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The Reaction of $[CoL_2]$ (L=5-Chloro- or 5-Nitro-8-quinolinolate Ion) with Nitrogen Monoxide

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$[CoL_2]\cdot nH_2O$ (L=5-chloro-8-quinolinolate ion, n=4; L=5-nitro-8-quinolinolate ion, n=5) reacted with nitrogen monoxide in CH_2Cl_2 at *ca.* 253 K to give $[CoL_2(NO)]$ with NO^- group. $[CoL_2(NO)]$ reacted further with nitrogen monoxide in 10 v% pyridine–DMF at room temperature to give $[CoL_2(NO_3)(py)]\cdot n\mathrm{DMF}\cdot 0.5\mathrm{py}$ (L=5-chloro-8-quinolinolate ion, n=0; L=5-nitro-8-quinolinolate ion, n=1) with liberation of dinitrogen oxide. $[CoL_2]\cdot nH_2O$ also reacted with nitrogen monoxide in the pyridine–DMF to give the same nitrato complexes. In pyridine, $[CoL_2]\cdot nH_2O$ gave $[CoL_2(NO_3)(py)]$. In DMF, $[CoL_2]\cdot nH_2O$ reacted with nitrogen monoxide at room temperature to give $[CoL_2(NO)]\cdot 0.5H_2O$ (L=5-chloro-8-quinolinolate ion) or $[CoL_2(NO_2)(DMF)]\cdot 2H_2O$ (L=5-nitro-8-quinolinolate ion).

Transition-metal complexes react with nitrogen monoxide, NO, causing the NO to disproportionate, or to give the nitrosyl or hyponitrito complexes. NO also reacts with transition-metal nitrosyls to bring about electrophilic attack by the NO on the coordinating NO or disproportionation of the NO, or to give the hyponitrito or further nitrosylated complexes. These reactions proceed separately or simultaneously, as the case may be.[1—3] Of the products obtained from the disproportionation, the product with most oxidized nitrogen atom has been reported to be nitrite ion. Recently, we reported that the reactions of NO with $[Co(qn)_2]$ (qn=8-quinolinolate ion) and $[Co(2mqn)_2]\cdot H_2O$ (2mqn=2-methyl-8-quinolinolate ion) in CH_2Cl_2 at room temperature caused disproportionation of the NO in the presence of the cobalt ion; $Co^{2+}+9NO \rightarrow Co^{3+}+NO^{+}+NO_2^-$(coord)$+NO_3^-$(coord)$+3N_2O$ (coord=coordinating), and $Co^{2+}+11NO \rightarrow Co^{+}+3NO^{+}+NO_2^-$(coord)$+NO_3^-$(coord)$+3N_2O$, respectively.[4,5] One of the features of the reactions is that the NO disproportionates to produce nitrate ion and nitrosyl cation.

In this paper, we report the reaction of $[Co(5cqn)_2]\cdot 4H_2O$ (5cqn=5-chloro-8-quinolinolate ion, $C_9H_5NOCl^-$), $[Co(5nqn)_2]\cdot 5H_2O$ (5nqn=5-nitro-8-quinolinolate ion, $C_9H_5N_2O_3^-$), or their nitrosyl complexes with NO in CH_2Cl_2, DMF, 10 v% pyridine–DMF, or pyridine. The reactions were characterized by NMR (^{13}C and ^{15}N), IR (including ^{15}N-isotopic shifts), and MS measurements.

Experimental

Materials. Dichloromethane was distilled and stored under argon over Zeorum A-4. DMF was purified by distilling under reduced pressure after dried over barium oxide, and stored under argon over Zeorum A-4. JIS-GR pyridine dried over Zeorum A-4 and JIS-GR diethyl ether were used without further purification. ^{15}NO was derived from $K^{15}NO_3$ (^{15}N atom%=99—99.7). Starting materials, $[Co(5cqn)_2]\cdot 4H_2O$ (Found: Co, 12.4. Calcd: Co, 12.1%) and $[Co(5nqn)_2]\cdot 5H_2O$ (Found: Co, 11.2. Calcd: Co, 11.1%) were prepared by the ordinary method.

Measurements. The C, H, N, and Cl contents of the products were analyzed by the Organic Analysis Center of the Institute of Physical and Chemical Research. The magnetic susceptibilities were measured by the Gouy method at room temperature.

