The Reaction of [CoL_2] or [$CoL_2(NO)$] (L=4-Methyl-8-quinolinolate Ion) with Nitrogen Monoxide

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(Received November 30, 1984)

[$Co(4mqn)_2$]·$2H_2O$ (4mqn=4-methyl-8-quinolinolate ion) reacted with nitrogen monoxide in CH_2Cl_2 or in DMF at room temperature to give [$Co(4mqn)_2(NO)$] (**1**). [$Co(4mqn)_2$]·$2H_2O$ and **1** reacted with nitrogen monoxide in 10 vol% pyridine-DMF and in pyridine at *ca.* 283—288 K to precipitate [$Co(4mqn)_2(NO)(py)$] (**2**). When the reaction was carried out at *ca.* 293—303 K, [$Co(4mqn)_2(NO_2)(py)$] (**3**) instead of **2** was precipitated. From the filtrates, [$Co(4mqn)_2(NO_3)(py)$]·py·$2H_2O$ (**4**) was obtained. The gaseous product of the reactions giving **2** and **4**, and **3** and **4**, was dinitrogen oxide. The stoichiometries of the reactions in the pyridine-DMF and in pyridine were confirmed by mass analyses for the residual nitrogen monoxide and the produced dinitrogen oxide.

A number of studies of the reactions of transition-metal or transition-metal nitrosyl complexes with nitrogen monoxide, NO, have been reported.[1)] However, there have been no careful examinations of the effects of the solvents used or those of the substituents of the ligands used on the reactions.

Bis(8-quinolinolato)cobalt(II) reacted with NO in CH_2Cl_2, which has a poor coordination ability, to give [$Co^{III}(qn)_2(NO)$] (qn=8-quinolinolate ion) with the NO^- group, and the nitrosyl reacted further with NO in CH_2Cl_2 to give [NO][$Co^{III}(qn)_2(NO_3)(NO_2)$], with the liberation of N_2O.[2)] In this reaction, the nitrosyl group forms the NO_2^- with a retention of the original Co–NO bond. On the other hand, bis(2-methyl-8-quinolinolato)cobalt(II) reacted with NO in CH_2Cl_2 to give $[NO]_3$[$Co^I(2mqn)_2(NO_3)(NO_2)$] and [$Co^0(2mqn)_2(NO)_2$] (2mqn=2-methyl-8-quinolinolate ion), with the liberation of N_2O.[3)] The difference in the reactions of NO with the corresponding cobalt ions seems to be due to the electron-donative power of the CH_3 group in the 2mqn.

In a solvent possessing a strong coordinating ability, such as pyridine, [$CoL_2(NO)$] with the NO^- group (L=5-chloro- or 5-nitro-8-quinolinolate ion) reacted with NO to give the nitrato complex, [$CoL_2(NO_3)(py)$], involving scrambling between the NO^- group and the NO.[4)]

The present paper will describe the reactions of [$Co(4mqn)_2$]·$2H_2O$ or [$Co(4mqn)_2(NO)$] (4mqn=4-methyl-8-quinolinolate ion) with NO in CH_2Cl_2, DMF, 10 vol% pyridine–DMF, or pyridine; the effects of the solvents and the substituents in the quinoline ring on the reactions are also discussed. The stoichiometries of the reactions are also examined on the basis of the determination of the relative molar ratio of the residual NO to the N_2O produced.

Experimental

The JIS-GR CH_2Cl_2, DMF, and pyridine were dried over Zeorum A-4, stored under argon, and carefully degassed by three cycles of freeze-pump-thaw prior to use. The JIS-GR diethyl ether used as a precipitation reagent was deaerated with dinitrogen before use. The ^{15}NO was prepared by the reaction of $K^{15}NO_3$ (^{15}N atom%=99) with concd H_2SO_4 and mercury. The 4-methyl-8-quinolinol was prepared from *o*-aminophenol and methyl vinyl ketone.[5)] The [$Co(4mqn)_2$]·$2H_2O$ was prepared by the ordinary method. Anal. ($CoC_{20}H_{20}O_4N_2$) Co, C, H, N.

