Syntheses, Structures, and Spectroscopic Properties of Cobalt(III) Complexes Containing 3- or 4-Pyridyl-Substituted Nitronyl and Imino Nitroxide Ligands

Masahiro Ogita,[a] Youhei Yamamoto,[a] Takayoshi Suzuki,[a] and Sumio Kaizaki*[a]

Keywords: Nitroxides / Radicals / Cobalt / NMR spectroscopy / Deoxygenation

---

Several new cobalt(III) complexes incorporating 4,4,5,5-tetramethyl-2-(3- or 4-pyridyl)imidazolin-1-oxyl 3-oxide (NIT*n*py) ($n = 3$ or 4) or 4,4,5,5-tetramethyl-2-(3- or 4-pyridyl)-imidazolin-1-oxyl (IM*n*py) have been prepared. The X-ray crystallographic analyses and the spectroscopic investigations have revealed that the nitronyl or imino nitroxides with the radical character are bound through the pyridyl-N atom to a Co^{III} center. There are some influences from the radical unpaired electron toward the Co^{III} complex moiety and those from the coordination of the Co^{III} ion toward the nature of these radicals which can be detected by ^{59}Co NMR and UV/Vis spectroscopy. Such observed changes coincide with the proposed spin density on the N atom of the pyridyl substituent. Furthermore, it was found that *trans*-$[Co(acac)_2(PPh_3)(NIT4py)]^+$ in methanol was gradually converted into the corresponding IM4py complex, while free NIT4py is stable in methanol. The Co^{II} species formed on the partial decomposition of the NIT4py complex in methanol seems to catalyze the deoxygenation of NIT4py to IM4py.

Introduction

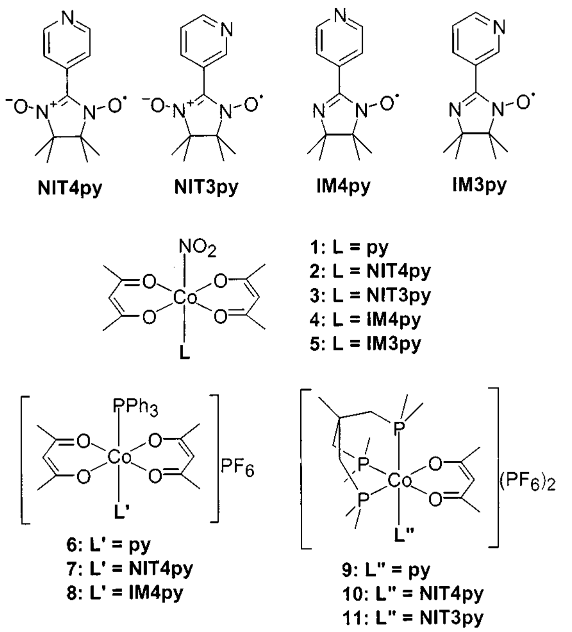
In the last two decades, the chemistry and magnetic properties of transition metal complexes containing imidazolin-1-oxyl 3-oxide (abbreviated as nitronyl nitroxide; NIT) or imidazolin-1-oxyl (imino nitroxide; IM) radicals have been examined extensively.[1−11] These studies have been aimed mainly at investigating the magnetic exchange interactions between the metal d (or f) and the radical unpaired electrons, and at designing and synthesizing molecular ferro/ferrimagnets. Therefore, most of the complexes studied were of paramagnetic metal ions such as Mn^{II}, Cu^{II}, Ni^{II},[1−5] Cr^{III},[5a] Co^{II},[6−8] and lanthanide(III).[9] Among the nitronyl or imino nitroxide radicals, the pyridyl-substituted derivatives are especially attractive and are utilized successfully, because the auxiliary donor ability of the pyridyl-N atom tends to assemble extended coordination compounds by binding to metal ions.[2a,10] The suitability of such pyridyl-substituted nitroxides with the metal ions has afforded new aspects of their paramagnetic and diamagnetic metal complexes. In our previous papers concerning paramagnetic metal radical complexes, we have reported on the structures, magnetic, and spectroscopic (UV/Vis absorption, MCD, resonance Raman, NMR) properties of the 2-pyridyl-substituted nitronyl nitroxide (NIT2py) or imino nitroxide (IM2py) complexes of Cr^{III}, Ni^{II}, Co^{II}, and Mn^{II}.[5,6] For diamagnetic metal complexes Oshio et al. have observed a large ferromagnetic or antiferromagnetic interaction between the two imino nitroxides through a diamagnetic metal center in tetrahedral Cu^{I}, Ag^{I} and square-planar Pd^{II} complexes.[11] Wei et al. have found a fairly large antiferromagnetic interaction in a polymeric Hg^{II} chain compound.[10] Recently, we described the X-ray structures and magnetic properties of the IM2py Zn^{II} complex and related complexes.[6] On the other hand, substitution-inert Co^{III} complexes incorporating the pyridyl-substituted nitronyl or imino nitroxides (NIT*n*py or IM*n*py) would exhibit a variety of coordination modes of the 3- or 4-pyridyl-substituted nitroxide radicals, or exert an influence from nonradical coligands. Such nitroxide radical Co^{III} complexes are expected to afford moderately or slightly magnetically coupled systems, where the spectroscopic properties could be regulated, as observed for the Ni^{II} and Cr^{III} complexes.[5] This is in contrast to semiquinone radical Co^{III} complexes, which are susceptible to reduction to Co^{II}.[12] Here, we report on the synthesis and structural characterization of *trans*-$[Co(acac)_2(NO_2\text{-}\kappa N)(L)]$, *trans*-$[Co(acac)_2(PPh_3)(L)]PF_6$, and $[Co(acac)(tdmme)(L)](PF_6)_2$ [acac = pentane-2,4-dionate; tdmme = 1,1,1-tris(dimethylphosphanylmethyl)-ethane; L = NIT4py, NIT3py, IM4py, and IM3py] (Scheme 1). We also report on the novel deoxygenation reaction of NIT4py in *trans*-$[Co(acac)_2(PPh_3)(NIT4py)]PF_6$, and on the attempts to prepare the bis(nitroxide) Co^{III} complexes.

---

[a] Department of Chemistry, Graduate School of Science, Osaka University,
Toyonaka 560-0043, Japan
Fax: (internat.) + 81-6/6850-5408
E-mail: kaizaki@chem.sci.osaka-u.ac.jp

Supporting information for this article is available on the WWW under http://www.eurjic.com or from the author.

1434−1948/02/0404−0886 $ 17.50+.50/0



Scheme 1. The nitronyl and imino nitroxides and their Co^{III} complexes, together with the reference pyridine complexes, prepared in this study

Results and Discussion

Bis(pentane-2,4-dionato)(nitrito-κ*N* or triphenylphosphane) Complexes

Although both 4- and 3-pyridyl-substituted nitroxide complexes, *trans*-[Co(acac)$_2$(NO$_2$-κ*N*)(L)] [L = NIT4py (**2**), IM4py (**4**), NIT3py (**3**), and IM3py (**5**)], were prepared from *trans*-Na[Co(acac)$_2$(NO$_2$-κ*N*)$_2$], the reaction of *trans*-[Co(acac)$_2$(PPh$_3$)$_2$]PF$_6$ with the nitroxides gave only the 4-pyridyl-substituted complexes, *trans*-[Co(acac)$_2$(PPh$_3$)(L′)]PF$_6$ [L′ = NIT4py (**7**) and IM4py (**8**)]. The formation of the 3-pyridyl-substituted nitroxide (NIT3py or IM3py)/PPh$_3$ complexes was not observed due to steric factors (vide infra). The *trans* geometry of the nitroxide complexes, as well as of the corresponding pyridine complexes of **1** and **6** was determined by ^{1}H NMR spectroscopy in CDCl$_3$. The spectra showed only one methyl and one methine proton resonances of the acac moiety with an intensity ratio of 6:1 (Table 1).

