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Nitrosyliron Complexes Containing 8-Quinolinolate or Its Derivatives**

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New nitrosyls, $[Fe(C_9H_6NO)_2(NO)]_2$($C_9H_6NO^-$=8-quinolinolate ion), $[Fe(C_{10}H_8NO)(NO)_2]$ ($C_{10}H_8NO^-$= 2-methyl-8-quinolinolate ion), and $[Fe(C_9H_5NOCl)_2(NO)(DMF)]$ ($C_9H_5NOCl^-$=5-chloro-8-quinolinolate ion) were isolated by the reaction of nitrogen monoxide with a mixture of iron(II) perchlorate and the corresponding quinolinol in methanol or methanol/DMF. They were characterized by IR, ^{57}Fe-Mössbauer, and magnetic measurements.

One of the present authors reported that $[Co(C_9H_6NO)_2(NO)]$ prepared by the reaction of nitrogen monoxide with a mixture of cobalt(II) chloride and 8-quinolinol in methanol, reacted further with nitrogen monoxide in dichloromethane at room temperature to precipitate $[NO][Co(C_9H_6NO)_2(NO_3)(NO_2)]$ with liberation of dinitrogen oxide. The reaction involved disproportionation of nitrogen monoxide and electrophilic attack by nitrogen monoxide on the coordinating nitrosyl group of the nitrosylcobalt complex.[1)]

In this paper, we report the syntheses and characterization of some new nitrosyliron complexes containing 8-quinolinolate ion, and its derivatives, 2-methyl-, or 5-chloro-8-quinolinolate ion, and also examine whether the obtained nitrosyliron complexes react further with nitrogen monoxide, as reported for $[Co(C_9H_6NO)_2(NO)]$.

Experimental

Materials. The nitrosyl complexes were synthesized and manipulated under nitrogen atmosphere or in a vacuum line. Commercial iron(II) perchlorate hexahydrate was treated with zinc powder in methanol to reduce any iron (III) present and dried over Zeorum A-4(Toyo Soda Ind. Co., Ltd.) before using. Organic solvents were dried over anhyd calcium sulfate or Zeorum A-4, distilled or deoxygenated in nitrogen or argon stream, and then degassed in a reaction vessel by a repetitive freeze-pump-thaw cycle. Nitrogen monoxide was derived from the reaction of potassium nitrate with mercury and concd sulfuric acid.

Preparation. Two mmol of iron(II) perchlorate in methanol (40 cm^3) was brought into contact with 5 mmol of nitrogen monoxide, which resulted in an instant color change to dark brown. Four mmol of 8-quinolinol or 2-methyl-8-quinolinol in methanol or DMF (10 cm^3) was poured into the dark brown solution; it was then stirred at *ca.* 0 °C for 1 h to precipitate the nitrosyl complexes. In the case of using 5-chloro- or 5-nitro-8-quinolinol, DMF was used instead of methanol as a solvent because they are sparingly soluble in methanol. A mixture of the dark brown solution and 4 mmol of the quinolinol in DMF(10 cm^3) was stirred at *ca.* −20 °C for 1 h. The product was collected by filtration, washed with diethyl ether, dried under vacuum for a minute, and then stored in nitrogen atmosphere. The ^{15}NO-substituted complexes(^{15}N atom% in NO=99.4) were prepared by the use of ^{15}NO derived from $K^{15}NO_3$. The elementary analyses and the yields of the obtained nitrosyls are shown in Table 1. The C, H, N, and Cl contents were analyzed by the Organic Analysis Center of the Institute of Physical and Chemical Research. The content of the iron was obtained by colorimetric determination.[2)]

Reaction of the Nitrosyl Complexes with Nitrogen Monoxide in Dichloromethane. Dichloromethane(20 cm^3) and 5 mmol of nitrogen monoxide were trapped into a reaction vessel containing *ca.* a half mmol of the nitrosyl complexes with the aid of liquid nitrogen. The frozen solution was melted and stirred at room temperature for several days. Gaseous materials in the reaction vessel were collected and identified by their IR bands. After the unreacted original nitrosyl had been filtered, the dichloromethane was removed from the filtrate at *ca.* −20 °C, and the residual product was characterized.

Measurements. The IR spectra in the solid state as Nujol and poly(chlorotrifluoroethylene) oil mulls, and of the dichloromethane solution were measured in the regions 200—4000 cm^{-1}, and 1500—2000 cm^{-1}, respectively. The gaseous materials were trapped into a calcium difluoride gas cell with the aid of liquid nitrogen, and identified on the basis of their IR bands.[3)] The magnetic susceptibility at room temperature was measured by the Gouy method.