The IR spectra of the solid products were measured on JASCO A-202 (400—4000 cm^{-1}) and JASCO IR-F (200—650 cm^{-1}) spectrometers. The isotopic shifts upon ^{15}N-substitution were carefully measured at 80 K. For identifying the gaseous products and examining the stoichiometry of the reaction in 10 vol% pyridine–DMF or in pyridine, a Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi data-processing system (M-003) was used; the IR bands of the gaseous materials and the ^{15}N-isotopic shifts[6)] in the 1000—4000 cm^{-1} region were also measured. The magnetic susceptibilities of the solid products were measured by the Gouy method at room temperature.

All the reactions were treated in a vacuum line. The representative scale and the procedure were as follows: NO (5.0 mmol) was trapped in a reaction vessel (*ca.* 150 cm^3) containing [$Co(4mqn)_2$]·$2H_2O$ (0.5 mmol) suspended or dissolved in the organic solvents (10 cm^3) with the aid of liquid nitrogen. The reaction vessel was shaken under running water until the frozen solution thawed, and then the contents were stirred for 1—3 d to obtain the precipitate. By dropping the filtrate into deoxygenated diethyl ether, another product was precipitated. These products were washed with diethyl ether and dried under a vacuum. When [$Co(4mqn)_2(NO)$] was used as the starting material, the degassed pyridine–DMF or pyridine was poured into the reaction vessel containing the nitrosyl complex, which had been kept at the temperature of liquid nitrogen, and then NO was trapped. The contents were stirred after having been thawed under running water.

Results and Discussion

The elementary analyses, the chemical formulae, and the yields of the solid products are shown in Table 1. All the compounds were diamagnetic, indicating that they are low-spin type cobalt(III) compounds, since the formal oxidation number of the coordinating NO in the nitrosyl compounds is −I, as will be discussed later. The compounds are stable in the solid state under air, but the nitrosyl compounds are unstable in the

Table 1. Elementary analyses and yields of the solid products

Complex (Color)	Yield/%		Elementary analysis				Reactant[a)]	Temperature	Solvent
			Co(%)	C(%)	H(%)	N(%)			
1 $[Co(4mqn)_2(NO)]$	60—90	Found	14.4	58.9	3.9	10.4	**A**		CH_2Cl_2
(dark green)		Found	14.0	59.2	3.9	10.3	**A**		DMF
		Calcd	14.6	59.3	4.0	10.4			
2 $[Co(4mqn)_2(NO)(py)]$	40—60	Found	11.9	60.9	4.5	11.4	**A**	b)	10vol%py-DMF
(yellowish khaki)	60	Found		60.9	4.4	11.7	**A**		py
		Found	11.9	61.7	4.4	11.6	**1**		10vol%py-DMF
	20	Found		60.3	4.3	11.6	**1**		py
		Calcd	12.2	62.0	4.4	11.6			
3 $[Co(4mqn)_2(NO_2)(py)]$	40	Found		60.2	4.4	11.5	**A**	c)	10vol%py-DMF
(yellowish khaki)	30—50	Found		59.4	4.3	11.4	**1**		10vol%py-DMF
		Calcd		60.0	4.2	11.2			
4 $[Co(4mqn)_2(NO_3)(py)]$	30—40	Found	9.4	56.8	4.5	11.3	**A**	b)	10vol%py-DMF
$\cdot py\cdot 2H_2O$	30	Found		57.6	4.5	11.0	**A**		py
(brownish khaki)	40—50	Found	9.2	56.4	4.4	11.1	**1**	c)	10vol%py-DMF
		Calcd	9.4	57.1	4.8 (4.4)[d)]	11.1			

a) **A**, $[Co(4mqn)_2]\cdot 2H_2O$. b) At *ca.* 283—288 K. c) At *ca.* 293—303 K. d) The hydrogen content on the assumption that the $2H_2O$ of **4** leaves during the preliminary treatment of the elementary analysis. 4mqn=4-methyl-8-quinolinolate ion.

dissolved state.