Table 1. ^{1}H NMR chemical shifts of the acac moiety in the Co^{III} complexes **1**−**8**

Compound	$-CH_3$[a]	$=CH-$[a]
1	2.12	5.33
2	2.11	5.33
3	2.19	5.35
4	2.12	5.33
5	2.12	5.32
6	1.78	4.89
7	1.74	4.91
8	1.79	4.90

[a] In CDCl$_3$. Chemical shifts (δ scale) are relative to TMS. For all compounds listed the intensity ratio of $-CH_3$ to $=CH-$ was found to be 6:1.

The structures of complexes **5**, **7**, and **8** were confirmed by X-ray analysis. The molecular structures of *trans*-[Co(acac)$_2$(NO$_2$-κ*N*)(IM3py)] (**5**) and *trans*-[Co(acac)$_2$(PPh$_3$)(NIT4py)]$^+$ in **7**·CH$_2$Cl$_2$ are shown in Figure 1. The crystal of **8**·CH$_2$Cl$_2$ is isomorphous to that of **7**·CH$_2$Cl$_2$ and the molecular structure of *trans*-[Co(acac)$_2$(PPh$_3$)(IM4py)]$^+$ in **8**·CH$_2$Cl$_2$ (Figure S1, Supporting Information) is very similar to that of the NIT4py complex, except for the absence

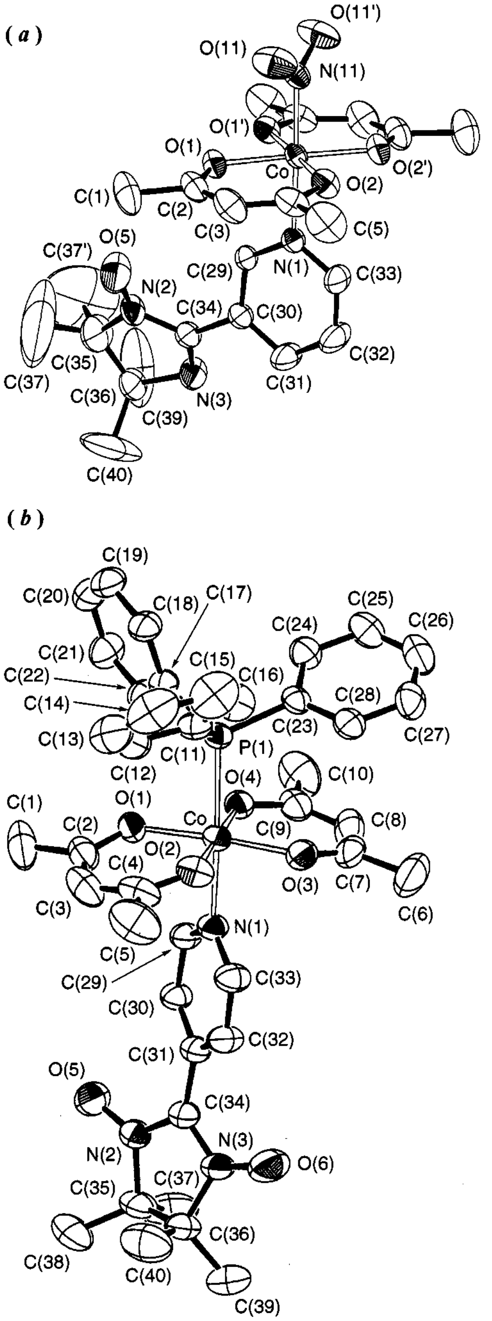


Figure 1. Perspective views of (*a*) *trans*-[Co(acac)$_2$(NO$_2$-κ*N*)(IM3py)] (**5**) (40% probability level) and (*b*) *trans*-[Co(acac)$_2$(PPh$_3$)(NIT4py)]$^+$ in **7**·CH$_2$Cl$_2$ (50% probability level); hydrogen atoms are omitted for clarity

of one O atom from the nitronyl nitroxide moiety. The pyridyl-substituted nitronyl or imino nitroxide is bound to a Co^{III} center via a pyridyl-N atom at the position *trans* to NO$_2$-κ*N* or PPh$_3$.

Selected bond lengths, bond angles, and dihedral angles between the least-squared planes are listed in Table 2. The structural parameters of the NIT4py moiety in **7** are similar to those of free NIT4py,[7b,13] and those of the other complexes containing monodentate pyridyl-N donating NIT4py.[1,2b,2c] The dihedral angle between the nitronyl nitroxide mean plane and the pyridyl ring in **7** [28.8(1)°] is slightly larger than those in free NIT4py (24.7°[7b] or 22.8°[13]). The N−O bond lengths in **7** [1.276(3) and 1.260(3) Å] are close to the typical bond lengths in the free nitronyl nitroxides.[7b,13,14] In contrast, the structural parameters of IM4py in **8**, IM3py in **5**, and the free 5-pyrimidyl or *m*-nitrophenyl imino nitroxide (IM5pym or IM*m*NP)[14a,15] are fairly different from one another. For example, the N−O bond length becomes shorter in the order **8** [1.295(6) Å] $>$ **5** [1.273(6) Å] $>$ IM5pym [1.268(4) Å] $>$ IM*m*NP (average 1.246 Å). The dihedral angle between the imino nitroxide mean plane and the pyridyl ring is 29.2(2) and 22.5(2)° for **5** and **8**, respectively, 19.1° for IM5pym,[14a] and 44.7 and 13.0° for two crystallographically independent IM*m*NP molecules.[15]

Table 2. Selected bond lengths [Å], bond angles [°], and dihedral angles [°] between the least-squared planes for the complexes

Compound[a]	**5**	**7**	**8**
Co−P(1)	−	2.2723(7)	2.269(1)
Co−O(1)	1.879(2)	1.873(2)	1.876(3)
Co−O(2)	1.889(2)	1.885(2)	1.880(3)
Co−O(3)	−	1.888(2)	1.882(3)
Co−O(4)	−	1.879(2)	1.882(3)
Co−N(1)	1.996(3)	2.021(2)	2.019(3)
Co−N(11)	1.902(3)	−	−
N(2)−O(5)	1.273(6)	1.276(3)	1.295(6)
N(3)−O(6)	−	1.260(3)	−
N(2)−C(34)	1.348(5)	1.347(4)	1.343(5)
N(3)−C(34)	1.306(5)	1.348(4)	1.306(5)
P(1)−Co−N(1)	−	175.47(6)	175.11(9)
N(1)−Co−N(11)	178.3(1)	−	−
O(1)−Co−O(2)	95.73(8)	94.59(9)	94.5(1)
O(3)−Co−O(4)	−	94.95(9)	95.0(1)
C(34)−N(2)−O(5)	125.2(4)	127.1(2)	127.5(4)
C(34)−N(3)−O(6)	−	126.3(2)	−
C(35)−N(2)−O(5)	127.2(4)	121.4(2)	121.5(4)
C(36)−N(3)−O(6)	−	122.3(3)	−
C(34)−N(2)−C(35)	107.6(3)	111.4(2)	110.0(4)
C(34)−N(3)−C(36)	109.4(4)	111.2(2)	108.2(4)
plane(Co−4O) vs. plane(acac 1)	4.0(1)	14.9(1)	16.5(2)
plane(Co−4O) vs. plane(acac 2)	−	9.5(1)	10.3(2)
plane(acac 1) vs. plane(acac 2)	−	24.3(1)	26.8(2)
plane(Co−4O) vs. plane(py)	90	84.53(9)	83.5(1)
plane(Co−4O) vs. plane(phenyl 1)	−	40.1(1)	40.8(2)
plane(Co−4O) vs. plane(phenyl 2)	−	72.7(1)	69.0(1)
plane(Co−4O) vs. plane(phenyl 3)	−	23.5(1)	22.8(1)
plane(py) vs. plane(nitroxide)	29.2(2)	28.8(1)	22.5(2)

[a] Plane(Co−4O) was defined by O(1), O(2), O(3 or 1′) and O(4 or 2′); plane(acac 1) by O(1), O(2), and C(2)−C(4); plane(acac 2) by O(3), O(4), and C(7)−C(9); plane(py) by N(1) and C(29)−C(33); plane(phenyl 1) by C(11)−C(16); plane(phenyl 2) by C(17)−C(22); plane(phenyl 3) by C(23)−C(28).

