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Reaction of Bis(4-methyl-8-quinolinolato)nitrosylpyridinecobalt(II) with Nitrogen Monoxide in Dichloromethane

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Synopsis. [Co(4mqn)$_2$(NO)(py)] (4mqn=4-methyl-8-quinolinolate ion, $C_{10}H_8NO^-$; py=pyridine) reacted with nitrogen monoxide in dichloromethane to produce a new compound, [NO][Co(4mqn)$_2$(NO$_3$)(py)], with liberation of dinitrogen oxide. The solid product was characterized by IR (including the ^{15}N-isotopic shifts), magnetic, and MS measurements.

It is well-known that transition-metal complexes react with nitrogen monoxide, NO, to make the NO disproportionation and transition-metal nitrosyls with NO$^-$ group also react with NO to cause electrophilic attack by NO on the nitrosyl group.[1,2]

We have reported the reaction of NO with [Co^{II}L$_2$] (L=8-quinolinolate ion or its derivatives) or [Co^{III}L$_2$(NO)] with NO$^-$ group in organic solvents.[3-6] In CH_2Cl_2 inhering poor coordinating ability to metal ion, [CoL$_2$] is nitrosylated or the nitrosyl group in the resulting nitrosyl complex reacts further with NO to give NO_3^-, NO_2^-, NO$^+$ (nitrosyl cation), and N_2O.[3,4] On the other hand, on the reaction of [CoL$_2$] with NO in pyridine having strong coordinating ability, [CoL$_2$] is nitrosylated followed by electrophilic attack of NO on the nitrosyl group to give NO_3^- or NO_2^-, and N_2O.[5,6]

In this paper, we report the reaction of [Co(4mqn)$_2$(NO)(py)] (4mqn=4-methyl-8-quinolinolate ion, py=pyridine) with NO in CH_2Cl_2. The solid product was [NO][Co(4mqn)$_2$(NO$_3$)(py)], the gaseous one being N_2O. The reaction is shown as follows;

$$\mathrm{Co^{3+} + NO^-(coord) + 5NO \longrightarrow Co^{2+} + NO^+}$$
$$\mathrm{+\,NO_3^-(coord) + 2N_2O}\ (\mathrm{coord} = \mathrm{coordinating}).$$

Experimental

Dichloromethane was dried over Zeorum A-4, distilled and stored under argon. Nitrogen[^{15}N] monoxide was derived from K^{15}NO$_3$ (^{15}N atom%=99). The reactants, [Co(4mqn)$_2$(NO)(py)] with NO$^-$ group and its ^{15}NO-labeled compound (^{15}N atom%=99), were prepared according to the literature.[6] Anal. ($CoC_{25}H_{21}O_3N_4$) Co, C, H, N.

The reactions were carried out using a vacuum line. Dichloromethane was degassed by three cycles of freeze-pump-thaw before use. The degassed CH_2Cl_2 (10 cm^3) was transferred to the reaction vessel containing the nitrosyl complex (0.3 mmol) and NO (5 mmol) which had been kept at the temperature of liquid nitrogen. The contents were stirred for ca. 50 h at room temperature after having been thawed under running water. The original yellowish khaki complex reacted rapidly with NO to give dark brown solution and gradually precipitate a khaki product in process of the reaction. The product was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 60% (ca. 100 mg). Found: Co, 11.1; C, 54.6; H, 3.9; N, 12.8%. Calcd for [NO][Co($C_{10}H_8NO$)$_2$(NO$_3$)(C_5H_5N)] ($CoC_{25}H_{21}O_6N_5$): Co, 10.8; C, 55.0; H, 4.0; N, 12.8%.

The magnetic susceptibility of the solid product was measured by the Gouy method. The IR spectra of the solid products were measured as Nujol and poly(chlorotrifluoroethylene) oil mulls in the 200—4000 cm^{-1} region. 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 (including ^{15}N-isotopic shifts) in the 1000—4000 cm^{-1} region.[6] The negative SIMS (secondary ion mass spectrometry) spectrum of the solid product was measured by the mass spectrometer with a SIMS unit and a negative ion measurement unit. The product was dissolved or suspended in a glycerol/3-mercapto-1,2-propanediol, glycerol/sulfolane, or diethanolamine/3-mercapto-1,2-propanediol matrix, and placed on a silver plate probe tip. Xenon was used to produce the primary ion.[7]

Results and Discussion

The khaki product in the solid state is stable in air but is decomposed in polar organic solvents such as DMF and DMSO.

The IR spectrum of the solid product showed some absorption bands characteristic of nitrosyl cation and

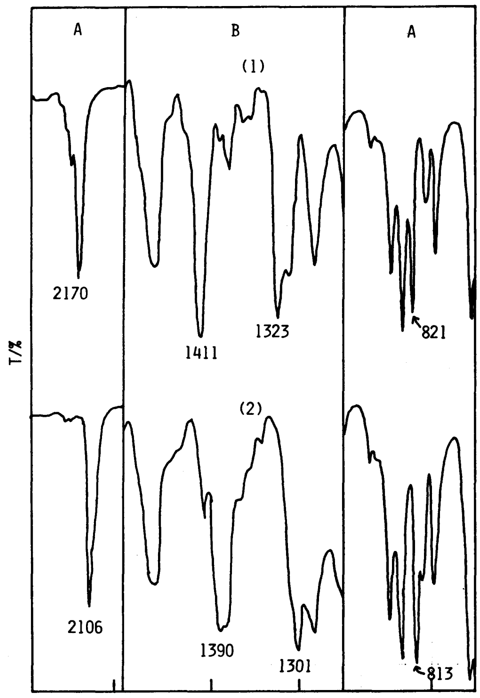

Fig. 1. IR spectra of [NO][Co(4mqn)$_2$(NO$_3$)(py)] (4mqn=4-methyl-8-quinolinolate ion, py=pyridine). (1): ^{14}N-complex, (2): ^{15}N-complex (^{15}N atom%=99). A region: Nujol mull, B region: poly(chlorotrifluoroethylene) oil mull.