Reaction of $[Co(4mqn)_2]\cdot 2H_2O$ with NO in CH_2Cl_2 or in DMF. $[Co(4mqn)_2]\cdot 2H_2O$ reacted with NO to precipitate $[Co(4mqn)_2(NO)]$ (**1**). No further reaction proceeded in CH_2Cl_2; however, in DMF **1** reacted further with NO to give a clear, reddish-brown solution, with the liberation of N_2O. However, the precipitate obtained by adding the solution to diethyl ether could not be characterized.

The IR bands at 1658(vs), 551(s), and 537(s) cm^{-1} for **1** shifted down by 31, 6, and 7 cm^{-1} respectively upon ^{15}N-substitution. The 1658 cm^{-1} band was assigned to the N–O stretching vibration, and the 551 and 537 cm^{-1} bands, to the skeletal vibrations between the cobalt and the NO group.[7)] The wave numbers of the N–O stretching band and the electrophilic attack of NO on the NO group, as will be mentioned later, suggest that **1** is an NO^- complex.[4,7)] The reaction giving **1** can be regarded as an oxidative addition of NO to cobalt(II).

Reaction of $[Co(4mqn)_2]\cdot 2H_2O$ or $[Co(4mqn)_2(NO)]$ with NO in 10 vol% Pyridine-DMF or in Pyridine. The gaseous product was always only N_2O.

Reaction at ca. 283—288 K: $[Co(4mqn)_2]\cdot 2H_2O$ reacted with NO to precipitate $[Co(4mqn)_2(NO)(py)]$ (**2**). The N–O stretching and the skeletal vibrations between the cobalt and the NO group were observed at 1616, 558, and 431 cm^{-1}. The wave numbers of the N–O stretching vibration for **1**, 1658 cm^{-1}, shifted down to 1616 cm^{-1} by the coordination of pyridine to the cobalt ion. The 321(s) cm^{-1} band of **2** could be assigned to the Co–N(pyridine) stretching vibration by a careful comparison of the IR spectrum for **2** with that for **1**.[8)]

By adding the filtrate to deaerated diethyl ether, a brownish khaki product, **4**, was precipitated. This product was not clearly characterized. The IR band at 823(w) cm^{-1} shifted to 810 cm^{-1} upon ^{15}N-substitution, but no isotopic shifts for any other bands could be observed.[9)]

The stoichiometries of the reactions to be discussed later can be reasonably explained on the assumption that **4** contains a nitrate ion. If so, the 823 cm^{-1} band can be assigned to the out-of-plane bending of NO_3^-.[4)] The 321 cm^{-1} (s) band was assigned to the Co–N (pyridine) stretching vibration, as had been **2**. By the reactions of $[CoL_2]$ (L=5-chloro- or 5-nitro-8-quinolinolate ion) with NO in the same solvents, $[CoL_2(NO_3)(py)]$ was isolated.[4)] **4** seems to be $[Co(4mqn)_2(NO_3)(py)]\cdot py\cdot 2H_2O$ considering the similarities of the reactions, the elementary analysis, the IR spectrum, and the stoichiometry of the reaction. The bands characteristic of a coordinating nitrate ion, with the exception of the 823 cm^{-1} band, seem to be hidden under the strong absorptions due to the 4mqn and pyridine. The water of crystallization in **4** may come from a small quantity of water contained in diethyl ether.

The reaction of $[Co(4mqn)_2]\cdot 2H_2O$ with NO consists of a nitrosylation reaction ($Co^{2+}+NO\rightarrow Co^{3+}+NO^-$) and the disproportionation of NO to NO_3^- and N_2O ($Co^{2+}+5NO\rightarrow Co^{3+}+NO_3^-+2N_2O$).

$[Co(4mqn)_2(NO)]$ reacted with NO to give the same products, **2** and **4**. The reaction can be described as $Co^{3+}+NO^-+4NO\rightarrow Co^{3+}+NO_3^-+2N_2O$.