The structures of the *trans*-Co(acac)$_2$(PPh$_3$) moiety in **7** and **8** are similar to those in *trans*-[Co(acac)$_2$(PPh$_3$)(H$_2$O)]PF$_6$[16a] and *trans*-[Co(acac)$_2$(PPh$_3$)(atmp)]PF$_6$ (atmp = 4-amino-2,2,6,6-tetramethylpiperidine-κ*N*^{4}).[16b] In particular, the acac ligands in the equatorial positions bend away from the axial PPh$_3$ group, due to the steric effects presented by the bulky axial PPh$_3$ group. The dihedral angle between the two acac planes are 24.3(1) and 26.8(2)° in **7** and **8**, respectively. The Co−P bond lengths, 2.2723(7) in **7** and 2.269(1) Å in **8**, are similar to those in *trans*-[Co(acac)$_2$(PPh$_3$)(H$_2$O)]PF$_6$ [2.243(1) Å] and *trans*-[Co(acac)$_2$(PPh$_3$)(atmp)]PF$_6$ [2.295(2) Å].

The pyridyl ring of NIT4py or IM*n*py in **5**, **7**, and **8** is oriented toward the cleft between the two equatorial acac ligands (Figure 1 and Figure S1). This orientation would minimize the sterically repulsive interaction between the planar pyridyl moiety of the nitroxide and the equatorial acac planes. Comparison with the structures of complexes **5**, **7**, and **8** suggests that in the hypothetical complex, *trans*-[Co(acac)$_2$(PPh$_3$)(NIT3py or IM3py)]$^+$, severe steric interaction exists between the nitroxide part of the coordinated NIT3py or IM3py and the equatorial acac planes which would bend away from the axial PPh$_3$ group due to steric hindrance. This seems to be the reason for the unsuccessful syntheses of the 3-pyridyl-substituted nitroxide complexes for PPh$_3$ derivatives.

(Tripodal tridentate phosphane)(pentane-2,4-dionato) Complexes

For spectroscopic purposes (vide infra), we have also attempted to prepare the NIT4py and NIT3py complexes which incorporates tripodal tridentate phosphane,

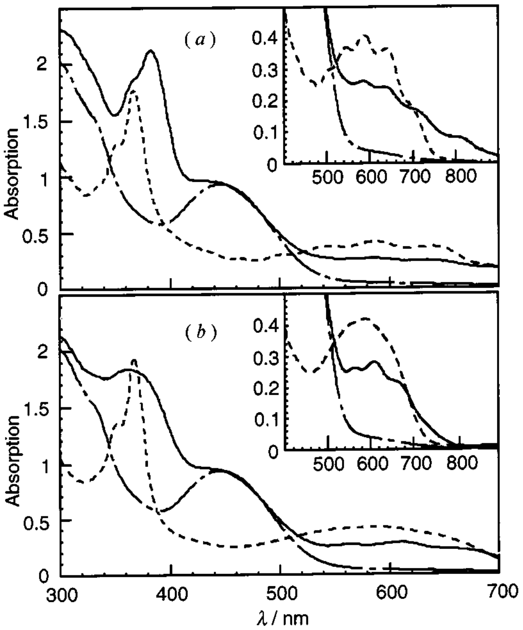


Figure 2. UV/Vis spectra in the solid state: (*a*) complex **9** (− · −), complex **10** (——), and NIT4py (− − − −); (*b*) complex **9** (− · −), complex **11** (——), and NIT3py (− − − −)

tdmme.[17] The reaction of [Co(acac)(tdmme)(CH_3CN)](PF_6)$_2$ (**12**) and L′′ (L′′ = py, NIT4py, or NIT3py) in methanol afforded powder products of [Co(acac)(tdmme)(L′′)](PF_6)$_2$ (**9−11**). The UV/Vis spectra of the products in the solid state showed distinct changes from the superimposed spectra of the starting materials (Figure 2 and Table 3). These compounds were insoluble in dichloromethane, chloroform, and methanol, and fairly soluble in acetonitrile. However, the absorption spectra of compounds **9−11** in acetonitrile showed apparent shifts from those in the solid, and coincided with the superimposed spectra of complex **12** and free L′′. These facts indicate that in acetonitrile NIT*n*py (or py) dissociates from the Co^{III} center giving a mixture of the acetonitrile complex **12** and free L′′. This lability is probably due to the strong *trans* influence of tdmme.[17]

Deoxygenation of NIT4py to IM4py in the PPh_3 Complex

Ullman reported that heating nitronyl nitroxides with PPh_3 in benzene affords the corresponding imino nitroxides in high yields.[18] In view of this fact, the successful synthesis of complex **7** from *trans*-[Co(acac)$_2$(PPh_3)$_2$]PF_6 seems to be strange since free PPh_3 is produced in the reaction mixture. Under the experimental conditions employed (in dichloromethane at room temperature for several hours), detectable deoxygenation of NIT*n*py to IM*n*py was not observed. Further, refluxing NIT4py with PPh_3 in dichloromethane, chloroform, or methanol for several hours did not result in any UV/Vis spectral change. The isolated complex **7** was also stable on refluxing in dichloromethane or chloroform for several hours. However, when a methanol solution of **7** was allowed to stand at room temperature for 1 d, the UV/Vis and ESR spectra of the solution changed to those corresponding to the IM4py complex **8**. On refluxing the methanol solution, deoxygenation of NIT4py in complex **7** was completed within 10 min (Figure 3). A prolonged reaction in boiling methanol resulted in the decomposition of IM4py; a very weak ESR signal of IM4py was seen after 1 d.

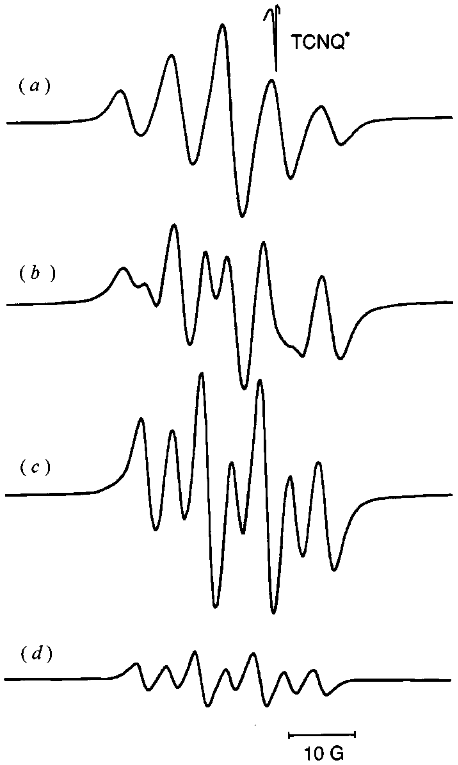


Figure 3. The ESR spectra of complex **7** (*a*) in dichloromethane, (*b*) in methanol, (*c*) in refluxing methanol for 10 min, and (*d*) in refluxing methanol for 24 h

The reagent that is responsible for the deoxygenation of NIT4py in complex **7** was investigated. As described above, a methanol solution of NIT4py alone, or together with PPh_3, did not result in such a deoxygenation reaction. The following Sephadex LH-20 chromatographic behavior in methanol suggests that complex **7** exists as a dissociated equilibrium mixture. Of the two bands separated from the