The IR spectra in the solid state were measured as Nujol and poly(chlorotrifluoroethylene) oil mulls on a JASCO A-202 and a JASCO IR-F spectrometers in the region 200—4000 cm^{-1}. Since the solid products showed a number of the bands due to the coordinating quinolinolate ions, the isotopic shifts upon ^{15}N-substitution were carefully measured at 80 K using a Liquid Nitrogen Cooling Unit-DN 70 (Oxford Instruments) in many cases.

The gaseous products from the reaction of the cobalt or nitrosylcobalt complex with NO were identified by a Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi M-003 data processing system and by the IR bands and their ^{15}N-isotopic shifts.[6] A relative molar ratio of the residual NO to the produced N_2O was measured by the mass spectrometer for examining stoichiometry of the reaction.

Nitrogen-15 NMR spectra of the obtained nitrato and nitro complexes were measured at 308—353 K in the Fourier transform mode with proton decoupling using a JEOL FX-90Q spectrometer operating at 9.04 MHz. For measuring the ^{15}N NMR spectra were used the samples with $^{15}NO_2^-$ and $^{15}NO_3^-$ (^{15}N atom%=99—99.7). Chemical shifts were referenced to the NH_4^+ signal of a saturated aqueous $^{15}NH_4{}^{15}NO_3$ solution employed as the external standard, and were converted to the liquid ammonia scale by addition of 20.68 ppm.[7] The saturated solutions in DMSO-d_6 were placed in egg-shaped sample tubes, and a sweep width of 5.0 kHz over 8 K data points was used. A pulse width corresponding to a tip angle of 30° and a repetition time of 4 s was used; 1—2 K transients were required for an adequate signal-to-noise ratio. Carbon-13 NMR spectra were recorded on the same spectrometer at 308—353 K at 22.5 MHz using the same solution. The chemical shifts were referenced to internal TMS. The spectral width was typically 5000 Hz with 8 K data points for acquisition. A pulse width of 15 µs (45°) and a delay of 3 s were used; 500—1000 transients were accumulated in the region where the resonances of the quinolinolato and py ligands were observed.

The UV spectra were run on a Hitachi 340 spectrometer.

Reaction with Nitrogen Monoxide. All reactions were carried out in a vacuum line equipped with greaseless valves and O-ring joints. The organic solvents were carefully degassed by three cycles of freeze-pump-thaw or deaerated with argon or dinitrogen before use.

Reaction of $[Co(5cqn)_2]\cdot 4H_2O$ or $[Co(5nqn)_2]\cdot 5H_2O$ with NO in CH_2Cl_2: The starting cobalt(II) complexes (0.5—1 mmol) suspended in CH_2Cl_2 (20 cm^3) was brought into contact with NO (5—10 mmol) and stirred for 7 d at *ca.* 253 K to obtain $[Co(5cqn)_2(NO)]$, **1**, or $[Co(5nqn)_2(NO)]$, **2**. The product was collected by filtration, washed with diethyl ether, and then dried under vacuum.

Reaction of $[Co(5cqn)_2]\cdot 4H_2O$ or $[Co(5cqn)_2(NO)]$ with NO in DMF, 10 v% Pyridine-DMF, or Pyridine: NO (5 mmol) was trapped into a reaction vessel containing $[Co(5cqn)_2]\cdot 4H_2O$ (0.25 mmol) dissolved in DMF (10 cm^3), and the solution was stirred at room temperature for 1 d. A small amount of **3** was obtained.

When the pyridine-DMF (10 cm^3) were used instead of DMF, **4** was precipitated by dropping deoxygenated diethyl ether (200 cm^3) in a clear reddish brown solution obtained by the reaction of NO (5 mmol) with $[Co(5cqn)_2]\cdot 4H_2O$ or $[Co(5cqn)_2(NO)]$ (0.25 mmol). The elementary analyses and the IR spectra for the product from $[Co(5cqn)_2]\cdot 4H_2O$ were the same as those for the product from $[Co(5cqn)_2(NO)]$. In pyridine (10 cm^3), $[Co(5cqn)_2]\cdot 4H_2O$ (0.25 mmol) reacted with NO (5 mmol) to give a clear reddish brown solution, to which **5** was precipitated by adding deoxygenated diethyl ether.

