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Synthesis and Property of Nitrosyl Cobalt and Nitrosyl Iron Complexes with some Quadridentate Ligands

YOSHIHIKO NUMATA, KOOICHI KUBOKURA, YASUOMI NONAKA, HISASHI OKAWA* and SIGEO KIDA
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan

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Nitrosyl cobalt and nitrosyl iron complexes, Co(J–R)NO (R = en, pn, ph), Fe(J–R)NO (R = ph, mph) and Fe(bza-ph)NO, were synthesized, where H_2(J–R) are Jäger-type ligands with bridging group R (en = ethylene; pn = 1,2-propylene; ph = o-phenylene; mph = 4-methyl-o-phenylene) combining two imino-nitrogens and H_2(bza-ph) is N,N'-bis(2-benzoylethylidene)-o-phenylenediamine. Co(J–R)NO showed a N–O stretching band in the region 1663–1698 cm^{-1}. The nitrosyl iron complexes had subnormal magnetic moments at room temperature and showed two ν_{NO} bands. Based on the measurements of magnetic moments in the temperature range 80–300 K, these complexes were revealed to be in a spin equilibrium between the s = 3/2 and s = 1/2 states. N–O frequencies and ESR parameters of the complexes were discussed in terms of electron-withdrawing effect of the acetyl group attached to the Jäger-type ligands.

Introduction

Much attention has been devoted to cobalt(II) complexes with quadridentate Schiff bases as models of natural oxygen carriers. Previously, we showed that the cobalt(II) complexes with Jäger-type ligands can reversibly bind molecular oxygen at room temperature [1]. These complexes markedly differ in oxygenation reaction from N,N'-disalicylideneethylenediaminatocobalt(II) (Co(salen)), N,N'-bis(1-acetonylethylidene)ethylenediaminatocobalt(II) (Co(acacen)) and their homologues, whose oxygenated complexes are only stable in solution at low temperature and irreversibly oxidized at room temperature [2, 3]. The characteristic of the cobalt(II) complexes with Jäger-type ligands may be attributed to the acetyl group attached to the γ-position, which attracts electrons from the cobalt(II) ion through the π-conjugated system of the ligand and lowers the *d*-orbital energy. The importance of mesomeric effect of the substituent on the electron density at the central metal ion is also known for the nickel(II) complexes with the N_4-macrocycles derived from Jäger-type type ligands [4].

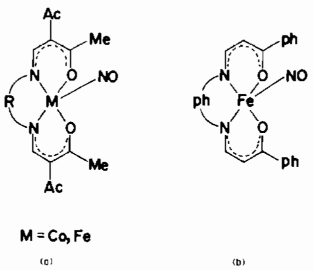

Fig. 1. Structure of (a) M(J–R)NO and (b) Fe(bza-ph)NO.

In this study, nitrosyl cobalt and nitrosyl iron complexes, Co(J–R)NO (R = en, pn, ph) and Fe(J–R)NO (R = ph, mph) (Fig. 1), were synthesized and their vibrational and ESR spectra were examined in terms of the electron-withdrawing effect of the acetyl group, where H_2(J–R) denotes Jäger-type ligands with ethylene (R = en), 1,2-propylene (pn), *o*-phenylene (ph) or 4–methyl-*o*-phenylene (mph) group combining two imino nitrogens. Nitrosyl iron complex, Fe(bza-ph)NO, with N,N'-bis(2-benzoylethylidene)-*o*-phenylenediamine (H_2bza-ph) was also prepared or comparison with Fe(J–R)NO. The nitrosyl iron complexes obtained in this study have subnormal magnetic moments at room temperature and their infrared spectra show two N–O stretching bands. In order to clarify these phenomena, magnetic susceptibilities of the complexes were investigated in a temperature range 80–300 K.

Experimental

Syntheses

Jäger-type ligands, H_2(J-en), H_2(J-pn), H_2(J-ph) and H_2(J-mph), were synthesized after the method described in the literature [5]. H_2(bza-ph) was prepared by the method given in the literature [6, 7].

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*Author to whom correspondence should be addressed.

Synthetic method of Co(J-en), Co(J-pn) and Co(J-ph) has been described in the previous paper [1].

All procedures for preparing the complexes given below were carried out in an atmosphere of nitrogen.