Table 3. Absorption spectroscopic data of the free nitroxides and the Co^{III} complexes

Compounds	Solvent	10^{-3} σ [cm^{-1}] (ε [dm^3 mol^{-1} cm^{-1}])
NIT4py	CH_2Cl_2	14[a] (80), 15.5[a] (175), 16.8 (230), 18[a] (180), 19.5[a] (80), 27.3 (16300), 28.5[a] (7400), 35.7[a] (8500), 38.2[a] (8800)
NIT3py	CH_2Cl_2	14.5[a] (190), 16.1 (476), 17.1 (489), 18.5[a] (300), 27.3 (17600), 28.5[a] (9600), 37.8 (10600), 40[a] (10000)
IM4py	CH_2Cl_2	17.8[a] (50), 19.5[a] (120), 21.1[a] (240), 22.4 (315), 23.5 (300), 25[a] (260), 33.3 (4400), 34.8[a] (3900), 37.4[a] (3800)
IM3py[b]	CH_2Cl_2	17.8[a], 19.7[a], 21.3[a], 22.6, 23.8[a], 25.1[a], 33[a], 37.5[a]
1	CH_2Cl_2	18.8 (157), 29.5 (8500)
2	CH_2Cl_2	12.5[a] (40), 14.3[a] (75), 16[a] (150), 18.4 (227), 26.5 (17600), 27.6[a] (13000)
3	CH_2Cl_2	14.4[a] (80), 15.8[a] (260), 17.3 (364), 18.3[a] (345), 27.0 (12000), 28.7 (12400)
4	CH_2Cl_2	18.5[a] (280), 20.0 (360), 29.5 (10800), 37.5 (33500)
5	CH_2Cl_2	17.8[a] (150), 19.5 (270), 21.0[a] (420), 29.5 (9200), 37.5 (29400)
6	CH_2Cl_2	18.7[a] (267), 30.3 (16000)
7	CH_2Cl_2	12.2[a] (50), 14[a] (80), 18.6[a] (370), 26.4 (19446), 27.8[a] (17000), 30.0 (22500), 33.8[a] (26500)
8	CH_2Cl_2	16.2[a] (180), 18.2[a] (430), 30.5 (20300)
9[b]	solid	22.5, 33.7[a]
10[b]	solid	14.9[a], 16.5, 17.8, 22.8[a], 27.8, 33.3[a], 38.3
11[b]	solid	12.5[a], 14.2[a], 15.8, 17.2, 22.9[a], 26.3, 33.7, 38.2
12	py	22.4 (910), 30.2[a] (3140)
	CH_3CN	23.1 (835), 30.7[a] (3200), 34.1 (10800), 39.4[a] (24700)

[a] Shoulder. [b] These data were measured qualitatively.

adsorbed products, the faster developing green band was a mixture of complex **7** and *trans*-[Co(acac)$_2$(PPh$_3$)(H$_2$O)]PF$_6$,[16a] whereas the slower developing blue eluate was free NIT4py. Thus, the aquated complex, [Co(acac)$_2$(PPh$_3$)(H$_2$O)]$^+$ would mainly contribute to the deoxygenation of NIT4py. In fact, NIT4py itself is catalyzed to form deoxygenated IM4py by a methanol solution of the triphenylphosphane complex *trans*-[Co(acac)$_2$(PPh$_3$)(H$_2$O)]PF$_6$, but not by a methanol solution of the dimethylphenylphosphane complex *trans*-[Co(acac)$_2$(PMe$_2$Ph)(H$_2$O)]PF$_6$ and the Co^{II} complex [Co^{II}(acac)$_2$(H$_2$O)$_2$]. The Co^{III}−PPh$_3$ complex, *trans*-[Co(acac)$_2$(PPh$_3$)(H$_2$O)]PF$_6$ slowly decomposes to give Co^{II} species, while *trans*-[Co(acac)$_2$(PMe$_2$Ph)(H$_2$O)]PF$_6$ is stable in methanol.[16a,19] Thus, the decomposed, yet uncharacterized Co^{II} products may be a catalyst for the deoxygenation process.

Attempts to Prepare Bis(nitronyl or imino nitroxide)bis(pentane-2,4-dionato) Complexes

Although the reaction of *trans*-[Co(acac)$_2$(PPh$_3$)$_2$]PF$_6$ with NIT3py in dichloromethane did not proceed, a similar reaction with twice the equimolar amounts of NIT3py in methanol showed a gradual change in color from dark red to brown. The elemental analysis and the spectroscopic data of the brown product indicate the formation of a complicated mixture of bis(NIT3py)-, (NIT3py)(IM3py)-, and bis(IM3py)-bis(acac)cobalt(III) complexes (Figure S2, Supporting Information), as suggested from the reaction conditions for the deoxygenation of NIT3py to IM3py as described above. The formation of IM3py could not be avoided under these reaction conditions.

An attempt to oxidize an ethanolic solution of *trans*-[Co^{II}(acac)$_2$(NIT*n*py or IM*n*py)$_2$][7b] with acidic PbO$_2$ resulted in the formation of a mixture of bis(NIT*n*py or IM*n*py) complexes (Figure S2), as in the case started from the Co^{III} complex. It is noted that in the reactions with PbO$_2$, NIT*n*py still deoxygenates to give IM*n*py.

ESR Spectra and Magnetic Properties

The ESR spectra of the Co^{III} NIT*n*py (**2**, **3**, **7**) and IM*n*py (**4**, **5**, **8**) complexes give a well-resolved quintuplet and septuplet signal, respectively (Figure S3, Supporting Information), as observed for free NIT*n*py and IM*n*py.[1,21] The *g* and *A* values of the Co^{III} complexes are close to those of the free nitroxide (Table 4). This fact indicates that the radical unpaired electron of the nitroxide is not significantly influenced by the coordination to a diamagnetic Co^{III} ion through the substituted pyridyl-N atom. This is also suggested by the variable-temperature magnetic measurements in the solid state, the overall profiles of the temperature dependence of the molar magnetic susceptibilities of the Co^{III} complexes are found to be similar to those of the free nitroxides (Figure S4, Supporting Information).

NMR Spectra

The ^{1}H NMR signals of the acac or PPh$_3$ moiety in the Co(acac)$_2$(NO$_2$-κ*N* or PPh$_3$) unit of **2**, **3**, **7**, and **8** were found to become broad. Since the observed broad signals did not show any shift from those of the parent complexes (Table 1), the line-broadening on coordination of NIT*n*py or IM*n*py via the pyridyl-N atom results from the dipolar relaxation (through space) mechanism, but not from the contact (through bond) mechanism. This is also related to the difference in broadening between the NIT3py and NIT4py complexes, the former being larger than the latter. The distance from the radical moiety in NIT3py to the protons in the coligands is shorter than for NIT4py, and accounts for the difference in line broadening in terms of the dipolar relaxation.

Table 4. ESR spectral parameters

Compounds[a]	Solvent	*g*	A$_1$	A$_2$
NIT4py	H$_2$O	2.007	8.2	−
2	CH$_2$Cl$_2$	2.007	7.3	−
7	CH$_2$Cl$_2$	2.007	7.3	−
NIT3py	H$_2$O	2.006	7.9	−
3	CH$_2$Cl$_2$	2.006	7.2	−
IM4py	H$_2$O	2.005	9.4	4.2
4	CH$_2$Cl$_2$	2.006	9.0	4.4
8	CH$_2$Cl$_2$	2.006	9.2	4.4
IM3py	H$_2$O	2.006	9.4	4.2
5	CH$_2$Cl$_2$	2.006	9.2	4.3

[a] H_0 = 3360 Gauss, 9.45 GHz, room temp., A_1, A_2 in Gauss.

