_3)(NO_2)(qn)_2]\cdot 0.5\,DMF$, but the compound could not be identified in spite of the further attempts for purification. The disproportionation of NO to nitrosyl cation, $N_2O$, and nitrate or nitrite ion would probably occurred in DMF.

Elementary analyses and chemical formulae for the complexes, **4**—**7**, obtained from the reactions in 10 vol% pyridine-DMF, pyridine, and $CH_2Cl_2$ are shown in Table 1. The water of crystallization seems to come from a small amount of water contained in diethyl ether and pyridine.

The bands characteristic of a coordinating $NO_3^-$ were confirmed by the $^{15}$N-isotopic shifts.[8—10] For **4**, the medium band at 1400 cm$^{-1}$ assignable to the $NO_2$ antisymmetric stretching of $NO_3^-$ shifted to and overlapped with the strong band at ca. 1370 cm$^{-1}$ due to 8-quinolinolato ligands upon the $^{15}$N-substitution, while the $NO_2$ symmetric stretching band of $NO_3^-$ hidden with the strong band at 1320 cm$^{-1}$ due to 8-quinolinolato ligands shifted to 1298 cm$^{-1}$ upon the $^{15}$N-substitution. The same phenomenon was also observed for **5**, **6**, and **7**. For these compounds, the medium band at 1413 cm$^{-1}$ assignable to the $NO_2$ antisymmetric stretching shifted to and overlapped with the strong band at ca. 1370 cm$^{-1}$, and the $NO_2$ symmetric stretching band hidden with the strong

Table 1. Elementary Analyses and Yields of the Solid Products[a]

| | Compound (Color) | Yield/% | | Co/% | C/% | H/% | N/% |
|---|---|---|---|---|---|---|---|
| **4** | $[Co(NO_3)(qn)_2(DMF)]\cdot py$ | 29—43 | Found | 10.2 | 55.1 | 3.8 | 11.8 |
| | (Brown) | | Calcd | 10.5 | 55.6 | 4.3 | 12.5 |
| **5** | $[Co(NO_3)(qn)_2(py)]\cdot py\cdot 3H_2O$ | 20—26 | Found | 9.7 | 54.8 | 3.9 | 11.4 |
| | (Reddish brown) | | Calcd | 9.5 | 54.1 | 4.5<br>(3.9)[b] | 11.3 |
| **6** | $[Co(NO_3)(qn)_2(py)]\cdot py\cdot H_2O$ | 68—90 | Found | 9.9 | 57.3 | 4.0 | 11.6 |
| | (Yellowish brown) | | Calcd | 10.1 | 57.4 | 4.1 | 12.0 |
| **7** | $[Co(NO_3)(qn)_2(py)]\cdot 2H_2O$ | 35—46 | Found | 11.0 | 53.5 | 3.4 | 10.9 |
| | (Yellowish brown) | | Calcd | 11.3 | 52.7 | 4.0<br>(3.3)[b] | 10.7 |

a) qn=8-quinolinolate ion. b) The hydrogen content on the assumption that $3H_2O$ of **5** and $2H_2O$ of **7** leave during the preliminary treatments of the elementary analyses.

band at 1325 $cm^{-1}$ due to 8-quinolinolato ligands shifted to 1303 $cm^{-1}$. Separation of the two stretching bands due to the nitrato ligand was less than 100 $cm^{-1}$, indicating that the nitrate ion coordinates as a unidentate ligand.[16] The wavenumber of the IR bands characteristic of the coordinating $NO_3^-$ of **4** is different from that of **5**, **6**, and **7**. Complex **4** is sparingly soluble in common organic solvents compared with **5**, **6**, and **7**. Thus, the medium band at 1670 $cm^{-1}$ of **4** was assigned to the CO stretching vibration due to coordinating DMF although the wavenumber is in the uncoordinating region.[14]