Fe(J-en)

H_2(J-en) (10.0 g), iron(II) acetate (4.0 g) and sodium acetate (1.4 g) were added in ethanol (100 ml) and the mixture was stirred at *ca.* 70 °C for 2 h and left stand overnight. Brown crystals thus obtained were collected and recrystallized from ethanol. Found: C, 49.99; H, 5.40; N, 8.26%. Calcd for $C_{14}H_{18}N_2O_4Fe$: C, 50.32; H, 5.43; N, 8.38%.

Fe(J-ph)

A mixture of H_2(J-ph) (5.0 g) and iron(II) acetate (2.5 g) in ethanol (100 ml) was stirred at *ca.* 70 °C for 2 h. After being left standing overnight, the product was collected and recrystallized from ethanol to give dark violet prisms. Found: C, 56.48; H, 4.63; N, 7.26%. Calcd for $C_{18}H_{18}N_2O_4Fe$: C, 56.57; H, 4.75; N, 7.33%.

Fe(J-mph)·½H_2O

This complex was obtained as dark violet prisms in the same way as Fe(J-ph). Found: C, 56.97; H, 5.21; N, 6.68%. Calcd for $C_{19}H_{21}N_2O_{4.5}Fe$: C, 56.32; H, 5.22; N, 6.91%.

Fe(bza-ph)

A mixture of H_2bza-ph (1.5 g) and iron(II) acetate (0.7 g) in ethanol (30 ml) was stirred under gently reflux for 1 h. The volume of the solution was concentrated to *ca.* 15 ml and allowed to stand overnight to give dark green crystals. Found: C, 68.18; H, 4.33; N, 6.58%. Calcd for $C_{24}H_{18}N_2O_2Fe$: C, 68.27; H, 4.30; N, 6.63%.

Co(J-en)NO

To a solution of Co(J-en) (0.5 g) in dichloromethane (30 ml) was introduced a stream of nitrogen monoxide, which was generated and purified after the method in the literature [8]. The solution became brown. Then, nitrogen gas bubbled through this solution to expell nitrogen monoxide. When petroleum ether was added to the solution, brown prisms separated. Found: C, 45.37; H, 4.87; N, 11.20%. Calcd for $C_{14}H_{18}N_3O_5Co$: C, 45.79; H, 4.94; N, 11.44%.

Co(J-pn)NO

This complex was obtained as brown prisms in the same way as Co(J-en)NO. Found: C, 46.83; H, 5.12; N, 11.12%. Calcd for $C_{15}H_{20}N_3O_5Co$: C, 47.25; H, 5.29; N, 11.02%.

Co(J-ph)NO

This complex was obtained as dark brown prisms in the same way as that of Co(J-en)NO. Found: C, 51.69; H, 4.27; N, 10.02%. Calcd for $C_{18}H_{16}N_3O_5Co$: C, 52.06; H, 4.37; N, 10.12%.

Fe(J-ph)NO

The synthetic method of this complex is practically the same as that of Co(J-en)NO except for the use of Fe(J-ph) instead of Co(J-en). The product forms brownish black prisms. Found: C, 52.26; H, 4.21; N, 10.06%. Calcd for $C_{18}H_{18}N_3O_5Fe$: C, 52.45; H, 4.40; N, 10.01%.

Fe(J-mph)NO

This complex was obtained as reddish black prisms in the same way as Fe(J-ph)NO. Found: C, 52.94; H, 4.84; N, 9.60%. Calcd for $C_{19}H_{20}N_3O_5Fe$: C, 53.54; H, 4.73; N, 9.86%.

Fe(bza-ph)NO

This complex was obtained as reddish black prisms in the same way as Fe(J-ph)NO. Found: C, 63.51; H, 4.01; N, 9.02%. Calcd for $C_{24}H_{18}N_3O_3Fe$: C, 63.74; H, 4.01; N, 9.29%.

Measurements

Infrared spectra were measured in the range 4000–650 cm^{-1} with a Hitachi Infrared Spectrophotometer Model 215 on KBr pellets. Electronic spectra were measured with a Shimazu Multipurpose Spectrophotometer Model MSP-5000. ESR spectra were measured with a JES-ME-3 Spectrometer by an X-band. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80–300 K. The apparatus was calibrated by the use of HgCo(NCS)$_4$. Effective magnetic moments were calculated by the expression, $\mu_{eff} = 2.828 \times [(\chi_A - N\alpha)T]^{1/2}$, where χ_A is the molar magnetic susceptibility corrected for diamagnetism by the use of Pascal's constants and $N\alpha$ the temperature-independent paramagnetism.

