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Reaction of Bis(2-methyl-8-quinolinolato)cobalt(II) with Nitrogen Monoxide[†]

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Synopsis. $[Co(C_{10}H_8NO)_2]\cdot H_2O$ ($C_{10}H_8NO^-$=2-methyl-8-quinolinolate ion) reacted with nitrogen monoxide in dichloromethane to give unstable compounds, $[Co(C_{10}H_8NO)_2(NO)_2]$ and $[NO]_3[Co(C_{10}H_8NO)_2(NO_3)(NO_2)]$ with liberation of dinitrogen oxide. The compounds were characterized by ^{15}N-isotopic effect observed on the IR spectra.

Nitrogen monoxide reacts with low-valent transition-metal complexes to give the nitrosyls or to cause a disproportionation of nitrogen monoxide.[1-3] Recently, one of the authors reported that $[Co(C_9H_6NO)_2]$ ($C_9H_6NO^-$=8-quinolinolate ion) reacted with nitrogen monoxide in dichloromethane at room temperature to give $[NO][Co^{III}(C_9H_6NO)_2(NO_3)(NO_2)]$ with liberation of dinitrogen oxide via $[Co^{III}(C_9H_6NO)_2(NO)]$.[4] The reaction involves a nitrosylation followed by an electrophilic attack of nitrogen monoxide on the coordinating nitrosyl group, and a disproportionation of nitrogen monoxide to $[NO]^+$, NO_3^-, and dinitrogen oxide.

In this paper, we report a reaction of $[Co(C_{10}H_8NO)_2]\cdot H_2O$ ($C_{10}H_8NO^-$ = 2-methyl-8-quinolinolate ion) with nitrogen monoxide in dichloromethane, pyridine, 10 vol% pyridine–DMF, or DMF.

The reaction was performed using a vacuum line, and the solid products were manipulated under nitrogen atmosphere as soon as possible. Starting material, $[Co(C_{10}H_8NO)_2]\cdot H_2O$ was synthesized by ordinary method. Nitrogen[^{15}N] monoxide was derived from potassium nitrate[^{15}N] (^{15}N atom%=99.7). The gaseous product was identified by mass spectrometer, and the IR bands and their ^{15}N-isotopic shifts.[5]

$[Co(C_{10}H_8NO)_2]\cdot H_2O$ (0.5 mmol) suspended in dichloromethane (20 cm^3) degassed by three cycles of freeze-pump-thaw was brought into contact with nitrogen monoxide (5 mmol), and stirred for 1 d at room temperature or for 7 d at *ca.* −20 °C. The suspended $[Co(C_{10}H_8NO)_2]\cdot H_2O$ changed from original orange to russet. The yield of the russet compound (**1**) was *ca.* 70% based on the starting material. The liberated gas was only dinitrogen oxide under the experimental conditions.

Compound **1** could not be purified since the compound in the solid state was gradually decomposed with liberation of nitrogen monoxide even under nitrogen atmosphere, and was also unstable in deoxygenated DMF or dichloromethane. The elementary analyses consisted with $Co_1C_{20}H_{16}N_7O_{10}$. Found: Co, 10.3; C, 42.3; H, 2.7; N, 17.5%. Calcd: Co, 10.3; C, 41.9; H, 2.8; N, 17.1%. The IR spectra of compound **1** at 80 K showed several absorption bands characteristic of nitrosyl cations, coordinating nitro, and nitrate ions in addition to the coordinating 2-methyl-8-quinolinolate ions, as shown in Fig. 1. The 2109(vs) cm^{-1} band shifted to 2040 cm^{-1} upon ^{15}N-substitution, and was assigned to the N–O stretching vibration due to the nitrosyl cations.[5] The 1280(w)[6], 820(sh)[6], 641(w), 582(w), and 422(w) cm^{-1} bands also shifted to 1260 (sh)[6], 812(m), 635(w), 576(w), and 416(w) cm^{-1}, respectively, and were assigned to the symmetric N–O stretching of NO_3^-, the symmetric NO_2 deformation of NO_2^- or the rocking of NO_3^-, the antisymmetric or symmetric NO_2 deformation of NO_3^-, the NO_2 wagging of NO_2^-, and the Co–NO_2 stretching vibrations, respectively, from wave numbers of the bands and their ^{15}N-isotopic shifts.[4,5] The bands at 1330(sh)[6] cm^{-1} for the ^{14}N-labelled compound and at 1347(m) cm^{-1} for the ^{15}N-one could be assigned to the antisymmetric or symmetric N–O stretching of NO_2^-, and the antisymmetric N–O stretching of NO_3^-.