Reaction at ca. 293—303 K: Both $[Co(4mqn)_2]\cdot 2H_2O$ and **1** reacted with NO to precipitate $[Co(4mqn)_2(NO_2)(py)]$ (**3**). The terminal N–O stretching band of the nitrosyl complex could not be observed. The 1402(s) and 1314(s) cm^{-1} bands shifted to 1383 and 1291 cm^{-1} respectively upon ^{15}N-substitution (see Fig. 1). These bands can be assigned to the N–O stretching bands characteristic of the coordinating nitro ion.[4)] The strong band at 320 cm^{-1} is the Co–N(pyridine) stretch-

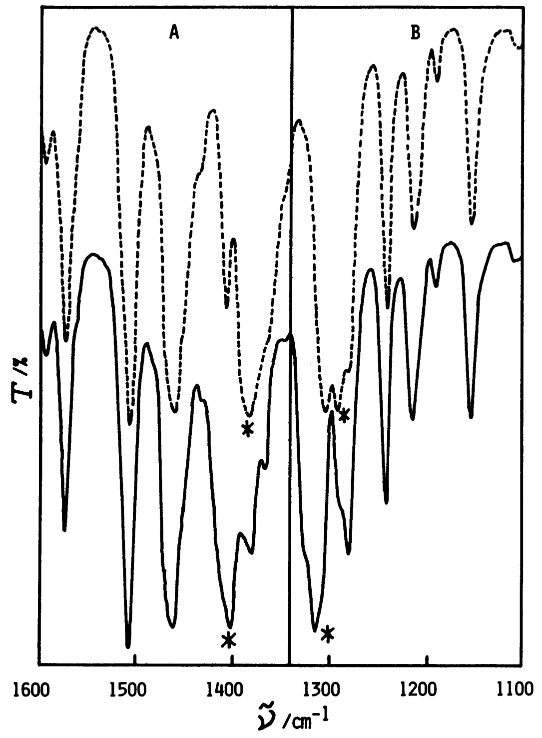


Fig. 1. IR spectra of [Co(4mqn)$_2$(NO$_2$)(py)] (4mqn=4-methyl-8-quinolinolate ion).
——: ^{14}NO$_2$ complex, -----: ^{15}NO$_2$ complex (^{15}N atom%=99).
* indicates the N–O stretching band characteristic of the coordinating nitro ion. The bands due to the nitro ion, and the bands due to the coordinating 4mqn and pyridine partially overlapped.
A region: poly(chlorotrifluoroethylene) oil mull, B region: Nujol mull.

ing vibration. The precipitate from the filtrate was **4**, like that prepared at a low temperature. The stoichiometry of the reaction reasonably explains that **3** and **4** contain a NO_2^- and a NO_3^- respectively, as will be discussed later.

The reaction of [Co(4mqn)$_2$]·2H$_2$O with NO can be regarded as the disproportionations of NO to NO_2^- and N_2O ($Co^{2+}+3NO \rightarrow Co^{3+}+NO_2^-+N_2O$) and to NO_3^- and N_2O ($Co^{2+}+5NO \rightarrow Co^{3+}+NO_3^-+2N_2O$), involving the oxidation of Co^{2+} to Co^{3+}.

On the reaction of **1** with NO, the coordinating NO^- group was electrophilically attacked by NO to give NO_2^- and NO_3^-, with the liberation of N_2O: $Co^{3+}+NO^-+2NO \rightarrow Co^{3+}+NO_2^-+N_2O$ and $Co^{3+}+NO^-+4NO \rightarrow Co^{3+}+NO_3^-+2N_2O$.

Characterization of Reactions. The stoichiometries of the reactions in the pyridine-DMF and in pyridine were also examined. The relative molar ratios of the residual NO to the gaseous product, N$_2$O, were calculated from the reaction formulae, based on the yields of the solid products. The reaction formulae are shown in the last item. The observed ratios agreed with the calculated ones, shown in Table 2, indicating that the reactions shown in the last item proceed.