TABLE 1. ELEMENTARY ANALYSES AND YIELDS OF THE NITROSYLS

	Compound	Color	Yield/%		Fe(%)	C(%)	H(%)	N(%)	Cl(%)
1	$[Fe(C_9H_5NOCl)_2(NO)(DMF)]$	Dark khaki	34	Found	10.7	47.5	2.9	10.0	15.7
				Calcd	10.8	48.5	3.3	10.9	13.7
2	$[Fe(C_{10}H_8NO)(NO)_2]$	Chocolate	24	Found	20.0	44.9	3.1	14.4	—
				Calcd	20.4	43.8	2.9	15.3	—
3	$[Fe(C_9H_6NO)_2(NO)]_2$	Dark green	20	Found	14.8	57.8	3.2	10.8	—
				Calcd	14.9	57.8	3.2	11.2	—

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The magnetic susceptibility for $[Fe(C_9H_6NO)_2(NO)]_2$ was measured by the Faraday method in the temperature range from 83 K to room temperature. The apparatus was calibrated by $[Fe(H_2O)_6]SO_4 \cdot (NH_4)_2SO_4$. The ^{57}Fe-Mössbauer spectra were measured at 80 K under vacuum by using a ^{57}Co(Pt) source moving in a constant acceleration mode. The isomer shift are relative to metallic iron foil.

Results and Discussion

It is very remarkable that different types of the nitrosyl complexes were isolated under the same preparative conditions. Nitrosyliron containing 5-nitro-8-quinolinolate ion could not be isolated under the present experimental conditions, dark green $[Fe(C_9H_5N_2O_3)_3] \cdot 1/2DMF$ being precipitated instead. Found: Fe, 8.3; C, 49.3; H, 2.8; N, 13.4%. Calcd: Fe, 8.5; C, 51.8; H, 2.8; N, 13.8%.

All the nitrosyls in the solid state were stable in nitrogen atmosphere, but compounds **1** and **2** were unstable at room temperature in a vacuum and nitrogen monoxide was liberated. The nitrosyls were also unstable in deoxygenated organic solvents such as dichloromethane, chloroform, acetone, THF, and DMSO, giving off nitrogen monoxide. Hence, they could not be recrystallized.

IR Spectra. *$[Fe(C_9H_5NOCl)_2(NO)(DMF)]$ (**1**)*: Upon ^{15}NO-substitution, the IR bands at 1710(vs)[4] and 440(w) cm^{-1} shifted to 1679 and 434 cm^{-1}, respectively. The former was assigned to the N–O stretching vibration and the latter to one of the FeNO skeletal vibrations.[5] A shoulder band at 1655 cm^{-1} overlapping with the N–O stretching band was observed for both the ^{14}NO- and ^{15}NO-complexes, and was assigned to the C–O stretching vibration of DMF. It has been reported that the C–O stretching band at 1670 cm^{-1} for free DMF shifted to 1625—1650 cm^{-1} on coordination.[6,7] Thus, the DMF of the present nitrosyl seems to coordinate to the iron.

*$[Fe(C_{10}H_8NO)(NO)_2]$ (**2**)*: The IR bands at 1758 (vs), 1685(vs), 543(w), 519(s), 511(w), and 379(s) cm^{-1} shifted to 1722, 1649, 539, 515, 500, and 369 cm^{-1}, respectively, upon ^{15}NO-substitution, which suggests the presence of a $Fe(NO)_2$ skeleton. Although the wave numbers of the N–O stretching bands in the region 1760—1650 cm^{-1} shifted upwards by *ca.* 7 cm^{-1} at 80 K, relative intensity of the bands at room temperature did not change at 80 K.

Four-coordinate compounds containing a monopositive dinitrosyliron group such as the present nitrosyl have already been reported. $[N(PPh_3)_2][FeX_2(NO)_2]$ (X=Cl, Br, or I)[8] and $[Fe(L'H)(NO)_2]$ ($L' = {}^-SCH_2CH_2N(CH_3)CH_2CH_2CH_2N(CH_3)CH_2CH_2S^-$)[9] show two N–O stretching bands in the region 1700—1780 cm^{-1} as observed for the present nitrosyl. X-Ray diffraction studies show that four-coordinate compounds with monopositive dinitrosyliron have flattened tetrahedral geometry with two equivalent nitrosyl groups, and the Fe–N–O angles are in the range 160—175°.[9,10] Thus, the present nitrosyl also is probably a pseudotetrahedral complex with almost linear Fe–N–O groups.