The $^{13}C$ NMR spectra of **4**, **5**, and **7** could not be measured clearly due to their solubilities. The resonances of **6** in chloroform-*d* were observed in the region 112—165 ppm which coincided with the regions, 112—153 ppm for 8-quinolinol and 123—150 ppm for pyridine.[17] Number of the observed signals was 25. Assuming that **6** contains two kinds of the coordinating 8-quinolinolate ions, and a coordinating and a free pyridine, number of the expected resonances becomes 24. The resonances at 123.84, 136.09, and 149.74 ppm were almost equal to those at 123.66, 135.71, and 149.85 ppm for free pyridine, respectively.[17] The other resonances could not be assigned because the spectrum was very complicated. The NMR data shows that **6** is $[Co(NO_3)(qn)_2(py)]\cdot py\cdot H_2O$ in which the nitrato ligand is in cis-position to the pyridine. The $^{15}N$ NMR spectra of **5**, **6**, and **7** in DMSO-$d_6$ showed a single resonance at 380.15, 380.42, and 380.15 ppm, respectively. These values were comparable to 380.26 ppm of a DMSO-$d_6$ solution of $K^{15}NO_3$ at 333 K.[8] The $^{15}N$ resonance of the nitrato ligand was found in the same region as that of free nitrate ion because the coordination of the nitrate ion to the cobalt ion is through the oxygen atom.[18]

The compounds except **7** were diamagnetic but **7** showed slightly paramagnetism ($\mu_B$=0.85 BM at 290 K), indicating that they are low spin type cobalt(III) compounds. No further investigation of the magnetic susceptibility of **7** was carried out.

**Characterization of Reactions.** The reactions of **1** and **2** with NO in the pyridine medium can be shown as follows; $Co^{2+}+5NO\rightarrow Co^{3+}+NO_3^-(coord)+2N_2O$ (coord=coordinating) and $Co^{3+}+NO^-(coord)+4NO \rightarrow Co^{3+}+NO_3^-(coord)+2N_2O$, respectively. These reactions were observed for the corresponding 5-chloro- or 5-nitro-8-quinolinolato complex.[8] **3** could be immediately prepared by reacting **1** with NO in pyridine or by dissolving **2** in pyridine. **3** reacted further with NO in the pyridine medium to prepare the nitrato complexes; $Co^{3+}+NO^-(coord)+4NO\rightarrow Co^{3+}+NO_3^-(coord)+2N_2O$. Thus **3** is probably an intermediate in the reaction of **1** or **2** with NO as observed for the corresponding 4-methyl-8-quinolinolato complex.[9] The reaction of **3** with NO in $CH_2Cl_2$ can be also shown as follows; $Co^{3+}+NO^-(coord)+4NO\rightarrow Co^{3+}+NO_3^-$ (coord)$+2N_2O$. On the other hand, **1** reacted with NO in $CH_2Cl_2$ to prepare **2** ($Co^{2+}+NO\rightarrow Co^{3+}+NO^-(coord)$) and then **2** reacted further with NO to precipitate $[NO][Co(NO_3)(NO_2)(qn)_2]$.

The stoichiometry of the reaction of **2** or **3** with NO in 10 vol% pyridine-DMF or pyridine and that of **3** with NO in $CH_2Cl_2$ were examined by measuring the relative molar ratio of the residual NO to the produced $N_2O$ and by considering the yields of the solid products. However, the stoichiometry could not be confirmed as well as for the reaction of the corresponding 5-chloro- or 5-nitro-8-quinolinolato complex with NO.[8] The observed data suggest that side reactions which could not be characterized may consume the produced $N_2O$.

For examining the reaction of **2** or **3** with NO in 10 vol% pyridine-DMF or pyridine and the reaction of **3** with NO in $CH_2Cl_2$, the following combinations of nitrogen isotopes were used: ($^{14}NO$ complex)-($^{15}NO$ gas) and ($^{15}NO$ complex)-($^{14}NO$ gas). The mass analyses showed that the relative molar ratio of $^{14}NO$ to $^{15}NO$ in the residual NO gas was almost equal to that of starting $^{14}NO$ to $^{15}NO$, indicating that the perfect $^{14}N$-$^{15}N$ scramble between NO gas and the coordinating NO group occurred; **2** or **3** decomposes to liberate NO, the liberated NO together with an original reactant NO reacts with the resulting Co(II) complex to prepare the NO complex, and then the NO complex reacts further with NO to prepare the nitrato complex