The elementary analyses and the IR spectra suggest that compound **1** is $[NO]_3[Co(C_{10}H_8NO)_2(NO_3)(NO_2)]$ containing monopositive cobalt ion. A number of nomopositive cobalt-complexes with π-acceptor ligands have been reported so far, and they are in general air-sensitive and diamagnetic.[7] On the other hand, as the ligands in compound **1** are not π-acceptor ones,[8] an electronic configuration of the cobalt ion in compound **1** is expected to be high-spin d^8. The effective magnetic moment of compound **1** was 3.7±0.1 BM (at 296 K), and was larger than the value, 2.8—3.5 BM observed for the first row transition-metal ions with high-spin d^8 configuration.[9] Hence, it is taken into consideration that compound **1** may be contaminated by paramagnetic substances such as the unreacted starting material or uncharacterized decom-

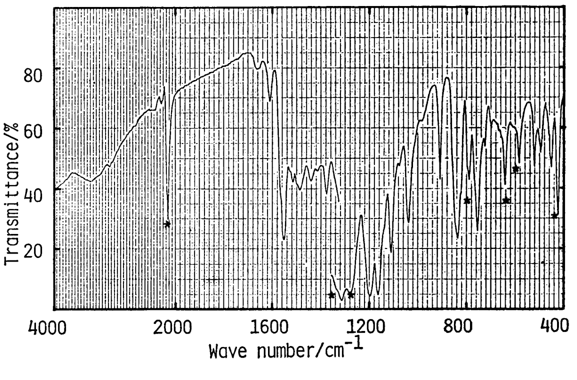

Fig. 1. IR spectrum of $[NO]_3[Co(C_{10}H_8NO)_2(NO_3)(NO_2)]$. * indicates the band shifted upon ^{15}N-substitution.

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posed one, although it could not be confirmed.

After compound **1** had been filtered from the reaction solution stirred at *ca.* −20 °C, the solvent, dichloromethane, was removed in keeping the filtrate at lower than 0 °C to obtain violet product, $[Co(C_{10}H_8NO)_2(NO)_2]$ (**2**). Yield, 10%. Found: C, 53.6; H, 3.6; N, 12.3%. Calcd: C, 55.2; H, 3.7; N, 12.9%. Compound **2** was even more unstable than compound **1**, and could not be purified. The IR spectra showed that compound **2** was contaminated by compound **1**. The IR bands at 1840(vs) and 1760(vs) cm^{-1} shifted to 1805 and 1730 cm^{-1}, respectively, upon ^{15}NO-substitution. These bands could be assigned to the N–O stretching vibrations of the coordinating nitrosyl groups.[8] The wave number of the N–O stretching vibrations show that the formal oxidation number of the coordinating nitrosyl group is +I, and hence that of the cobalt is zero.[8] The N–O stretching vibrations for $[Fe(C_{10}H_8NO)(NO)_2]$ with the formal oxidation number of Fe^{-I} were observed at 1758 and 1685 cm^{-1}.[8] The N–O stretching bands for compound **2** are higher than those for the iron nitrosyl, which reflects that π^*-electron on the nitrosyl group is more drawn to the cobalt than to the iron due to difference of their nuclear charges.

The yields of compounds **1** and **2** were *ca.* 30 and 50%, respectively, in the case of stirring at *ca.* −20 °C for 1 d; the yield of compound **2** was larger than that of compound **1** in the initial stage of the reaction. Compound **2** reacted with nitrogen monoxide in dichloromethane to precipitate compound **1**. These suggest that $[Co(C_{10}H_8NO)_2]\cdot H_2O$ reacted with nitrogen monoxide to form compound **2**, and then it reacted further with nitrogen monoxide to precipitate compound **1** with liberation of dinitrogen oxide. However, it can not be denied that $[Co(C_{10}H_8NO)_2]\cdot H_2O$ reacted with nitrogen monoxide to produce compound **1** directly.

The Co^{II} in the starting material was reduced to Co^{I} or Co^{0} by nitrogen monoxide on the present study, while on the reaction of $[Co(C_9H_6NO)_2]$ with nitrogen monoxide, the Co^{II} was oxidized to Co^{III}.[4] The difference in the reaction of nitrogen monoxide with the cobalt ion seems to be due to electron-donating power of methyl groups in 2-methyl-8-quinolinolate ions.

A reaction of $[Co(C_{10}H_8NO)_2]\cdot H_2O$ with nitrogen monoxide in pyridine, 10 vol% pyridine–DMF, or DMF was tried on the same scale as in dichloromethane. In pyridine and the pyridine–DMF, $[Co(C_{10}H_8NO)_2]\cdot H_2O$ did not reacted with nitrogen monoxide, instead only the pyridine adduct being isolated. In DMF, $[Co(C_{10}H_8NO)_2]\cdot H_2O$ reacted with nitrogen monoxide to give a deep red solution with liberation of dinitrogen oxide. Deoxygenated diethyl ether (150 cm^3) was added to the solution to precipitate a russet product. However, the russet product did not give constant elementary analyses. The IR spectra of the compound was seemingly same as those of compound **1** except an addition of a 1660 cm^{-1} band assignable to the C–O stretching vibration of DMF to the spectra of compound **1**.

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