*$[Fe(C_9H_6NO)_2(NO)]_2$ (**3**)*: Upon ^{15}NO-substitution, the IR bands at 1740(vs), 1667(vs), and 373(m) cm^{-1} shifted to 1711, 1643, and 362 cm^{-1}, respectively, and the 540 cm^{-1} band(sh) also shifted and became concealed by the foot of the very strong band at 520 cm^{-1}, due to the coordinating 8-quinolinolate ions. The bands at 1740 and 1667 cm^{-1} could be assigned to the N–O stretching vibrations, and the bands at 540 and 373 cm^{-1} to the FeNO skeletal ones.

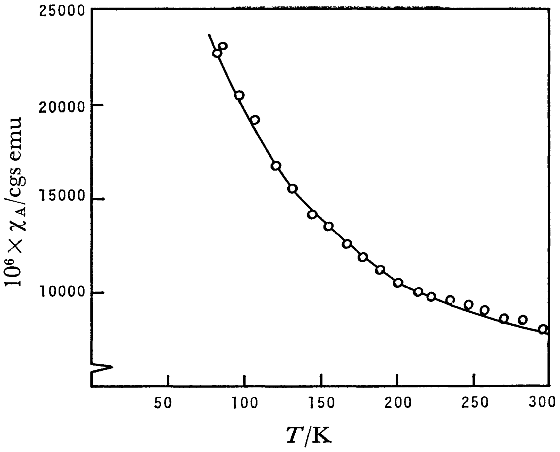

Fig. 1. Temperature dependence of atomic susceptibility of $[Fe(C_9H_6NO)_2(NO)]_2$.
The solid curve was calculated from Eq. 1 with $g = 2.25 \pm 0.01$ and $-J = 4.4 \pm 0.5$ cm^{-1}.

In the case of a dimer complex, $[Fe(TDBM)_2(NO)]_2$ ($TDBM^-$ = diphenylpropane-1-onate-3-thionate ion), where two of the iron atoms are bridged through the sulfur atoms of two TDBM and each iron atom has a coordination number of six, the N–O stretching vibrations are observed at 1675 and 1780 cm^{-1}.[11] For a spin-equilibrium complex, [Fe(salen)(NO)] ($salen^{2-}$ = *N,N'*-disalicylideneethylenediaminate ion) with two N–O stretching bands, the relative intensity of the N–O bands changes with lowering temperature.[12,13] Geometry-equilibrium complexes, $[CoCl_2(NO)L_2]$ (L= phosphine derivatives) also show two N–O stretching bands; their relative intensity changes with temperature.[14,15]

On the other hand, the relative intensity of the N–O stretching bands for the present nitrosyl at 80 K was almost equal to that at room temperature although the bands shifted upwards by *ca.* 5 cm^{-1} at 80 K. The separation of the two bands is too large to be due to the solid state effect. The wave numbers of the two bands show that both nitrosyl groups are terminal.[16] Thus, the two N–O stretching bands suggest that the terminal nitrosyl groups are in different chemical environments.

Magnetism. According to the notation introduced by Enemark and Feltham,[17] both compounds, **1** and **3**, contain $\{Fe(NO)\}^7$, and compound **2** contains $\{Fe(NO)_2\}^9$; here the superscripts show the number of the *d*-electrons in the iron when the nitrosyl ligand is formally assumed to be NO^+.

The effective magnetic moment of compound **2** was 1.97 BM (at 292 K), which was comparable to that of $[N(PPh_3)_2][FeX_2(NO)_2]$ where the dinitrosyliron is the $\{Fe(NO)_2\}^9$ species.[8] The effective magnetic moments of compounds **1** and **3** were 4.21 (at 291 K) and 4.43 BM (at 285 K), respectively, and the values correspond to those observed for first row transition-

Table 2. Mössbauer parameters of the nitrosyls at 80 K

	Compound	$\delta^{a,b)}$ / mm s^{-1}	$\Delta E_Q{}^{b)}$ / mm s^{-1}	$\Gamma_1{}^{b)}$ / mm s^{-1}	$\Gamma_2{}^{b)}$ / mm s^{-1}
1	$[Fe(C_9H_5NOCl)_2(NO)(DMF)]$	0.68	1.32	0.49	0.36
2	$[Fe(C_{10}H_8NO)(NO)_2]$	0.47	0.88	0.28	0.30
3	$[Fe(C_9H_6NO)_2(NO)]_2$	0.45	0.69	0.48	0.49

a) The isomer shift is relative to metallic iron foil. b) The values are accurate within ±0.03 mm s^{-1}. Γ_1, line width of a lower energy peak; Γ_2, line width of a higher energy peak.