Table 5. ^{59}Co NMR spectroscopic data

Compound[a]	Solvent	δ	Δ$_{1/2}$ [Hz]
1	CDCl$_3$	10633	1200
2	CDCl$_3$	10700	11000
3	CDCl$_3$	10585	2600
4	CDCl$_3$	10624	4500
5	CDCl$_3$	10606	2000
6	CDCl$_3$	9800	2000
7	CDCl$_3$	9837	12000
8	CDCl$_3$	9780	5900
trans-[Co(acac)$_2$(py)$_2$]PF$_6$	CD$_3$CN	13260	
trans-[Co(acac)$_2$(NIT4py)$_2$]BF$_4$[b]	CD$_3$CN	13352	
trans-[Co(acac)$_2$(NIT4py)(IM4py)]BF$_4$[b]	CD$_3$CN	13284	
trans-[Co(acac)$_2$(IM4py)$_2$]BF$_4$[b]	CD$_3$CN	13231	

[a] Chemical shifts (δ scale) are relative to K$_3$[Co(CN)$_6$]. [b] Could not be isolated.

Table 5 presents the ^{59}Co NMR parameters of the pyridine and nitroxide complexes. The ^{59}Co NMR chemical shifts of the PPh$_3$ complexes with py, NIT4py, and IM4py are located at a higher field than those of the corresponding NO$_2$-κ*N* complexes. The ^{59}Co NMR resonances of the nitroxide complexes are relatively broader as compared with the py complexes. For the NIT*n*py complexes **2**, **3**, and **7**, the ^{59}Co NMR signals on coordination of NIT3py and NIT4py shift to a higher and lower field, respectively, from those of the corresponding py complexes. The line-broadening for the NIT3py complex is small and considerably larger for the NIT4py complex (Figure S5, Supporting Information). These observations coincide with the ^{1}H

NMR behavior of the *meta*- and *para*-protons in the phenyl group of NITPh[22] and NITPhOH,[23] and also with the experimental and theoretical spin density (and sign) at these positions.[14,24]

The ^{59}Co NMR resonances of the IM*n*py complexes **3**, **4**, and **8** show slightly higher field shifts with less broadening than the corresponding NIT*n*py complexes. This also coincides with the difference in the spin density between the imino and nitronyl nitroxides.[14,15] Thus, the ^{59}Co NMR chemical shifts reflect the spin density and sign on the pyridyl-N atom of NIT*n*py or IM*n*py, although the shift values are relatively small, in accordance with the small spin density on the N atom.

UV/Vis Absorption Spectra

The UV/Vis spectra of complexes **2**−**5**, **7**, and **8** give a complicated pattern due to the overlap with the intraligand bands for the nitroxides and the Co(acac)$_2$(NO$_2$-κ*N* or PPh$_3$) moieties (Figure S6, Supporting Information). Thus, it is difficult to evaluate the coordination effect on the ligand-field d−d transitions of the Co^{III} ion and on the intraligand transitions of the radical moiety in these complexes by comparison with the spectra of the py complexes **1** and **6**. This difficulty may be overcome if the d−d bands are shifted to a shorter wavelength where the nitronyl nitroxides are transparent. This can be achieved with the use of a tripodal tridentate phosphane tdmme instead of PPh$_3$ and one acac ligand, since the ligand-field strength of tdmme is much larger than that of PPh$_3$ and acac.[17] Since the complexes [Co(acac)(tdmme)(L′′)](PF$_6$)$_2$ (**9**−**11**) are unstable in acetonitrile, the following UV/Vis spectra were measured in the solid state. The ligand-field d−d band of the py complex **9** appears at 22200 cm^{-1}, as expected from the difference in the ligand-field strengths between tdmme and (acac)(PPh$_3$). It is noted that the d−d transition of the NIT*n*py complex **10** or **11** is observed at the same position as that of the py complex **9** (Figure 2). Therefore, the radical unpaired electron of NIT*n*py exerts no influence on the d−d transition energy of the Co^{III} complexes. However, there are explicit perturbations for the broad vibronic band at 15000−18000 cm^{-1} upon coordination, and a very sharp strong band following the higher energy component around 27000 cm^{-1}, due to the n→π* and π→π* transitions of the nitronyl nitroxide moiety, respectively.[1] In the NIT4py complex **10** [Figure 2 (*a*)], the n→π* and π→π* bands are red-shifted by 1300 and 1100 cm^{-1}, respectively. In contrast, the NIT3py complex **11** [Figure 2 (*b*)] gives a slightly red-shifted (500 cm^{-1}) n→π* transition band, however, the π→π* band is shifted by a negligible amount, but is remarkably broad.

This perturbation is confirmed by subtracting the UV/Vis spectra of the NIT*n*py complexes from the py complex, which gives the spectrum of the perturbed nitroxide in the complex. For the NIT*n*py complexes, comparisons of both the difference spectra of complexes **2** (subtracted from **1**) and **3** (subtracted from **1**) with the spectra of free nitroxides (Figure 4) gives a similar result as the above tdmme complexes. Further, the difference spectrum of the PPh$_3$ complex **7** (subtracted from **6**) gives the same result (Figure S7, Supporting Information). Thus, it is concluded that the n→π* and π→π* transition bands are red-shifted (by ca. 800 cm^{-1}) on coordination of NIT4py to the Co^{III} ion via the pyridyl-N atom, while these bands show a slight shift and band-broadening when NIT3py is coordinated. These differences in perturbation between the NIT4py and NIT3py complexes may result from the difference in spin density (and sign) at the pyridyl-N atom, as found in the ^{59}Co NMR chemical shifts of complexes **2** and **3** (vide supra). Another reason is considered to be related to the difference in perturbation on the NIT*n*py SOMO π* orbitals through π-back-bonding from the Co^{III} t$_{2g}$ orbital to the pyridyl π* orbital, in view of the plausible inherent interaction of the π-systems between the NIT*n*py and the pyridyl group. This interaction is suggested by the lower frequency shift of both the n→π* and π→π* transitions by 1000−2000 cm^{-1}, on going from NITMe to NIT*n*py.[1]

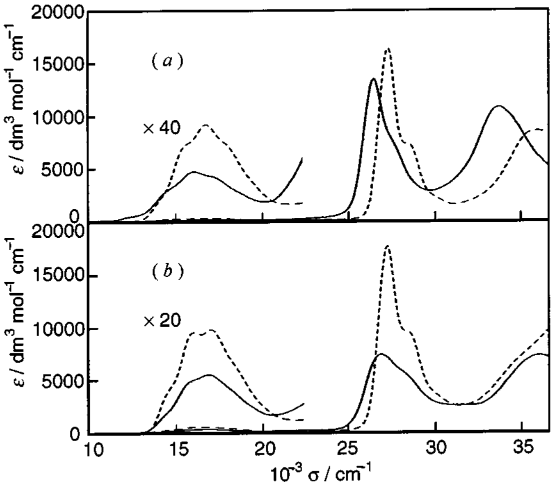


Figure 4. The difference absorption spectra of (*a*) complex **2** − complex **1** and (*b*) complex **3** − complex **1** (——), together with the UV/Vis spectra of NIT4py and NIT3py (– – – –), respectively

We have also made a similar analysis for the IM*n*py complexes (Figure S8, Supporting Information). Although the n(N−O)→π* transition band in the IM4py complexes **4** and **8** shows a distinct red-shift and that in the IM3py complex **5** does not shift, the results are not so clear, because the absorption spectra are much more complicated.