For examining the mechanism of the reaction of **1** with NO in the pyridine-DMF at *ca.* 288 K, the following isotopic combinations were used; *A*, (the ^{14}NO complex)-(^{15}NO gas) and *B*, (the ^{15}NO complex)-(^{14}NO gas). In the case of *A*, the molar ratio of ^{14}NO to ^{15}NO observed in the residual NO gas was almost equal to that of ^{14}NO to ^{15}NO contained in the reaction system. The same phenomenon was also observed for the case of *B*. Moreover, [Co(4mqn)$_2$(^{14}NO)] reacted with ^{15}NO to give [Co(4mqn)$_2$(^{14,15}NO)(py)], showing the ^{14}N–O and ^{15}N–O stretching bands. On a reaction at a higher temperature (*ca.* 298 K), the same ^{14}N–^{15}N scrambling as that at a lower temperature was observed.

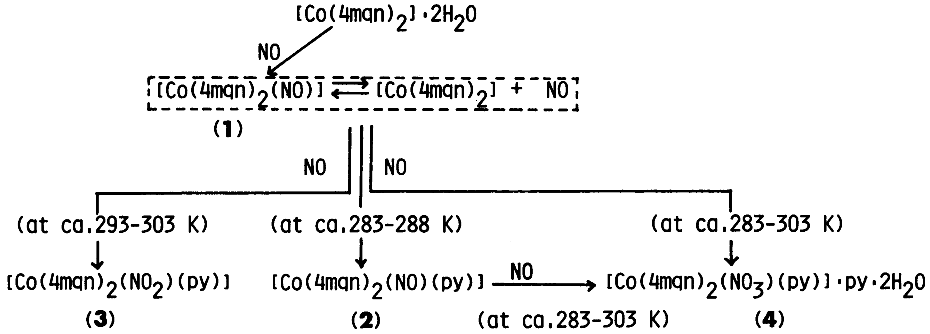
These facts suggest that **1** decomposes perfectly to the cobalt(II) complex, [Co(4mqn)$_2$], and NO, and that the resulting NO gas, together with NO gas, an original reactant, reacts again with [Co(4mqn)$_2$] to give **1**. A part of the **1** is precipitated as **2** at a low temperature. On the other hand, at a high temperature, **1** reacts further with NO to give **3**. This reaction seems to proceed with a cleavage of the Co–NO bond, because the coordination of pyridine unstabilizes the Co–NO bond in the dissolved state.[4] The remaining part of **1** in the dissolved state reacts with NO to give **4**.

When a smaller amount of **1**, for example, 0.2 mmol, was used without changing the amounts of NO and the pyridine-DMF, only **4** was obtained. **2** reacted with NO in the pyridine-DMF on the same scale as has

Table 2. Stoichiometry of the reaction

Reactants		Solid products		NO/N$_2$O[c]		Solvent
				Found	Calcd	
At a low temperature[a]						
A(0.50)[d]	NO(5.0)	**2**(0.18)	**4**(0.20)	9.4	9.6	10vol%py-DMF
A(0.50)	NO(5.0)	**2**(0.31)	**4**(0.17)	11	11	py
1(0.75)	NO(5.0)	**2**(0.54)	**4**(0.20)	9.2	10	py
1(0.33)	NO(5.0)	**2**(0.07)	**4**(0.22)	11	9.4	py
At a high temperature[b]						
A(0.50)	NO(5.0)	**3**(0.21)	**4**(0.17)	6.8	6.4	10vol%py-DMF
1(0.50)	NO(5.0)	**3**(0.24)	**4**(0.19)	6.1	6.1	10vol%py-DMF

a) At *ca.* 283—288K. b) At *ca.* 293—303K. c) Relative molar ratio of the residual NO to the produced N$_2$O. d) mmol unit. **A**, [Co(4mqn)$_2$]·2H$_2$O. **1**, [Co(4mqn)$_2$(NO)]. **2**, [Co(4mqn)$_2$(NO)(py)]. **3**, [Co(4mqn)$_2$(NO$_2$)(py)]. **4**, [Co(4mqn)$_2$(NO$_3$)(py)]·py·2H$_2$O. 4mqn=4-methyl-8-quinolinolate ion.