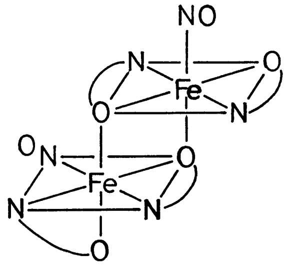

Fig. 2. One of the possible structures for $[Fe(C_9H_6NO)_2(NO)]_2$.
N-O: 8-Quinolinolate ion.

metal ions with high-spin d^7 configurations.[18] The magnetic moment of compound **3** decreased gradually with lowering temperature from 4.4 (at 285 K) to 4.0 BM (at 83 K); this decrease suggests the presence of antiferromagnetic exchange interaction between the iron ions.[19] The temperature dependence of the magnetic susceptibility is shown in Fig. 1.

The molecular weight of compound **3** could not be measured because it is unstable in the examined organic solvents. The two N–O stretching bands of compound **3** can not deny the possibility that it is a dimer. Thus, by assuming that compound **3** was a binuclear complex containing two iron ions with $S=3/2$, the susceptibility data were fit to Eq. 1, which was reported by Earnshaw and Lewis:[20]

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[\frac{14+5\exp(-6J/kT)+\exp(-10J/kT)}{7+5\exp(-6J/kT)+3\exp(-10J/kT)+\exp(-12J/kT)}\right] + N\alpha. \quad (1)$$

$N\alpha$ was neglected in the fitting. The experimental data fit Eq. 1 with $g=2.25\pm0.01$ and the exchange integral, $-J=4.4\pm0.5$ cm^{-1}. The negative J suggests that there is some antiferromagnetic interaction between the two iron ions in the assumed binuclear complex, $[Fe(C_9H_6NO)_2(NO)]_2$.

The value of J for compound **3** was comparable to those reported for $[Fe(salen)Cl]_2$ and its analogs with a binuclear moiety, $\mathrm{Fe^{III}}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Fe^{III}}$.[19] On the other hand, the value of $-J$ for $[Fe(salen)]_2O$ and its analogs containing a $\mathrm{Fe^{III}}$-O-$\mathrm{Fe^{III}}$ system with an Fe–O–Fe angle of *ca.* 160° have been reported to be 87—100 cm^{-1}.[21] This value of J shows that the $\mathrm{Fe}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Fe}$ system is less favorable for transmitting the exchange interaction than the Fe–O–Fe one. The formal oxidation number of the iron for compound **3** is considered to be +I as discussed later. There is no data for the J value of the iron(I) complexes. Although the J value for the iron(I) complex can not be directly compared with those for the iron(III) complexes, the J value suggests the possibility that compound **3** is a dimer in which two of the iron atoms are bridged through the oxygen atoms of two 8-quinolinolate ions to form a $\mathrm{Fe^{I}}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Fe^{I}}$ moiety. One of the possible structures for compound **3** is shown in Fig. 2.

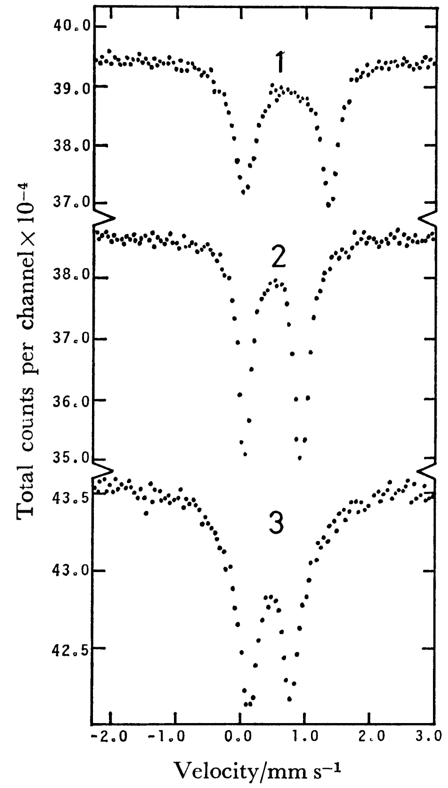

Fig. 3. Mössbauer spectra of the nitrosyls at 80 K.
1: $[Fe(C_9H_5NOCl)_2(NO)(DMF)]$, **2**: $[Fe(C_{10}H_8NO)(NO)_2]$, **3**: $[Fe(C_9H_6NO)_2(NO)]_2$.