The intensity enhancement of the spin-forbidden $^{1}A_{1}\rightarrow{}^{3}T_{2}$, $^{3}T_{1}$ ligand-field transitions is expected as a result of the magnetic exchange coupling with the doublet ground state of the nitroxide radical and the triplet excited state of Co^{III}. This intensity enhancement is also found for the intraligand singlet−triplet transition in diamagnetic bipyridine, due to the nearby paramagnetic Cr^{III} ion in [Cr(mal)$_2$(bpy)]$^{-}$.[25] However, in the predicted region for the $^{1}A_{1}\rightarrow{}^{3}T_{2}$, $^{3}T_{1}$ transitions, only one shoulder is observed for complexes **2**, **7**, and **11** near 12500 cm^{-1}, which belongs to the lowest frequency vibronic component of the n→π* NIT*n*py intraligand transition, in terms of the above difference spectra. It is seen that the magnetic exchange coupling in this kind of nitroxide complex is not large enough to observe the spin-forbidden transition intensity enhancement. The chelated NIT2py or IM2py Co^{III} complexes may be such a candidate to give observable intensity enhancement. The research in this direction is currently under way in our laboratory.

Conclusion

Explicit perturbations are found in the ^{59}Co NMR chemical shifts resulting from the radical unpaired electron, and on the n→π* and π→π* transition bands of the nitroxide moieties as a result of coordination to the Co^{III} center, in several newly prepared Co^{III} complexes bearing 3- or 4-pyridyl-substituted nitronyl or imino nitroxides. The structural and magnetic properties do not show any significant changes from the corresponding pyridine complexes and/or from the free nitroxides. These perturbed properties reflect the radical spin density and sign on the pyridyl-N atom of NIT*n*py or IM*n*py and/or the π-back bonding which is fine-tuned by coordination. Attempts to prepare bis(NIT*n*py or IM*n*py) Co^{III} complexes resulted in the formation of a mixture of the NIT*n*py and IM*n*py complexes, due to the deoxygenation of NIT*n*py to IM*n*py, and the decomposition of the IM*n*py radicals.

Experimental Section

General Remarks: The nitronyl and imino nitroxides, NIT4py, NIT3py, IM4py, and IM3py,[18,20,21a,26] and the starting Co^{III} complexes, *trans*-Na[Co(acac)$_2$(NO$_2$-κ*N*)$_2$],[27a] *trans*-[Co(acac)$_2$(PPh$_3$)$_2$]PF$_6$,[19a] and [CoCl(acac)(tdmme)]PF$_6$,[17a] and the pyridine (py) complex, *trans*-[Co(acac)$_2$(NO$_2$-κ*N*)(py)] (**1**),[27b] were prepared by the literature methods. UV/Vis spectra were measured with a Perkin−Elmer Lambda 19 spectrophotometer at room temperature. The solid-state spectra in the form of Nujol mulls were obtained according to the method described by Lee et al.[28] The ^{1}H and ^{59}Co NMR spectra were recorded with a JEOL EX-270 or Lambda 500 spectrometer at 30 °C. The ^{59}Co chemical shifts were referenced from external [Co(acac)$_3$] (in CDCl$_3$; $\delta = 12625$).[16a,29] The ESR spectra were obtained with a JEOL JES-FE or JES RE1X spectrometer at ambient temperature. The magnetic susceptibility data were collected with a SQUID-based sample magnetometer using a QUANTUM Design model MPMS instrument. Data were corrected for the magnetization of the sample holder and for the diamagnetic contributions, which were estimated from Pascal's constants.

***trans*-[Co(acac)$_2$(NO$_2$-κ*N*)(L)] {L = NIT4py (2), NIT3py (3), IM4py (4), and IM3py (5)}:** A methanol solution (10 mL) of **L** (1.00 mmol) was added to an aqueous solution (50 mL) of *trans*-Na[Co(acac)$_2$(NO$_2$-κ*N*)$_2$] (1.00 mmol). The mixture was stirred at 30 °C for 10 min, and then cooled in an ice bath. The resulting red-brown precipitate was collected by filtration, and washed with a small amount of methanol and with diethyl ether. The crude product was recrystallized from chloroform/diethyl ether. **2**: Dark red-brown prismatic crystals, yield 0.38 g (70%). $C_{22}H_{30}CoN_4O_8$ (537.4): calcd. C 49.17, H 5.63, N 10.42; found C 48.09, H 5.50, N 10.20. **3**: Dark red-brown needle crystals, yield 0.27 g (50%). $C_{22}H_{30}CoN_4O_8$ (537.4): calcd. C 49.17, H 5.63, N 10.42; found C 48.15, H 5.65, N 10.24. **4**: Red powder, yield 0.42 g (80%). $C_{22}H_{30}CoN_4O_7$ (521.4): calcd. C 50.68, H 5.80, N 10.74; found C 49.90, H 5.66, N 11.15. **5**: Red columnar crystals, yield 0.26 g (50%). $C_{22}H_{30}CoN_4O_7$ (521.4): calcd. C 50.68, H 5.80, N 10.74; found C 49.92, H 5.66, N 10.68.

***trans*-[Co(acac)$_2$(PPh$_3$)(L′)]PF$_6$·*x*CH$_2$Cl$_2$ {L′ = py (6): *x* = 0, NIT4py (7): *x* = 1, and IM4py (8): *x* = 1}:** **L′** (1.00 mmol) was added to a red-purple dichloromethane solution (100 mL) of *trans*-[Co(acac)$_2$(PPh$_3$)$_2$]PF$_6$ (1.00 mmol) while stirring; the color of the mixture turned brown immediately. The solution was concentrated to dryness under reduced pressure, and the residue was thoroughly washed with diethyl ether (100 mL). The obtained brown solid was recrystallized either from dichloromethane/hexane or from dichloromethane/diethyl ether. **6**: Dark brown columnar crystals from CH_2Cl_2/C_6H_{14}, yield 0.67 g (90%). $C_{33}H_{34}CoF_6NO_4P_2$ (743.5): calcd. C 53.31, H 4.61, N 1.88; found C 52.98, H 4.52, N 2.10. **7**: Dark brown trigonal columnar crystals from CH_2Cl_2/Et_2O, yield 0.88 g (90%). $C_{41}H_{47}Cl_2CoF_6N_3O_6P_2$ (983.6): calcd. C 50.07, H 4.82, N 4.27; found C 49.54, H 4.80, N 4.42. **8**: Red plate crystals from CH_2Cl_2/C_6H_{14}, yield 0.87 g (90%). $C_{41}H_{47}Cl_2CoF_6N_3O_5P_2$ (967.6): calcd. C 50.89, H 4.90, N 4.34; found C 50.65, H 4.80, N 4.74.

[Co(acac)(tdmme)(L′′)](PF$_6$)$_2$·*x*H$_2$O {L′′ = py (9): *x* = 0, NIT4py (10): *x* = 1, and NIT3py (11): *x* = 1}: A methanol solution (15 mL) of AgPF$_6$ (1.61 mmol) was added to a solution of [Co(acac)Cl(tdmme)]PF$_6$ (1.60 mmol) in a mixture of methanol and acetonitrile (1:1, 50 mL) while stirring. The mixture was stirred in the dark for 2 h at room temperature, and the resulting white precipitate was filtered off. The precipitate was washed with acetonitrile (10 mL × 2), and the filtrate and washings were combined and concentrated to ca. 5 mL under reduced pressure. Diethyl ether vapor was diffused into the filtered concentrate in a desiccator, depositing red prismatic crystals of [Co(acac)(tdmme)(CH$_3$CN)](PF$_6$)$_2$ (**12**), yield 1.08 g (91%). $C_{18}H_{37}CoF_{12}NO_2P_5$ (741.3): calcd. C 29.17, H 5.03, N 1.89; found C 29.11, H 4.95, N 1.84. Compound **12** (1.00 mmol) was dissolved in acetonitrile (40 mL), and ligand **L′′** (4.00 mmol of py or 1.00 mmol of NIT*n*py) was added to the solution. After stirring for 20 min at room temperature, the solvents were evaporated to dryness under reduced pressure. The residue was thoroughly washed with methanol (10 mL) and dried in vacuo. **9**: Red powder, yield 0.38 g (95%). $C_{21}H_{39}CoF_{12}NO_2P_5$ (779.3): calcd. C 32.37, H 5.04, N 1.80; found C 32.21, H 4.95, N 1.85. **10**: Green powder, yield 0.89 g (96%). $C_{28}H_{52}CoF_{12}N_3O_5P_5$ (952.5): calcd. C 35.31, H 5.50, N 4.41; found C 35.29, H 5.32, N 4.36. **11**: Green powder, yield 0.90 g (96%). $C_{28}H_{52}CoF_{12}N_3O_5P_5$ (952.5): calcd. C 35.31, H 5.50, N 4.41; found C 34.82, H 5.33, N 4.23.