Reaction of $[Co(5nqn)_2]\cdot 5H_2O$ or $[Co(5nqn)_2(NO)]$ with NO in DMF, 10 v% Pyridine-DMF, or Pyridine: The reactions were carried out on the same scale as described in the preceding paragraph. A clear reddish brown solution obtained from the reaction of $[Co(5nqn)_2]\cdot 5H_2O$ with NO in DMF for 1—4 d was dropped in deoxygenated diethyl ether (100 cm^3) to precipitate **6**. When the pyridine-DMF (10 cm^3) was used instead of DMF, reddish brown suspention was obtained from the reaction of $[Co(5nqn)_2]\cdot 5H_2O$ or $[Co(5nqn)_2(NO)]$ with NO. The precipitated **7** was collected by filtration. The elementary analyses and the IR spectra for the product from $[Co(5nqn)_2]\cdot 5H_2O$ were the same as those for the product from $[Co(5nqn)_2(NO)]$. From the reaction of $[Co(5nqn)_2]\cdot 5H_2O$ with NO in pyridine, **8** was obtained as precipitate.

Results and Discussion

Characterization of the Solid Products. Elementary analyses and chemical formulae for the obtained complexes, **1—8**, are shown in Table 1. The complexes were diamagnetic, suggesting that all the solid products are low-spin type cobalt(III) complexes since the formal oxidation number of the coordinating NO group for the nitrosyl complexes is −I as mentioned later.

The nitrosyl complexes in the solid state were stable in air, but unstable in deoxygenated organic solvents such as CH_2Cl_2 and DMF to gradually decompose with liberation of NO. The nitro and nitrato complexes were stable in common organic solvents such as CH_2Cl_2, pyridine, DMF, and DMSO.

Reactions in CH_2Cl_2: The nitrosyls, **1** and **2**, were prepared at 253 K, but could not be isolated at above 273 K. Upon ^{15}N-substitution, the IR band at 1669 cm^{-1} (vs)[8] for **1** shifted to 1636 cm^{-1}, and the 1720 cm^{-1}

Table 1. Elementary analyses and yields of the solid products

Compound (Color)	Yield/%		Co(%)	C(%)	H(%)	N(%)	Cl(%)
1 $[Co(5cqn)_2(NO)]$	90	Found	13.2	48.4	2.3	9.4	16.1
(Dark green)		Calcd	13.2	48.5	2.3	9.4	15.9
2 $[Co(5nqn)_2(NO)]$	90	Found	11.9	45.7	2.2	14.2	
(Dark brown)		Calcd	12.6	46.3	2.2	15.0	
3 $[Co(5cqn)_2(NO)]\cdot 0.5H_2O$	Very low	Found		47.5	2.1	9.1	
(Dark green)		Calcd		47.5	2.4	9.2	
4 $[Co(5cqn)_2(NO_3)(py)]\cdot 0.5\,py$	10	Found (from **A**)	9.5	50.8	3.1	10.5	
(Khaki)	50	Found (from **1**)	9.6	51.1	3.0	10.4	11.9
		Calcd	9.8	51.3	3.0	10.6	11.8
5 $[Co(5cqn)_2(NO_3)(py)]$	90	Found		49.5	3.0	9.8	
(Khaki)		Calcd		49.6	2.7	10.1	
6 $[Co(5nqn)_2(NO_2)(DMF)]\cdot 2H_2O$	50	Found	9.9	42.7	3.4	14.0	
(Brown)		Calcd	10.0	42.6	3.6 (3.3)[a]	14.2	
7 $[Co(5nqn)_2(NO_3)(py)]\cdot DMF\cdot 0.5\,py$	40	Found (from **B**)		49.3	3.5	15.4	
(Brown)	50	Found (from **2**)	8.5	49.3	3.5	15.4	
		Calcd	8.5	49.5	3.6	15.2	
8 $[Co(5nqn)_2(NO_3)(py)]\cdot py$	60	Found		50.9	3.1	14.2	
(Brown)		Calcd		51.2	3.1	14.2	

A, $[Co(5cqn)_2]\cdot 4H_2O$; **B**, $[Co(5nqn)_2]\cdot 5H_2O$; 5cqn, 5-chloro-8-quinolinolate ion; 5nqn, 5-nitro-8-quinolinolate ion. a) The hydrogen content on the assumption that H_2O of **6** leaves during the preliminary treatments of the elementary analysis.