Table 2. Gaseous Species of the Reaction of $[Co(NO)(qn)_2]$ with NO Gas in Dichloromethane[a)]

| X: ($^{14}$NO complex)-($^{15}$NO gas)[b)] | | | Y: ($^{15}$NO complex)-($^{14}$NO gas)[c)] | | |
|---|---|---|---|---|---|
| *m/z* | intensity | (species) | *m/z* | intensity | (species) |
| 29 | 2850 | ($^{14}N^{15}N$) | 29 | 5570 | ($^{14}N^{15}N$) |
| 30 | 161100 | ($^{14}$NO 72%. $^{15}N^{15}N$ 28%) | 30 | 3810000 | ($^{14}$NO) |
| 31 | 1455000 | ($^{15}$NO) | 31 | 293500 | ($^{15}$NO) |
| 44 | 25910 | ($CO_2$)[d)] | 44 | 103500 | ($^{14}N^{14}NO$, $CO_2$) |
| 45 | 4080 | ($^{15}N^{14}NO$, $^{14}N^{15}NO$) | 45 | 3710 | ($^{15}N^{14}NO$, $^{14}N^{15}NO$) |
| 46 | 47160 | ($^{15}N^{15}NO$) | 46 | 291 | ($^{15}N^{15}NO$) |

a) qn=8-quinolinolate ion. b) The molar ratio of $^{15}$NO to $^{14}$NO is 9.0. c) The molar ratio of $^{14}$NO to $^{15}$NO is 9.6. d) Considering the isotopic condition of the X, the produced $^{14}N^{14}NO$ is negligible.

as observed for the corresponding 5-chloro-, 5-nitro-, and 4-methyl-8-quinolinolato complexes.[8,9)]

The reaction of **2** with NO in $CH_2Cl_2$ was investigated by measuring the $^{15}$N-isotopic effects on the IR spectra of the gaseous product ($N_2O$) and the solid one ($[NO][Co(NO_3)(NO_2)(qn)_2]$), and it was suggested that the NO group reacted with NO to give the $NO_2^-$ with a retention of the original Co–NO bond.[6)] However, a present detailed IR investigation showed that $CO_2$ in addition to $N_2O$ was produced by the reaction. Thus, the residual and produced gases for the following reaction combinations, X: ($^{14}$NO complex)-($^{15}$NO gas) and Y: ($^{15}$NO complex)-($^{14}$NO gas), were reinvestigated by the mass spectrometry.

The relative intensities of the peaks at $m/z$=28, 29, 30, 31, 44, 45, and 46 were measured. The intensities of the mass number 28 for the X and Y were left out of consideration because of a leakage of $N_2$ from atmosphere into the mass spectrometer. The representative data are shown in Table 2. The observed relative ratio of the mass number 30 to the 31 for the Y was 12.6±0.7. From the comparison of 12.6 with the calculated relative ratio of the starting $^{14}$NO to $^{15}$NO for the Y, 9.6, the retention of the original Co–NO bond was estimated to be ca. 25%. The value of 12.6 for the Y was larger than the observed relative ratio of the mass number 31 to the 30 for the X, 9.0±0.7, suggesting a possibility that $^{15}N^{15}N$ produced from the reaction in the X is contained in the mass number 30. It has been reported that $[Co(NO)(PPh_3)_3]$ reacted with NO in benzene or toluene having a poor coordinating ability to give $[Co(NO)_2(ONO)(PPh_3)]$ and $Ph_3PO$ with liberation of $N_2$ and $N_2O$.[5)] Thus production of $N_2$ seems to be taken account of for the present reaction. From the relative ratio, 12.6, for the Y, the $^{15}N^{15}N$ produced from the X was calculated to be ca. 28% of the intensity of the mass number 30 for the X. Considering the isotopic conditions of the X, the produced $^{14}N^{14}NO$ and $^{14}N^{14}N$ seem to be negligible. Thus the produced $N_2$ (mass numbers 29 and 30), $N_2O$ (mass numbers 45 and 46), $CO_2$ (mass number 44), and residual NO (mass numbers 30 and 31) for the X were calculated to be 2.8, 3.0, 1.6, and 92.6% of the intensities over the mass numbers 29—46, respectively. The relative ratio of the mass number 46 to the 45 for the X was 11.6 and that of the starting $^{15}$NO to $^{14}$NO of the X was 9.0, suggesting that the retention of the original NO group is ca. 22%. The value was comparable to that (ca. 25%) of the retention of the original Co–NO bond estimated from the mass number 30 to the 31 for the Y. The relative ratio of the mass number 31 to the 30 for the Y and that of the mass number 46 to the 45 for X were reproducible although that of the mass number 44 to the 45 for Y was not reproducible at every experiment because $CO_2$ is contained in the mass number 44 for the Y. The mass and IR spectrometries showed that $CO_2$ and $N_2$ in addition to $N_2O$ were produced by reacting **2** with NO in $CH_2Cl_2$. Carbon dioxide seems to come from the reaction of NO with $CH_2Cl_2$. However, the reaction mechanism and the stoichiometry could not be elucidated.