***trans*-[Co(acac)$_2$(py)$_2$]PF$_6$:** The bis(pyridine) complex *trans*-[Co(acac)$_2$(py)$_2$]PF$_6$ was prepared as follows. Acetic acid (1 mL) and PbO$_2$ (7.78 mmol) were added to an ethanol solution (200 mL) of *trans*-[Co^{II}(acac)$_2$(py)$_2$] (3.05 mmol). The mixture was stirred for 2 h at room temperature, and then filtered. The filtrate was concentrated to ca. 50 mL under reduced pressure, and an excess amount of solid NH$_4$PF$_6$ was added to the concentrate with vigorous stirring. The resulting pale brown precipitate was collected by filtration, and recrystallized from acetone/diethyl ether, affording red-brown needle crystals, yield 0.51 g (30%). $C_{20}H_{24}CoF_6N_2O_4P$ (560.3): calcd. C 42.87, H 4.32, N 5.00; found C 43.33, H 4.34, N 5.02.

Table 6. Crystallographic data for compounds **5**, **7**·CH_2Cl_2, and **8**·CH_2Cl_2

Compound	**5**	**7**·CH_2Cl_2	**8**·CH_2Cl_2
Empirical formula	$C_{22}H_{30}CoN_4O_7$	$C_{41}H_{47}Cl_2CoF_6N_3O_6P_2$	$C_{41}H_{47}Cl_2CoF_6N_3O_5P_2$
M	521.43	983.59	967.59
Crystal size [mm]	0.80×0.28×0.26	0.50×0.30×0.30	0.46×0.35×0.12
Crystal system	orthorhombic	triclinic	triclinic
Space group	*Pnma* (no. 62)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	13.892(2)	13.558(2)	13.371(3)
b [Å]	14.790(2)	14.654(2)	14.520(4)
c [Å]	12.889(2)	13.174(2)	13.148(6)
α [°]	90	103.35(1)	101.76(4)
β [°]	90	94.46(1)	93.41(4)
γ [°]	90	65.41(1)	68.27(2)
V [Å^3]	2648.3(6)	2315.2(6)	2321(1)
Z	4	2	2
D_c [Mg m^{-3}]	1.308	1.411	1.384
μ(Mo-K_α) [mm^{-1}]	0.693	0.626	0.622
$F(000)$	1092	1014	998
Transmission factors	0.967−1.000	0.883−1.000	0.832−1.000
Reflns/param ratio	3999/201	13503/558	13554/551
$R1$ [$\lvert F_o\rvert > 2\sigma(\lvert F_o\rvert)$]	0.049	0.054	0.077
wR (all reflns.)	0.153	0.170	0.254

Attempts To Prepare Bis(nitroxide) Complexes. − Method A: NIT*n*py (2.00 mmol) was added to a green methanol solution (150 mL) of *trans*-[Co(acac)$_2$(PPh$_3$)$_2$]PF$_6$ (1.00 mmol). The mixture was stirred at room temperature for 1 d, and the solvents evaporated to dryness under reduced pressure. The residue was extracted with a minimum amount of methanol, and diethyl ether was added to the filtered extract. The resulting precipitate was collected by filtration and washed with diethyl ether. − **Method B:** Acetic acid (1 mL) and PbO_2 (1.00 mmol) were added to an ethanol solution (150 mL) of *trans*-[Co^{II}(acac)$_2$(L)$_2$] (1.00 mmol), which was prepared from [Co(acac)$_2$(H$_2$O)$_2$] and **L** in methanol in a molar ratio of 1:2.[7b] The mixture was stirred for 2 h in an ice bath and then filtered. The filtrate was concentrated to ca. 30 mL under reduced pressure, mixed with an excess amount of a saturated ethanol solution of $NaBPh_4$ or $LiBF_4$, and stored in a refrigerator overnight. The crystalline product deposited was collected by filtration, and recrystallized either from acetone/diethyl ether (BPh_4 salt) or from acetonitrile/diethyl ether (BF_4 salt).

X-ray Crystallographic Study:[30] A suitable crystal of each compound **5**, **7**·CH_2Cl_2, **8**·CH_2Cl_2 was coated with enamel and used for an X-ray diffraction study. The X-ray intensities were measured with an automated Rigaku four-circle diffractometer AFC-5R or -7R [23 °C, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), 2 θ_{max} = 60°]. Absorption corrections were made by an empirical Ψ-scan method.[30a] The structures were solved by the usual heavy-atom method using the SHELXS-86 program,[30b] and refined on F^2 by full-matrix least squares with all independent reflections using the SHELXL-97 program.[30c] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated by riding models. All calculations were carried out using the teXsan software package.[30d] Selected crystallographic data are summarized in Table 6. The structures of **7**·CH_2Cl_2 and **8**·CH_2Cl_2 were successfully solved on the assumption of a centrosymmetric space group $P\bar{1}$. For the analysis of **8**·CH_2Cl_2, there is no electron density (larger than 1 e·Å^{-3}) around the imino-N, N(3), site of IM4py, although from the crystal packing point of view there is no difference between the O(5) and O(6) sites of the NIT4py group in **7**·CH_2Cl_2. For **5**, the Laue symmetry check and systematic absences ($0kl$, $k + l$ = odd; $hk0$, h = odd) indicated the space group was either *Pnma* or *Pn*2$_1$*a*. Initially the structure was solved based on the centrosymmetric space group *Pnma* with Z = 4. It was suggested that the complex possessed a crystallographically imposed plane of symmetry, on which Co, N(11) of nitrito-κ*N*, all atoms [N(1) and C(29)−C(33)] of the pyridyl ring, atoms C(34) and C(35) were located. The imino nitroxide moiety of IM3py was almost planar, but the plane was twisted against the pyridyl ring; this twist forces the N(2), N(3), O(5), C(36), C(39) and C(40) atoms to be positionally disordered over two positions related to the symmetry plane. Even though the space group was deduced to be the non-centrosymmetric *Pn*2$_1$*a*, such disorders could not be resolved. Consequently, the space group *Pnma* was adapted. The O atom of the nitroxide group was located at the *endo* position [N(2) site] relative to the Co atom, no electron-density (larger than 1 e·Å^{-3}) was observed at the corresponding *exo* position [N(3) site]. CCDC-168533 to -168535 (**5**, **7**·CH_2Cl_2, **8**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We gratefully acknowledge support of this research by Grant-in-Aids for Scientific Research (nos. 10304056 and 09740489) from the Ministry of Education, Science and Culture, Japan.

---

[1] A. Caneschi, D. Gatteschi, P. Rey, *Prog. Inorg. Chem.* **1991**, *39*, 331−429; and references therein.

[2] [2a] F. L. de Panthou, E. Belorizky, R. Calemczuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek, P. Rey, *J. Am. Chem. Soc.* **1995**, *117*, 11247−11253. [2b] A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, R. Sessoli, *Inorg. Chem.* **1990**, *29*, 1756−1760. [2c] A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, R. Sessoli, *Inorg. Chem.* **1990**, *29*, 4217−4223. [2d] A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Inorg. Chim. Acta* **1991**, *184*, 67−71. [2e] D. Luneau, G. Risoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi, J. Laugier, *Inorg. Chem.* **1993**, *32*, 5616−5622.