(vs) band for **2** shifted to 1688 cm^{-1}. These bands were assigned to the N–O stretching vibrations.[9] Difference in wave numbers of the N–O stretching vibrations for **1** and **2** arise from that electron-attractive power of the nitro group in the quinoline ring is larger than that of the chloro group. Of nitrosyl-cobalt complexes, the N–O stretching vibration of the NO$^-$ complexes are observed in the region 1570—1710 cm^{-1}, while that of the NO$^+$ complex at *ca.* 1850 cm^{-1}.[1,5] Thus, the present nitrosyls are the NO$^-$ complexes, which is also supported from an empirical rule in the value of the N–O stretching bands for transition-metal nitrosyl complexes proposed by Haymore and Ibers.[9] The reaction in CH_2Cl_2 can be regarded as an oxidative addition of NO to the Co^{2+}, $Co^{2+}+NO \rightarrow Co^{3+}+NO^-$(coord).

Reactions in DMF: The yield of **3** was very low. The IR spectrum was quite similar to that of **1**; the N–O stretching vibration was observed at 1667 cm^{-1}. The reaction over more than 2 d at room temperature made **3** decompose to uncharacterized product with liberation of N_2O.

The 3400(br) and the 1655 cm^{-1}(vs) bands for **6** could be assigned to the O–H stretching vibration of the water of crystallization and the C–O stretching one for the coordinating DMF, respectively.[10] The bands characteristic of the coordinating nitro group could be clearly observed; upon ^{15}N-substitution, the 792(w), 606(w), and 428 cm^{-1}(w) bands shifted to 787, 598, and 424 cm^{-1}, respectively, and were assinged to the NO_2 symmetric deformation, NO_2, wagging, and Co–NO_2 stretching vibrations, respectively.[4–6,11] However, the N–O stretching bands characteristic of the nitro group could not be observed because these bands were hidden under many strong bands due to the 5-nitro-8-quinolinolate ions. The reaction giving **6** was broken off halfway, and the obtained solution was poured into deoxygenated diethyl ether to precipitate a dark brown product. The IR spectrum showed the characteristic bands of **6** together with the 1720 cm^{-1} band assignable to the N–O stretching vibration of **2**. This suggests that [Co(5nqn)$_2$] reacts with NO to yield **2** followed by the further reaction of NO with the coordinating NO group of **2** to give the nitrite ion. Thus, the reaction may be shown as follows; $Co^{2+}+NO \rightarrow Co^{3+}+NO^-$(coord), NO^-(coord)$+2NO \rightarrow NO_2^-$(coord)$+N_2O$. Such electrophilic attack of NO on the coordinating NO group has already been reported by Gwost and Caulton.[12]

Reactions in 10 v% Pyridine-DMF or Pyridine: [Co(5cqn)$_2$]·4H_2O reacted with NO in the pyridine-DMF or in pyridine to give **4** or **5**, respectively, with liberation of N_2O. **1** gave also the same nitrato complex, **4**, in the pyridine-DMF. Table 2 shows wave numbers and the assignments of the bands on which ^{15}N-isotopic shifts were observed in the region 200—4000 cm^{-1}. The bands characteristic of a coordinating nitrate ion were observed for **4**. Separation of two N–O stretching bands due to the nitrate ion was less than 100 cm^{-1}, suggesting that the nitrate ion coordinates to the cobalt atom as a unidentate ligand.[4,5,13] **5** also showed one of the N–O stretching bands due to the coordinating nitrate ion at 1404 cm^{-1}(m). Upon ^{15}N-substitution, the another N–O stretching band could be observed at 1295 cm^{-1}(m, sh).