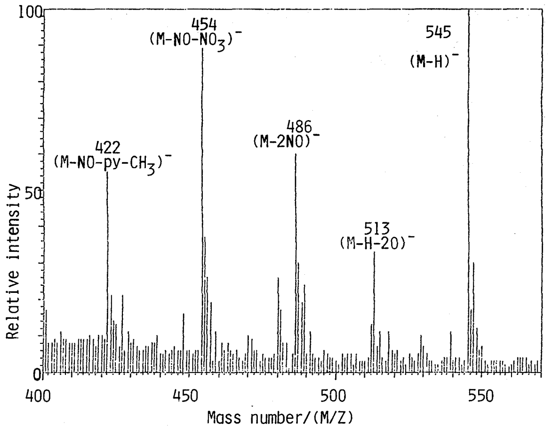

Fig. 2. Negative SIMS spectrum of [NO][Co(4mqn)$_2$-(NO$_3$)(py)] (4mqn=4-methyl-8-quinolinolate ion, py=pyridine) in the matrix, diethanolamine/3-mercapto-1,2-propanediol.

unidentate nitrate ion. These bands shifted downwards upon ^{15}N-substitution as shown in Fig. 1; the strong band at 2170 cm^{-1} shifted to 2106 cm^{-1}, and was assigned to the stretching vibration of nitrosyl cation.[3,4] The strong bands at 1411, 1323, and 821 cm^{-1} shifted to 1390, 1301, and 813 cm^{-1}, respectively, which were assigned to the NO$_2$ antisymmetric stretching, the symmetric stretching, and the out-of-plane bending vibrations of the NO$_3^-$, respectively.[3-6] The strong band at 327 cm^{-1} was assigned to the Co-N(pyridine) stretching vibration.[6]

The negative SIMS spectrum in diethanolamine/3-mercapto-1,2-propanediol showed the peaks at m/z= 545, 513, 486, 454, and 422. These ions correspond to (M−H)$^-$, (M−H−2O)$^-$, (M−NO−NO)$^-$, (M−NO−NO$_3$)$^-$, and (M−NO−py−CH$_3$)$^-$ where M is the molecular ion with m/z=546, respectively (see Fig. 2). These peaks were also observed in glycerol/3-mercapto-1,2-propanediol and glycerol/sulfolane matrices.

The elemental, IR, and MS analyses indicate that the solid compound is [NO][Co(4mqn)$_2$(NO$_3$)(py)] containing cobalt(II). The effective magnetic moment was 1.66 BM at 295 K, supporting low-spin d^7 configuration of the cobalt ion.

The IR and MS measurements clearly showed that the gaseous product was only dinitrogen oxide.

For tracing the nitrogen atoms in the reaction of the nitrosyl group with NO, the following isotopic combinations were used and the residual NO and the liberated N$_2$O were analysed by the mass spectrometer; A (the reaction of the ^{14}NO-complex with ^{15}NO gas) and B (the reaction of the ^{15}NO-complex with ^{14}NO gas). The molar ratio of ^{14}NO to ^{15} NO observed after the reaction was equal to that calculated from the amounts of the reactants before the reaction; the calculated and observed ratios in the case of A were 0.045 and 0.050±0.001, respectively, and those in the case of B, 19 and 20±3, respectively. This shows that the ^{14}N-^{15}N scrambling between the nitrosyl group and the NO gas occurred. Such a phenomenon has been observed for the reaction of [CoL$_2$(NO)] (L=8-quinolinolate ion or its derivatives) with NO in solvents having coordinating ability to metal ion.[5,6,8] The reproducibility of the same measurements for the liberated N$_2$O as the NO was poor, but the ^{14}N-^{15}N scrambling was also observed for N$_2$O. These scrambling phenomena suggest that the nitrosyl complex liberates NO in dissolution and the liberated NO together with original reactant, NO, reacts with the resulting cobalt(II) complex to attain the following equilibrium; Co$^{\mathrm{II}}$+NO$\rightleftarrows$Co$^{\mathrm{III}}$-NO$^-$.[5,6] Thus, the reaction mechanism could not be elucidated.

In CH$_2$Cl$_2$, [Co(4mqn)$_2$(NO)] did not react with NO. The N-O stretching bands of [Co(4mqn)$_2$(NO)] and [Co(4mqn)$_2$(NO)(py)] are observed at 1658 and 1616 cm^{-1}, respectively, suggesting that electrophilicity of the nitrosyl group in the latter is stronger than that in the former due to coordination of pyridine. Thus, even in solvent having poor coordinating ability, the electrophilic attack of NO on the nitrosyl group would proceed to produce NO$_3^-$, NO$^+$ (nitrosyl cation), and N$_2$O as observed for the reaction of [Co(qn)$_2$(NO)] (qn=8-quinolinolate ion) with NO in CH$_2$Cl$_2$.[3]

There is a possibility that [Co(4mqn)$_2$L(py)] (L= NO$_3^-$ or NO$_2^-$) is formed as a minor product in the present reaction considering our last paper.[6] However, the negative SIMS spectra showed no peaks corresponding to their molecular ion regions.

The present overall reaction can be represented as

$$\mathrm{Co^{3+} + NO^-(coord) + 5NO \longrightarrow Co^{2+} + NO^+}$$
$$\mathrm{+\ NO_3^-(coord) + 2N_2O(coord = coordinating).}$$

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