Results and Discussion

Reaction of Co(J–R) (R = en, pn, ph) with nitrogen monoxide formed nitrosyl complexes, Co(J–R)NO, in good yield. They are relatively stable in solid state. Magnetic measurements indicated that these complexes are diamagnetic. Electronic spectra of Co(J–R)NO were characterized by a strong absorption around 18,000 cm^{-1}, which is absent in the spectra of Co(J–R). A similar characteristic band was observed for Co(acacen)NO [9], which has a square-pyramidal configuration around the metal [10]. It seems reasonable to assign this band to a charge transfer band between NO and cobalt.

TABLE I. N–O Frequencies of Nitrosyl Cobalt Complexes.

	ν_{NO} (cm^{-1})	References
Co(J-en)NO	1663	This work
Co(J-pn)NO	1665	This work
Co(J-ph)NO	1698	This work
Co(acacen)NO	1654	9
Co(bzacen)NO	1635	9
Co(salen)NO	1624	11

TABLE II. N–O Frequencies of Nitrosyl Iron Complexes.

	ν_{NO} (cm^{-1})		References
Fe(J-ph)NO	1790	1715	This work
Fe(J-mph)NO	1790	1705	This work
Fe(bza-ph)NO	1730	1645	This work
Fe(salen)NO	1712	1630	15
Fe(5-NO_2salen)NO	1790	1715	15
[Fe(TMC)NO]$(BF_4)_2$	1840		16

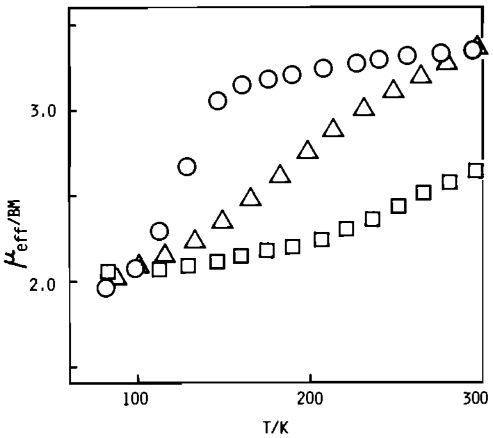

Fig. 2. Temperature variations of magnetic moments of (○) Fe(J-ph)NO, (△) Fe(J-mph)NO and (□) Fe(bza-ph)NO.

The N–O stretching band of Co(J–R)NO could easily be determined by comparing IR spectra of a nitrosyl complex and its NO-free complex. The N–O stretching frequencies of Co(J–R)NO and their related complexes [9, 11] are given in Table I. It is generally known that N–O frequencies of nitrosyl complexes markedly depend on the electronic state of the metal ion. For example, $[Co(CN)_5NO]^{3-}$ which is believed to be a cobalt(II) complex coordinated by NO^- ion, shows a ν_{NO} band at 1120 cm^{-1} [12]. On the other hand, $[Fe(CN)_5NO]^{2-}$, in which cobalt(II) is coordinated by NO^+, shows a ν_{NO} band at 1939 cm^{-1} [13]. Judging from the frequencies of the N–O stretching bands, it seems reasonable to assume that Co(J–R)NO are essentially cobalt(II) complexes coordinated by neutral NO molecule. The N–O stretching bands of the nitrosyl cobalt(II) complexes given in Table I are lower in frequency than that (1876 cm^{-1}) of NO molecule [14]. This might be attributed to π-backdonation from cobalt to NO.

Because of similarity in structure between Co(J–R)NO and Co(acacen)NO except for the substituents on the ligands, a comparison of the ν_{NO} bands of these complexes serves for evaluating the effect of the acetyl substituent in Co(J–R)NO. As is seen in Table I, the N–O stretching frequencies of Co(J–R)NO are higher than that of Co(acacen)NO. As we have already pointed out [1], it is likely that the metal *d*-orbitals in Co(J–R)NO are stabilized owing to the electron-withdrawing effect of the acetyl group, compared with those in Co(acacen)NO. Accordingly, π-backdonation from cobalt to NO decreases and the frequency of ν_{NO} increases.

Iron(II) complexes, Fe(J–R) (R = en, ph, mph) and Fe(bza-ph), prepared in this study are high-spin, whose magnetic moments are in the range 5.37–5.46 BM at room temperature. Electronic spectra of these complexes in dichloromethane are characterized by an absorption near 15,000 cm^{-1} with an extinction coefficient of *ca.* 50–70 mol^{-1} dm^3 cm^{-1}. This absorption band can be tentatively assigned to a *d–d* transition for iron(II) ion.