TABLE 2. WAVE NUMBERS AND THE ASSIGNMENTS OF COORDINATING NITRATE ION FOR [Co(5cqn)$_2$(NO$_3$)(py)]·0.5 py AND [Co(5nqn)$_2$(NO$_3$)(py)]·DMF·0.5 py AT 80 K

[Co(5cqn)$_2$(NO$_3$)(py)]·0.5 py

^{14}N-compound	^{15}N-compound	Assignment
1414 m	1385 sh$^{a)}$	N–O antisym str of NO_3^-
1330 m$^{a)}$	1300 m	N–O sym str of NO_3^-
832 sh$^{a)}$	820 s	Out-of-plane bend of NO_3^-
596 w	584 w	NO_2 sym bend or NO_2 antisym bend of NO_3^-

[Co(5nqn)$_2$(NO$_3$)(py)]·DMF·0.5 py

^{14}N-compound	^{15}N-compound	Assignment
1421 m	1393 m	N–O antisym str of NO_3^-
1328 m	1308 sh$^{a)}$	N–O sym str of NO_3^-
820 vs$^{a)}$	810 vs$^{a)}$	Out-of-plane bend of NO_3^-
600 vs$^{a)}$ 579 vs$^{a)}$	591 w 576 s, br$^{a)}$	NO_2 sym bend or NO_2 antisym bend of NO_3^-

a) The bands due to the nitrate ion and the strong bands due to the coordinating 5-chloro- or 5-nitro-8-quinolinolate ions partially overlapped.

Abbreviations: str = stretching, bend = bending, sym = symmetric, antisym = antisymmetric, vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Both [Co(5nqn)$_2$]·5H_2O and **2** gave the same nitrato-complex, **7**, in the pyridine-DMF. In Table 2 are also shown the IR bands characteristic of a unidentate nitrate ion for **7** with their ^{15}N-isotopic shifts. The strong band at 1670 cm^{-1} could be assigned to the C–O stretching vibration due to the uncoordinating DMF.[10] **8** obtained from the reaction in pyridine also showed two N–O stretching bands at 1425(m) and 1326 cm^{-1}(m) due to the unidentate nitrate ion.

The reaction of [CoL$_2$] and [CoL$_2$(NO)] with NO can be shown as follows; $Co^{2+}+5NO \rightarrow Co^{3+}+NO_3^-$(coord)$+2N_2O$, and $Co^{3+}+NO^-$(coord)$+4NO \rightarrow Co^{3+}+NO_3^-$(coord)$+2N_2O$, respectively.

DMF in **6** and **7** could be also confirmed by the ^{13}C NMR measurements as mentioned later. The IR measurements could not confirm pyridine in **4**, **5**, **7**, and **8**, but the ^{13}C NMR ones suggest that **4** and **5** contain pyridine.

UV Measurements: The electronic spectra for the nitro and nitrato complexes are shown in Table 3.

Table 3. Electronic spectra of the solid products

Compound[a)]	Solvent	σ/nm(ε/mol^{-1} dm^3 cm^{-1})
4	CH_2Cl_2	$330(4.93\times10^3)$, $346(5.14\times10^3)$ $428(7.68\times10^3)$, 560 sh(4.9×10^2)
6	CH_2Cl_2	$340(1.63\times10^4)$ $438(5.06\times10^4)$, 580 sh(5.7×10^2)
7	CH_2Cl_2	$344(1.59\times10^4)$ $442(4.35\times10^4)$, 560 sh(3.5×10^2)
8	10 v% py-DMF	$342(1.76\times10^4)$ $438(4.35\times10^4)$, 560 sh(2.9×10^2)
A	10 v% py-DMF	$352(5.78\times10^3)$, $418(7.65\times10^3)$
B	10 v% py-DMF	$344(1.26\times10^4)$, $444(4.30\times10^4)$

a) Abbreviations of the compounds are the same as those shown in Table 1.

The bands at 330—440 nm may be assigned to the charge transfer absorption between the coordinating 8-quinolinolate ion and the cobalt(III) ion as compared with the absorption maxima and intensities for the spectra of $[Co(5cqn)_2]$ or $[Co(5nqn)_2]$. The shoulder bands at 560—580 nm may be due to *d-d* absorption in the cobalt(III) ion.[14)]

NMR Measurements: Since the obtained nitrosyl complexes, **1** and **2**, were unstable in deoxygenated common organic solvents, the NMR spectra could not be measured. The ^{15}N and ^{13}C NMR measurements of the nitro and nitrato complexes, **4**—**8**, were tried in DMSO-d_6 at 308—353 K to alleviate their sparing solubility to DMSO and the high viscosity of the solution at room temperature (the solubility is less than 10^{-3} mol dm^{-3} at room temperature).

