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REACTION OF BIS(8-QUINOLINOLATO)NITROSYLCOBALT WITH NITROGEN OXIDE

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Reaction of $[Co(C_9H_6NO)_2(NO)]$ ($C_9H_6NO^-$ = 8-quinolinolate ion) with a large excess of nitrogen oxide in dichloromethane gives $[NO][Co(C_9H_6NO)_2(NO_3)(NO_2)]$ with liberation of dinitrogen oxide at room temperature. Investigations using nitrogen-15 labelled compounds suggest that the reaction is $^*NO^-$(coordinated) + 8NO $\longrightarrow$ $^*NO_2^-$(coordinated) + NO_3^-(coordinated) + $3N_2O$ + NO^+.

It has been reported that free NO disproportionates by reacting with transition-metal complexes [1] and coordinated NO^- reacts with free NO to give coordinated nitro group with liberation of N_2O.[2]

In the present study on the reaction of free NO with a new nitrosyl complex of cobalt, $[Co(C_9H_6NO)_2(NO)]$ formulated as NO^- complex, the author has found a new disproportionation reaction of free NO, and has confirmed by the use of nitrogen-15 labelled compounds that the nitrogen atom of the coordinated nitro group resulting from the reaction of the coordinated NO^- with free NO comes from that of the coordinated NO^-.

The parent complex $[Co(C_9H_6NO)_2(NO)]$: A new compound was isolated from the reaction of NO with a mixture of $CoCl_2 \cdot 6H_2O$ and 8-quinolinol in methanol. Found: Co, 15.5; C, 57.19; H, 3.22; N, 10.83%. Calcd for $CoC_{18}H_{12}N_3O_3$: Co, 15.62; C, 57.31; H, 3.21; N, 11.14%. μ_B = 1.70 B.M. (290 K). The compound in the solid state was stable in air, but was gradually decomposed in deoxygenated dichloromethane to give $[Co(C_9H_6NO)_2]$ with liberation of NO at room temperature. The N-O stretching vibration at 1650 cm^{-1} shifted to 1621 cm^{-1} upon ^{15}NO-substitution. Previous studies on the position of the N-O stretching vibration and its ^{15}N-isotopic shift for transition-metal nitrosyls by the present author and his co-workers suggest that the present nitrosyl is formulated as NO^- complex.[3]

Characterization of the reaction of $[Co(C_9H_6NO)_2(NO)]$ with NO : Ten mmol of NO was trapped into a reaction vessel containing 1 mmol of $[Co(C_9H_6NO)_2(NO)]$ dissolved in deoxygenated dichloromethane (40 cm^3) by cooling with liquid nitrogen. The reaction vessel was shaken under running water until the frozen solution thawed; and then the solution was allowed to stand for 3 - 5 d at room temperature. Dark violet powder precipitated was filtered off and dried under vacuum. The yield was 80%. Found: Co, 12.2; C, 44.73; H, 2.48; N, 14.37%. Calcd for $CoC_{18}H_{12}N_5O_8$: Co, 12.14; C, 44.55; H, 2.49; N, 14.43%. μ_B = 2.09 B.M. (292 K). The smaller the ratio of NO to the parent complex, the smaller the yield of the dark violet product, but the product formed was always the same. The compound in the solid state was stable in air, but was decomposed in deoxygenated common organic solvents such as methyl alcohol, N,N-dimethylformamide, and dimethyl sulfoxide. For investigating the reaction, the following four combinations of nitrogen isotopes were used: A,(^{14}NO complex)-(^{14}NO gas); B,(^{15}NO complex)-(^{15}NO gas); C,(^{14}NO complex)-(^{15}NO gas); and D,(^{15}NO complex)-(^{14}NO gas).

Gaseous products from the reaction were trapped in a calcium difluoride gas cell by cooling with liquid nitrogen, and were identified from their IR bands. The liberated gas was dinitrogen oxide; $^{14}N^{14}NO$ was derived from A and D, while $^{15}N^{15}NO$ from B and C.[4] This suggests that the nitrogen atom of the dinitrogen oxide exclusively originates from that of the NO gas.