Reactions of Fe(J-ph), Fe(J-mph) and Fe(bza-ph) with nitrogen monoxide yielded Fe(J-ph)NO, Fe(J-mph)NO and Fe(bza-ph)NO, respectively, in good yield. On the other hand, we were unsuccessful in synthesizing Fe(J-en)NO. It seems that the aromatic bridges bring about a special stabilizing effect on nitrosyl iron complex formation with Jäger-type ligands. Electronic spectra of the nitrosyl complexes are not well resolved. Magnetic moments of Fe(J-ph)NO, Fe(J-mph)NO and Fe(bza-ph)NO at room temperature are 3.34, 3.33 and 2.63 BM, respectively, which are quite uncommon for either high-spin (s = 3/2) and low-spin (s = 1/2) species.

The frequencies of ν_{NO} bands of the present nitrosyl iron complexes and their related complexes [15, 16] are given in Table II. Notably, the present complexes displayed two ν_{NO} bands. It is known that Fe(salen)NO and Fe(5-NO_2salen)NO (5-NO_2salen^{2-} = N,N′-bis(5-nitrosalicylidene)ethylenediamine dianion), which are crossover complexes between the s = 3/2 and s = 1/2 states, also show two ν_{NO} bands [15]. Thus, observations of two N–O stretching bands and subnormal magnetic moments suggest that the present complexes are in a spin–equilibrium. In order to verify this, magnetic susceptibilities were measured from liquid nitrogen temperature to room temperature. The moments are plotted against temperature and shown in Fig. 2. The effective magnetic moments decrease with lowering temperature to *ca.* 2.0 BM near liquid nitrogen temperature, which corresponds to the moment for one unpaired electron. Magnetic behaviors of the complexes may be well interpreted in terms of a spin equilibrium between the s = 3/2 and s = 1/2 states, in which only the spin doublet state is practically occupied near liquid nitrogen temperature. Earnshaw *et al.* [15] assigned the ν_{NO} band at 1712 cm^{-1} to the high-spin species and the band at 1630 cm^{-1} to the low-spin species for Co(salen)NO, based on measurements of IR spectra at liquid nitrogen and room temperatures.

Recently, the molecular structure of Fe(salen)NO was determined at 23° and –175 °C [17]. The complex has a tetragonal-pyramidal coordination geometry with the bent FeNO fragment at both temperatures. However, the structure at –175 °C has a smaller Fe–N–O angle, a smaller displacement of iron from the basal plane and a higher coplanarity of the salicylideneimine moiety, compared with the structure at room temperature. These structural changes result in a decrease of the molecular volume with lowering temperature. This fact is compatible with the observation of the ν_{NO} band at 1610 cm^{-1} for Fe(salen)NO even at room temperature under high pressure [17]. On the other hand, according to Hodges *et al.* [16], [Fe(TMC)NO](BF$_4$)$_2$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), which is another nitrosyl complex displaying a spin equilibrium, has an intermediate configuration between a square-pyramid and a trigonal-bipyramid with a linear FeNO group. The N-O frequency of this complex at room temperature is very high (1840 cm^{-1}). The IR spectrum exhibits no marked change upon cooling down to *ca.* –230 °C, except for a broadening the ν_{NO} band at 1840 cm^{-1}. This fact implies that the N–O stretching frequency of nitrosyl complex with a linear FeNO group does not greatly change even when the spin state is altered. Judging from a marked resemblance in N–O stretching mode between Fe(salen)NO and the present complexes, we assume that the present complexes possess a square-pyramidal configuration with a bent FeNO group. It seems that a structural change takes place in these complexes when temperature is lowered, and this change must occur more abruptly in Fe(J-ph)NO than Fe(J-mph)NO and Fe(bza-ph)NO, judging from the temperature dependences of magnetic moments given in Fig. 2.

In order to evaluate the electron-withdrawing effect of the acetyl substituent, we compared ν_{NO} frequencies of Fe(J–R)NO with that of Fe(bza-ph)NO. As is seen in Table II, Fe(J-ph)NO and Fe(J-mph)NO show ν_{NO} bands at 1790 and ~1710 cm^{-1}, which are higher than those (1730 and 1645 cm^{-1}) of Fe(bza-ph)NO, respectively. High ν_{NO} frequency for Fe(J–R)NO might indicate that the acetyl group attracts electrons from the metal ion thereby lowering the *d*-orbital energy and reducing the degree of π-backdonation.