**Effects of Solvents on Reactions.** Coordinating ability of the solvent to metal ion increases in the order $CH_2Cl_2$<DMF<pyridine. The present and the previous results[6–10)] showed that the 8-quinolinolato and its derivative complexes reacted with NO in the pyridine medium to produce $NO_2^-$ or $NO_3^-$ with liberation of $N_2O$. On the other hand, in $CH_2Cl_2$, the nitrosylation reactions proceeded.[6–10)] These phenomena can be explained as follows; in the solution having strong coordinating ability such as pyridine, a coordination of the solvent to the cobalt ion causes the coordinating NO to unstabilize and the NO group is easily attacked by NO, an electophile, to give $NO_3^-$ by way of $NO_2^-$ with liberation of $N_2O$.[9)] Some reactions in DMF could not be elucidated. The complicated reactions may proceed because a coordinating ability of DMF is in the position between $CH_2Cl_2$ and pyridine.

**Effects of Substituents in Quinoline Ring of Ligand on Reactions.** 2-Methyl- and 4-methyl-8-quinolinolato ligands are expected to behave as stronger electron donors than 5-chloro- and 5-nitro-8-quinolinolato ligands, and 5-nitro-8-quinolinolato ligand is a weakest electron donor in them. This was reflected in wavenumber of the NO stretching bands for the nitrosyl complexes having the same chemical formulae; 1658 cm$^{-1}$ for $[Co(NO)(4mqn)_2]$[9)]<1669 cm$^{-1}$ for $[Co(NO)(5cqn)_2]$[8)]<1720 cm$^{-1}$ for $[Co(NO)(5nqn)_2]$[8)] where 4mqn, 5cqn, and 5nqn are 4-methyl-, 5-chloro-, and 5-nitro-8-quinolinolate ions, respectively. In the case that 2-methyl-8-quinolinolate ion (2mqn) was used as the ligands, unstable $[Co(2mqn)_2(NO)_2]$ in which the formal oxidation numbers of the NO and the Co are +I and 0, respectively, was prepared.7) This seems to be due to strong electron-donating power of the methyl group in ortho position to the ligating N atom of 2mqn.

The wavenumber of the NO stretching bands for the $[Co(NO)L_2]$(L=8-quinolinolate ion and its derivatives) shows that nucleophilicity of the NO group decreases in the order 4mqn>5cqn>5nqn.

**Reactions in $CH_2Cl_2$:** For the reactions of $[CoL_2]\cdot 2H_2O$ with NO in $CH_2Cl_2$ having a poor coordination ability, the order of the nucleophilicity of the NO group caused by the substituent of the quinoline ring was clearly reflected in the solid products. For the 5nqn, 5cqn, and 4mqn complexes, only the nitrosylation reaction proceeded.8,9) On the other hand, the qn and 2mqn complexes were nitrosylated, and the NO group reacted further with NO to prepare $[NO][Co(NO_3)(NO_2)(qn)_2]$6) and $[NO]_3[Co(NO_3)(NO_2)(2mqn)_2]$,7) respectively. $[Co(NO)(qn)_2(py)]$, **3**, and $[Co(4mqn)_2(NO)(py)]$10) reacted further with NO to prepare the nitrato complexes, **6** and **7**, and $[NO][Co(4mqn)_2(NO_3)(py)]$, respectively. Increase of the nucleophilicity of the NO group caused by coordination of pyridine makes the NO group react with NO to give $NO_3^-$ although $[Co(NO)(4mqn)_2]$ did not react with NO. It is interesting that the formal oxidation states of the cobalt ions in $[NO][Co(NO_3)(NO_2)(qn)_2]$, $[NO][Co(NO_3)(4mqn)_2(py)]$, and $[NO]_3[Co(NO_3)(NO_2)(2mqn)_2]$ decrease from III to I with increase of electron-donating power of the 8-quinolinolato ligands.