The IR spectra of the isolated compounds were measured in the region 200 - 4000 cm^{-1}. Table 1 shows wave numbers and the assignments of the bands on which ^{15}N-isotopic shifts were observed. For both the compounds from A and D, a strong band at about 2150 cm^{-1} was observed, while for both the compounds from B and C the band shifted downwards by about 50 cm^{-1}. These bands were assigned to the N-O stretching vibration of nitrosonium ion, $[NO]^+$ because the N-O stretching vibration of ionic compounds of nitrosonium ion is generally observed in the 2150 - 2400 cm^{-1} region.[5] On the other hand, the N-O stretching vibration of coordinated NO^+ of $[Co(NO)(diars)_2]^{2+}$ (diars = 1,2-bis(dimethylarsino)benzene) formulated as NO^+ complex was observed by Feltham [6] at 1852 cm^{-1}. Of the bands characteristic of nitro complex, one of the N-O stretching vibrations, the wagging vibration, and the Co-N stretching vibration were observed in the present work; and the IR spectra for the compounds from A and C, and from B and D showed that the nitro group coordinated to the cobalt atom through the nitrogen atom as $^{14}NO_2^-$ and $^{15}NO_2^-$, respectively. Two N-O stretching vibrations characteristic of

Table 1. Wave numbers and assignments of $[NO][Co(C_9H_6NO)_2(NO_3)(NO_2)]$

Reaction systems				Assignments
A	B	C	D	
2148 vs	2098 vs 2085 sh	2094 vs 2080 s	2148 vs	N-O str of $[NO]^+$
1410 m	1390 m	1395 m,sh	1410 m	N-O str of NO_3^-
1312 s,br	1295 s,sh	1320 s	1290 s,br	N-O str of NO_2^-
1312 s,br	1276 s,br	1270 sh	1310 s	N-O str of NO_3^-
602 m[a)]	588 sh[a)]	597 m,br[a)]	588 sh[a)]	NO_2 wag of NO_2^-
421 m	411 m	421 m	416 w,br	Co-NO_2 str

Abbreviations: str=stretching, wag=wagging, vs=very strong, s=strong, m=medium, w=weak, sh=shoulder, br=broad. a) The band overlaps with one of the bands due to the 8-quinolinolate ion.

coordinated nitrate ion were also observed. The separation of the bands was about 100 cm^{-1}, which suggested that the nitrate ion coordinates to the cobalt atom as a unidentate.[7)] The IR spectra for the compounds from A and D, and from B and C showed that the nitrate ion was present as $^{14}NO_3^-$ and $^{15}NO_3^-$, respectively. The position of the bands due to the nitro and nitrate group and the ^{15}N-isotopic shifts were almost equal to those observed for their cobalt, platinum, and iridium complexes.[8)] Other bands due to the nitro and nitrate ions were interfered with by the strong bands due to the coordinated 8-quinolinolate ions. The IR measurements suggested that the cobalt atom for the dark violet product had a coordination number of six.

Both the parent complex and the dark violet product were paramagnetic, and reproducibility of the observed effective magnetic moments was better than ± 0.03 B.M. Both the observed values of the compounds were intermediate of the values expected from their high-spin and low-spin states, thus both the compounds may be in spin-equilibrium as observed for five-coordinate iron nitrosyls [9)] and cobalt(II) complexes with a coordination number of six.[10)]

The ^{15}N-isotopic studies and the elementary analyses show that the isolated compound is $[NO][Co(C_9H_6NO)_2(NO_3)(NO_2)]$, that NO^- of the parent complex is oxidized by NO gas to form NO_2^-, and that the NO gas is reduced by the NO^- to form N_2O: $^*NO^- + 2NO \longrightarrow {}^*NO_2^- + N_2O$ as reported in Ref. 2. Furthermore, NO gas disproportionates to NO_3^-, NO^+, and N_2O in such a reaction system:

$6NO \longrightarrow NO_3^- + NO^+ + 2N_2O$.

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