Scheme 1. Reaction of [Co(4mqn)$_2$]·$2H_2O$ or [Co(4mqn)$_2$(NO)] with NO in 10vol% py–DMF or in py.
(4mqn = 4-methyl-8-quinolinolate ion).

been described in the Experimental section to give only **4**, but to leave the unreacted **2** behind at both low and high temperatures. These facts suggest that **2** in the dissolved state reacts with NO to produce **4**, while **3** does not come from **2**. **3** hardly dissolved at all in the pyridine–DMF or in pyridine; hence, it did not react with NO to be recovered quantitatively. This indicates that **4** does not come from **3**. The reactions of [Co(4mqn)$_2$]·$2H_2O$ and [Co(4mqn)$_2$(NO)] with NO are summarized in Scheme 1.

The critical temperature in the preparation of **2** or **3** was ambiguous. At 288—293 K, **2**, **3**, or their mixture was precipitated in subtly different conditions on that occasion.

In CH_2Cl_2, the reaction of [Co(4mqn)$_2$]·$2H_2O$ with NO was expected to be similar to that of [Co(2mqn)$_2$]·H_2O with NO because of the electron-donative power of the CH_3 group in the ligands.[3] However, the reaction gave only [Co(4mqn)$_2$(NO)], and no further reaction with NO could be found such as was observed for the reactions of [CoL$_2$] (L=5-chloro- or 5-nitro-8-quinolinolate ion) with NO.[4]

As for the reactions of [Co(4mqn)$_2$]·$2H_2O$ or [Co(4mqn)$_2$(NO)] with NO in 10vol% pyridine–DMF and in pyridine, [Co(4mqn)$_2$(NO)(py)] and [Co(4mqn)$_2$(NO$_2$)(py)] were prepared with [Co(4mqn)$_2$(NO$_3$)(py)]·py·$2H_2O$ at low and high temperatures respectively, although [CoL$_2$] and [CoL$_2$(NO)] (L=8-quinolinolate, 5-chloro-, or 5-nitro-8-quinolinolate ion) reacted with NO in the same solvents to produce [CoL$_2$(NO$_3$)(py)]. No remarkable effects of the substituent in the quinoline ring on the reactions could be found except for the solubilities of the obtained compounds. The nitro complex, [Co(4mqn)$_2$(NO$_2$)(py)], in the present study may be isolated because of its sparing solubility, since it is generally expected that, after [CoL$_2$] has been nitrosylated, the NO^- group reacts with NO to give NO_3^- by way of NO_2^-.[4]

The present reaction in DMF could not be elucidated as observed for the reactions of [CoL$_2$] (L=2-methyl- or 5-chloro-8-quinolinolate ion) with NO because the coordinating ability of DMF is not stronger than that of pyridine, and so complicated reactions may occur.

In the present study, the stoichiometries of the reactions in the pyridine–DMF and in pyridine were confirmed because all the products could be identified. It is very interesting that NO^- or NO_2^- is formed, together with NO_3^-, by the disproportionation of NO with a difference in the reaction temperature.

References

1) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974); K. G. Caulton, *ibid.*, **14**, 317 (1975); J. A. McCleverty, *Chem. Rev.*, **79**, 53 (1979); K. K. Pandey, *Coord. Chem. Rev.*, **51**, 69 (1983).

2) E. Miki, *Chem. Lett.*, **1980**, 835.

3) E. Miki, K. Saito, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **56**, 3515 (1983).

4) E. Miki, K. Ishimaru, K. Mizumachi, T. Ishimori, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **58**, 962 (1985).

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

6) J. Laane and J. R. Ohlsen, "Characterization of Nitrogen Oxides by Vibrational Spectroscopy," in "Progress in Inorganic Chemistry," ed by S. J. Lippard, An Interscience Publication by John Wiley & Sons, New York (1980), Vol. 27, pp. 465—513.

7) E. Miki, H. Okamura, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **51**, 1768 (1978), and the references cited therein.

8) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

9) The carbon-13 and nitrogen-15 NMR measurements for **4** in DMSO-d_6 were performed at *ca.* 333 K to increase its low solubility to DMSO and decrease the high viscosity of the solution at room temperature, but **4** decomposed in DMSO to precipitate an uncharacterized product. The experimental conditions were the same as those described in Ref. 4.