**Reactions in 10 vol% Pyridine-DMF or Pyridine:** $[CoL_2]\cdot nH_2O$ or $[Co(NO)L_2]$ reacted with NO in 10 vol% pyridine-DMF or pyridine to prepare the nitrato complexes by way of the nitro ones. No remarkable effect of the substituent in the quinoline ring on the reactions could be found in the pyridine medium because pyridine is a strong electron donor and is superior to the electronic effect due to the substituent. In the case that L is 4mqn, the reaction intermediate, $[Co(4mqn)_2(NO)(py)]$ or $[Co(4mqn)_2(NO_2)(py)]$, was precipitated with a difference in the reaction temperature, and the final product, $[Co(4mqn)_2(NO_3)(py)]$, was obtained from the filtrates.9) Isolations of the nitrosyl and the nitro complexes seem to be due to their low solubilities under the experimental conditions. $[Co(2mqn)_2]\cdot 2H_2O$ did not react with NO, instead only the pyridine adduct being isolated.7)

**Reactions in DMF:** The reactions in DMF were complicated and could not be characterized for the most part because the coordination ability of DMF is in the position between $CH_2Cl_2$ and pyridine. $[Co(5cqn)_2]\cdot 4H_2O$ and $[Co(4mqn)_2]\cdot 2H_2O$ reacted with NO to precipitate their nitrosyl complexes. On the other hand, the 5nqn complex reacted with NO to prepare $[Co(NO_2)(5nqn)_2(DMF)]$ although 5nqn is a weakest electron donor, suggesting that the resulting NO complex reacted further with NO to form $NO_2^-$ because a coordination of DMF to the cobalt ion increases a nucleophilicity of the NO group.

The metal-induced NO disproportionation reaction was studied on the cobalt complexes containing a series of the 8-quinolinolate ion. In $CH_2Cl_2$ having a poor coordinating ability, the NO disproportionation reaction was largely controlled by the electronic effect of the substituent in the quinoline ring of the ligand, however in pyridine having a strong coordinating ability the reaction was controlled by the strong electronic effect of the solvent.

**Positive SIMS Spectra.** The spectra of the starting materials (**1**, **2**, and **3**) and the products (**4**, **5**, **6**, and **7**) were measured. However, the detailed information about their structures could not be obtained. Instead, interestingly several new cluster ions containing two or more Co atoms were observed. The representative data are as follows. For **1** and **2**, $m/z$ 203 $(CoL)^+$ (rel intensity 82), 348 $(CoL_2+H)^+$ (94), 406 $(Co_2L_2)^+$ (51), 550 $(Co_2L_3)^+$ (100), 695 $(Co_2L_4+H)^+$ (33), 753 $(Co_3L_4)^+$ (<1), 897 $(Co_3L_5)^+$ (4), 1042 $(C_3L_6+H)^+$ (<1), 1100 $(Co_4L_6)^+$ (<1), 1244 $(Co_4L_7$ (<1), 1388 $(Co_4L_8)^+$ (<1), and 1447 $(Co_5L_8)^+$ (<1), where L is qn. For **3**, **4**, **5**, **6**, and **7**, $m/z$ 203 $(CoL)^+$ (69), 348 $(CoL_2+H)^+$ (96), 406 $(Co_2L_2)^+$ (58), 426 $(CoL_2P)^+$ (10), 505 $(CoL_2P_2)^+$ (16), 550 $(Co_2L_3)^+$ (100), 566 $(Co_2L_2P_2+2H)^+$ (7), 609 $(Co_3L_3)^+$ (3), 625 $(Co_3L_2P_2+2H)^+$ (5), 695 $(Co_2L_4+H)^+$ (4), 753 $(Co_3L_4)^+$ (6), 768 $(Co_3L_3P_2+H)^+$ (3), 897 $(Co_3L_5)^+$ (9), 913 $(Co_3L_4P_2+2H)^+$ (<1), 972 $(Co_4L_4P_2+2H)^+$ (<1), 1042 $(Co_3L_6+H)^+$ (1), 1100 $(Co_4L_6)^+$ (<1), 1115 $(Co_4L_5P_2+H)^+$ (<1), 1162 $(Co_5L_6+2H)^+$ (<1), 1244 $(Co_4L_7)^+$ (<1), 1260 $(Co_4L_6P_2+2H)^+$ (<1), 1319 $(Co_5L_6P_2+2H)^+$ (<1), and 1462 $(Co_5L_7P_2+H)^+$ (<1), where P is pyridine.

The species originated from the compounds containing pyridine, **3**, **4**, **5**, **6**, and **7** consist of the species containing pyridine and those originated from the compounds without pyridine, **1** and **2**. The species containing nitrate ion and nitrosyl group could not be observed. The relative intensities of the cluster ions larger than $m/z$=900 were less than 1. Recently, such a phenomenon has been reported by Dean et al.19) The cluster ions may be produced by the cascade reactions between the original compound and the cobalt-containing fragment ions.

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