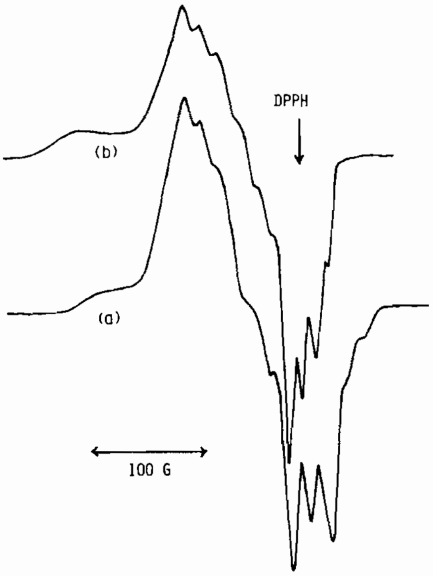

Fig. 3. ESR spectra of (a) Fe(J-ph)NO and (b) Fe(bza-ph)NO in a frozen solution (in a 1:1 mixture of toluene and chloroform at 78 K).

ESR spectra of Fe(J-ph)NO, Fe(J-mph)NO and Fe(bza-ph)NO were measured in a frozen solution (in a 1:1 mixture of toluene and chloroform) at liquid nitrogen temperature. The spectra of Fe(J-ph)NO and Fe(bza-ph)NO are shown in Fig. 3. The spectrum of Fe(J-mph)NO is almost the same as that of Fe(J-ph)NO. ESR bands observed are attributed to a low-spin species, since measurements were carried out at liquid nitrogen temperature. The spectra of Fe(J-ph)NO and Fe(bza-ph)NO resemble in shape each other and exhibit a superhyperfine structure due to ^{14}N nucleus of nitrogen monoxide. However, Fe(J-ph)NO displays a larger anisotropy compared with Fe(bza-ph)NO. This fact implies that the contribution from iron *d*-orbital to the molecular orbital containing an unpaired electron is larger in Fe(J-ph)NO than in Fe(bza-ph)NO. This is in line with our view that the energy of the metal *d*-orbital of Fe(J–R)NO is lowered by an electron-withdrawing effect of the acetyl substituent. It is to be noticed that ESR spectra of the present complexes bear a marked resemblance to that of Fe(TPP)NO [18]. This adds a strong support for the square-pyramidal structure with a bent FeNO fragment for the present complexes, since the same structure was demonstrated for Fe(TPP)NO from X-ray analysis [19].

The ESR spectrum of Fe(J-ph)NO in the presence of excess pyridine (Fig. 4) indicates that Fe(J-ph)-

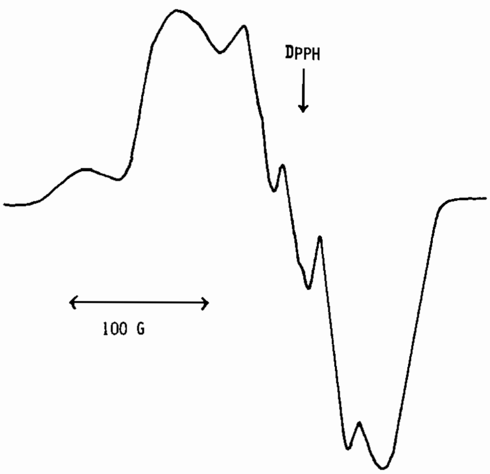

Fig. 4. ESR spectrum of Fe(J-ph)NO in the presence of excess pyridine (in 1:1 mixture of toluene and chloroform at 78 K).

NOpy is formed in this solution. It shows a rhombic pattern with ^{14}N superhyperfine splitting due to nitrogen monoxide in g_z region. The principal g-values and superhyperfine coupling constant are as follows: $g_1 = 2.060$, g_2 $(=g_z) = 2.008$, $g_3 = 1.971$, and $A_N = 35$ gauss. It is to be noted that the ESR parameters are very similar to those for nitrosyl derivatives of hemoproteins, such as ferrous catalase [20], ferrous myoglobin [20, 21] and ferrous hemoglobin [20, 21–24], except for a slightly smaller anisotropy of g value and a slightly larger superhyperfine coupling constant due to ^{14}N nucleus for the present complexes. It is likely that the orbital containing an unpaired electron of Fe(J-ph)NOpy possesses a lower metal character than those of nitrosyl hemoproteins. This suggests that metal d-orbitals for hemoproteins are much stabilized compared with those for Fe(J–R), owing to electron-delocalization due to the π-conjugated system of porphyrin.

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