The ^{15}N NMR spectra of the nitrato complexes, **4**, **5**, **7**, and **8**, showed a single resonance at 379.34, 388.06, 379.72, and 375.56 ppm, respectively. These values were comparable to 376.25 ppm of $^{15}NO_3^-$ in a saturated aqueous solution of $^{15}NH_4{}^{15}NO_3$, and 380.26 ppm of a DMSO-d_6 solution of $K^{15}NO_3$ (0.28 mg/0.35 cm^3) at 333 K. The ^{15}N NMR resonance of the nitro complex, **6**, was also observed at 371.12 ppm and the coordinating nitro ion showed a high-field resonance by 240 ppm compared with 610 ppm of free nitrite ion. Such a phenomenon has been found for $[RhCl(NO_2)(NO)L_2]$(L=phosphine derivatives).[15)] On the other hand, the ^{15}N resonance of the coordinating nitrate ion was found in the same region as that of free nitrate ion. Because the coordination of the nitrate ion to the cobalt(III) ion is through the oxygen atom, the shifts are small as observed for nitrato complexes of various metals.[16)]

The ^{13}C NMR spectra of **4** and **5** were very complicated (see Fig. 1), and thus could not be clearly assigned. The resonances were observed in the region 112—166 ppm which coincided with the regions, 111—153 ppm for 5-chloro-8-quinolinol and 123—150 ppm for pyridine.[17)] Number of the observed signals for **4** was 25, and that for **5** was 22. Assuming that **4** contains two kinds of the coordinating 5-chloro-8-quiolinolate ions, a coordinating pyridine, and a free pyridine, number of the expected resonances becomes 24. Also, assuming that **5** consists of two kinds of the coordinating 5-chloro-8-quinolinolate ions and a coordinating pyridine, number of the expected signals becomes 21. The NMR data suggest that among **4** and **5**, the nitrato ligand is in *cis*-position to the pyridine. The ^{13}C NMR spectra of **6**, **7**, and **8** could not be measured clearly due to their solubilities, but two kinds of 5-nitro-8-quinolinolate ions seems to exist. The resonances due to DMF in **6** and **7** could be observed. The resonances at 28.97 and 33.90, and at 160.96 ppm for **6** could be assinged to the methyl carbons, and the carbonyl carbon, respectively.[17)] The resonances at 30.66, 35.65, and 162.20 ppm for **7** were almost equal to those at 31.17, 36.27, and 162.39 ppm for free DMF, respectively.[17)]

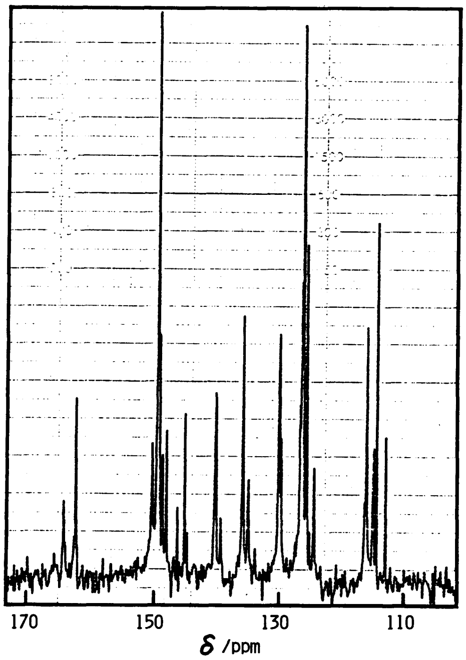


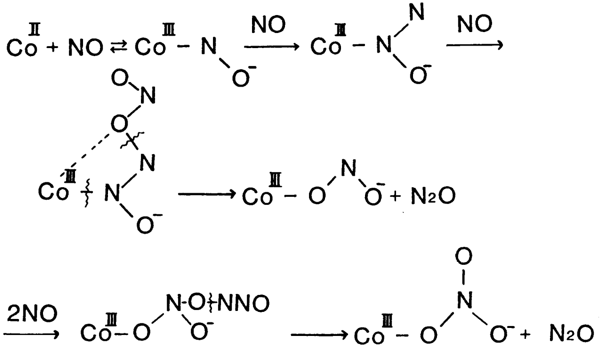
Fig. 1. ^{13}C NMR spectrum of $[Co(5cqn)_2(NO_3)(py)]\cdot0.5py$ in DMSO-d_6; standard, internal TMS.