^{57}Fe-Mössbauer Spectra. The Mössbauer spectra and the derived parameters of the nitrosyls are shown in Fig. 3 and Table 2, respectively. The spectrum of compound **2** consisted of a single and symmetrical doublet with line widths of *ca.* 0.3 mm s^{-1}, whereas that of compound **1** consisted of an unsymmetrical doublet with line widths of more than 0.3 mm s^{-1}. This suggests the presence of some impurity that may be derived from compound **1** which is not stable under these conditions. Compound **3** showed a symmetrical doublet but its line widths are broader than those of

compound **2**. The line broadening can be reasonably explained by supposing that compound **3** is a dimer, as shown in Fig. 2; the two sites of the irons are in very similar chemical environments, so the Mössbauer spectra are expected to be almost equal to each other. Such spectra are overlapped to give the line broadening.

Studies on the wave numbers of the N–O stretching vibration and its ^{15}N-isotopic shift for transition-metal nitrosyls indicate that the nitrosyl ligand of the present nitrosyls formally coordinates as NO^+ to the iron.[5] Thus, the formal oxidation number of the iron for both compounds **1** and **3** is +I, and that for compound **2** is −I. One might expect that the isomer shift observed for the iron compounds with such electronic structures are higher than those for high-spin iron(III) compounds (d^6, $S=2$). The isomer shift for $[Fe(H_2O)_5(NO)]SO_4$ (Fe^+, $S=3/2$) has been observed at *ca.* 1.3 mm s^{-1} at room temperature.[22] However, the isomer shifts for the present nitrosyls were observed in the region of those for Fe^{2+} ($S=0$), Fe^{3+} ($S=1/2$), or Fe^{3+} ($S=5/2$) ions.[23] The results can be explained as follows; strong π-acidity of NO^+ causes a decrease of the 3d-electron density of iron, and thus the isomer shifts for the nitrosyls decreases.[23] The smaller isomer shifts of compounds **1** and **3**, compared with that of $[Fe(H_2O)_5(NO)]SO_4$, indicate the increase in π-acceptor ability of the ligands in compounds **1** and **3**. The close values of the isomer shifts for compound **2** and compounds **1** and **3** may be due to strong π-back donation of two nitrosyl groups in compound **2**. The value of the isomer shift for compound **2** is comparable to those reported for dinitrosyliron compounds, $LYFe(NO)_2$ ($L=C_5H_{11}N$, Ph_3P, Ph_3As, or Ph_3Sb; $Y=Br$ or I).[24]

The quadrupole splittings for the present nitrosyl compounds arise not only from the extra electrons in 3*d* orbitals, which can distort the symmetry of the total environment of iron atom, but also from the differences in strength of the π-acceptor of the ligands. Therefore, the larger quadrupole splitting for compound **1**, compared with that of compound **3**, indicates that the distortion from the octahedral symmetry in compound **1** is larger than that in compound **3**. Although compounds **1** and **3** seem to have the high-spin configuration from the magnetic results, the Mössbauer data shows the presence of strong π-back donation leading to low-spin configuration. This discrepancy seems worthy of further investigation.

Reaction of the Nitrosyl Complexes with Nitrogen Monoxide in Dichloromethane. It has been reported that nitrogen monoxide disproportionates by reacting with transition-metal complexes to give nitrosyl nitrite and hyponitrito complexes, and that nitrosyl complexes with a NO^- group reacts with nitrogen monoxide to form nitro complexes with liberation of dinitrogen oxide.[1,25]

Compound **3** was stable in dichloromethane saturated with nitrogen monoxide, and the product from the filtrate was identified to be the original compound **3**. Compounds **1** and **2** decomposed to give unidentified products, but dinitrogen oxide could not be observed in the reaction vessel. Products from compounds **1** and **2** showed no N–O stretching bands assignable to $[NO]^+$, coordinating nitrosyl, nitrite or hyponitrite groups.

Thus, for all the present nitrosyl compounds, the disproportionation of nitrogen monoxide or the electrophilic attack by nitrogen monoxide on a coordinating nitrosyl group could not be observed. These facts are consistent with the idea that the present nitrosyls are formally NO^+-complexes.

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