Gaseous Products. Gaseous product from the reaction in DMF, the pyridine–DMF, or pyridine was only N_2O. It has been reported that N_2 together with N_2O was liberated on disproportionation of NO in the presence of transition-metal complex.[3)] N_2 was not liberated under the present experimental conditions.

For the reaction giving **4**, **5**, or **8**, the stoichiometry was examined by measuring the relative molar ratio of the residual NO to the produced N_2O. The molar ratio of NO to the cobalt complex was 20.0, and the cobalt complex and the organic solvent used were 0.25 mmol and 10 cm^3, respectively. The ratio observed was generally larger than that calculated on the assumption that the reaction proceeded completely, and the reproducibility was not always good. The yield of the solid product calculated from the observed ratio was smaller than the yield obtained actually. These suggest that the total reaction with NO is not simple, and side reactions which could not be identified may consume the produced N_2O.

Effects of Organic Solvents on the Reactions. On the reaction of $[Co(qn)_2(NO)]$ (qn=8-quinolinolate ion) with NO in CH_2Cl_2 having very poor coordinating ability to metal ion, NO attacks the coordinating nitrosyl group, NO^-, electrophilically to give NO_2^- with retention of the Co–NO bond; the nitrogen atom in the nitro group comes from the nitrosyl group. This was confirmed by ^{15}N-labelled experiments.4)

For examining the mechanism of the reaction of the nitrosyl complex, **1**, or **2**, with NO in the pyridine–DMF, the following combinations of nitrogen isotopes were used; A, (^{14}NO-complex)–(^{15}NO gas) and B, (^{15}NO-complex)–(^{14}NO gas). The molar ratio of the NO to the nitrosyl complex was *ca.* 6—7. In the case of A, the mass analysis showed that the relative molar ratio of ^{14}NO to ^{15}NO in the residual NO was almost equal to that of the ^{14}NO-complex to the ^{15}NO gas. The experiment using the isotopes suggests that the ^{14}NO-complex decomposes almost perfectly to liberate ^{14}NO and the liberated ^{14}NO together with ^{15}NO, original reactant, reacts with the resulting cobalt(II) complex to give the nitrato complex. In the case of B was also found the same phenomena as observed for the case A. The ^{14}N–^{15}N scramble was observed for the reaction of the nitrosyl complex with NO, hence the reaction mechanism could not be elucidated from the isotopic experiments. In solution containing strong σ-donor Lewis base such as pyridine, after the Co–NO bond in the original nitrosyl complex was broken and the resulting cobalt(II) complex was nitrosylated again, NO reacts with the NO^- group to give NO_2^- and N_2O with cleavage of the Co–NO bond, and the NO_2^- reacts further with NO to give NO_3^- and N_2O. Coordination of pyridine to the cobalt ion seems to unstabilize the Co–NO bond. The proposed mechanism for the reaction is pictured (Scheme 1).



Scheme 1. Proposed reaction mechanism.

The reaction of the nitrosyl complex with NO in DMF could not be elucidated. Since coordinating ability of DMF to metal ion is weaker than that of pyridine, the complicated reactions may proceed.

On the reaction of $[CoL_2]$ with NO in pyridine and 10 v% pyridine–DMF, the disproportionation of NO to NO_3^- and N_2O involving an oxidation of cobalt(II) to cobalt(III) was observed. The reaction is considered to be initiated from a nitrosylation of $[CoL_2]$ followed by the reaction of the resulting nitrosyl complex with NO as mentioned above. The reaction giving **6** is considered as follows; after $[Co(5nqn)_2]$ was nitrosylated, the resulting NO^- group seems to react further with NO to give NO_2^- without cleavage of the Co–NO bond, because DMF is not so strong Lewis base as break the Co–NO bond.

On metal-induced NO disproportionations which has been reported so far, the product with most oxidized nitrogen atom is nitrite ion.3) In a series of our reaction system4,5) including the present study, nitrate ion was produced. This phenomenon is considered to be usual on the disproportionation, especially in solvent with strong coordinating ability such as pyridine.

A number of studies on the disproportionation of NO have been reported,3) but the stoichiometry of the reaction has been mentioned for only a few examples.2,18) Since this type of the reaction is very complicated, it seems likely that stoichiometry of the total reaction can not be elucidated in many cases.

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