[3] [3a] D. Luneau, P. Rey, J. Laugier, P. Fries, A. Caneschi, D.

Gatteschi, R. Sessoli, *J. Am. Chem. Soc.* **1991**, *113*, 1245–1251. [3b] D. Luneau, P. Rey, J. Laugier, E. Belorizky, A. Conge, *Inorg. Chem.* **1992**, *31*, 3578–3584. [3c] K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer, *J. Am. Chem. Soc.* **2000**, *122*, 718–719.

[4] [4a] P. F. Richardson, R. W. Kreilick, *J. Am. Chem. Soc.* **1977**, *99*, 8183–8187. [4b] P. F. Richardson, R. W. Kreilick, *J. Phys. Chem.* **1978**, *82*, 1149–1151.

[5] [5a] T. Yoshida, K. Kanamori, S. Takamizawa, W. Mori, S. Kaizaki, *Chem. Lett.* **1997**, 603–604. [5b] T. Yoshida, S. Kaizaki, *Inorg. Chem.* **1999**, *38*, 1054–1058. [5c] T. Yoshida, T. Suzuki, K. Kanamori, S. Kaizaki, *Inorg. Chem.* **1999**, *38*, 1059–1068.

[6] [6a] Y. Yamamoto, T. Suzuki, S. Kaizaki, *J. Chem. Soc., Dalton Trans.* **2001**, 1566–1572. [6b] Y. Yamamoto, T. Yoshida, T. Suzuki, S. Kaizaki, *Inorg. Chim. Acta* **2001**, *325*, 187–192. [6c] Y. Yamamoto, T. Suzuki, S. Kaizaki, *J. Chem. Soc., Dalton Trans.* **2001**, 2943–2950.

[7] [7a] C.-F. Huang, H.-H. Wei, *J. Chin. Chem. Soc. (Taipei)* **1997**, *44*, 439–443. [7b] H.-H. Wei, H.-Y. Wong, G.-H. Lee, Y. Wang, *J. Chin. Chem. Soc. (Taipei)* **1996**, *43*, 253–259.

[8] [8a] B.-W. Sun, Q.-H. Zhao, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, X.-K. Yao, H.-G. Wang, *Can. J. Chem.* **2000**, *78*, 322–327. [8b] A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, *Inorg. Chem.* **1988**, *27*, 1553–1557.

[9] [9a] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, *Inorg. Chem.* **1990**, *29*, 4223–4228. [9b] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, *Inorg. Chem.* **1992**, *31*, 741–746. [9c] C. Benelli, A. Caneschi, D. Gatteschi, R. Sessoli, *Inorg. Chem.* **1993**, *32*, 4797–4801. [9d] J.-P. Sutter, M. L. Kahn, S. Golhen, L. Ouahab, O. Kahn, *Chem. Eur. J.* **1998**, *4*, 571–576. [9e] C. Lescop, D. Luneau, G. Bussière, M. Triest, C. Reber, *Inorg. Chem.* **2000**, *39*, 3740–3741.

[10] C.-J. Lee, C.-H. Huang, H.-H. Wei, Y.-H. Liu, G.-H. Lee, Y. Wang, *J. Chem. Soc., Dalton Trans.* **1998**, 171–176.

[11] [11a] H. Oshio, T. Watanabe, A. Ohto, T. Ito, T. Ikoma, S. Tero-Kubota, *Inorg. Chem.* **1997**, *36*, 3014–3021. [11b] H. Oshio, T. Watanabe, A. Ohto, T. Ito, U. Nagashima, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 670–671. [11c] H. Oshio, A. Ohto, T. Ito, *Chem. Commun.* **1996**, 1541–1542.

[12] L. I. Simándi, T. Barna, G. Argay, T. L. Simándi, *Inorg. Chem.* **1995**, *34*, 6337–6340.

[13] K. Awaga, T. Inabe, Y. Maruyama, *Chem. Phys. Lett.* **1992**, *190*, 349–352.

[14] [14a] F. L. de Panthou, D. Luneau, J. Laugier, P. Rey, *J. Am. Chem. Soc.* **1993**, *115*, 9095–9100. [14b] F. M. Romero, R. Ziessel, M. Bonnet, Y. Pontillan, E. Ressouche, J. Schweizer, B. Delley, A. Grand, C. Paulsen, *J. Am. Chem. Soc.* **2000**, *122*, 1298–1309. [14c] A. Zheludev, V. Barone, M. Bonnet, B. Delley, A. Grand, E. Ressouche, P. Rey, R. Subra, J. Schweizer, *J. Am. Chem. Soc.* **1994**, *116*, 2019–2027. [14d] A. Zheludev, M. Bonnet, E. Ressouche, J. Schweizer, M. Wan, H. Wang, *J. Magn. Magn. Mater.* **1994**, *135*, 147–160.

[15] A. Zheludev, M. Bonnet, B. Delley, A. Grand, D. Luneau, L. Örström, E. Ressouche, P. Rey, J. Schweizer, *J. Magn. Magn. Mater.* **1995**, *145*, 293–305.

[16] [16a] T. Suzuki, S. Kaizaki, K. Kashiwabara, *Inorg. Chim. Acta* **2000**, *298*, 131–140. [16b] T. Suzuki, M. Ogita, S. Kaizaki, *Acta Crystallogr., Sect. C* **2000**, *56*, 532–533.

[17] [17a] T. Suzuki, T. Imamura, S. Kaizaki, K. Kashiwabara, *Polyhedron*, in press. [17b] T. Ando, M. Kita, K. Kashiwabara, J. Fujita, S. Kurachi, S. Ohba, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2748–2755.

[18] E. F. Ullman, L. Call, J. H. Osiecki, *J. Org. Chem.* **1970**, *35*, 3623–3631.

[19] [19a] K. Katoh, H. Sugiura, K. Kashiwabara, J. Fujita, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3580–3586. [19b] K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, M. Shibata, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 149–155.

[20] T. Akita, Y. Mazaki, K. Kobayashi, N. Koga, H. Iwamura, *J. Org. Chem.* **1995**, *60*, 2092–2098.

[21] [21a] E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, R. Darcy, *J. Am. Chem. Soc.* **1972**, *94*, 7049–7059. [21b] J. N. Helbert, P. W. Kopt, E. H. Poindexter, B. E. Wagner, *J. Chem. Soc., Dalton Trans.* **1975**, 998–1006.

[22] M. S. Davis, K. Morokuma, R. W. Kreilick, *J. Am. Chem. Soc.* **1972**, *94*, 5588–5592.

[23] H. Heise, F. H. Köhler, F. Mota, J. J. Novoa, J. Veciana, *J. Am. Chem. Soc.* **1999**, *121*, 9659–9667.

[24] [24a] S. Yamanaka, T. Kawakami, S. Yamada, H. Nagao, M. Nakano, K. Yamaguchi, *Chem. Phys. Lett.* **1995**, *240*, 268–277. [24b] K. Yamaguchi, M. Okuyama, J. Maki, T. Noro, H. Namimoto, M. Nakano, T. Fueno, K. Nakasuji, *Chem. Phys. Lett.* **1992**, *190*, 353–360.

[25] T. Ohno, S. Kato, S. Kaizaki, I. Hanazaki, *Inorg. Chem.* **1986**, *25*, 3853–3858.

[26] [26a] M. Lamchen, T. W. Mittag, *J. Chem. Soc., C* **1966**, 2300–2303. [26b] J. H. Osiecki, E. F. Ullman, *J. Am. Chem. Soc.* **1968**, *90*, 1078–1079. [26c] G. Ulrich, R. Ziessel, *Tetrahedron Lett.* **1994**, *35*, 1215–1218. [26d] G. Ulrich, R. Ziessel, D. Luneau, P. Rey, *Tetrahedron Lett.* **1994**, *35*, 1211–1214.

[27] [27a] L. J. Boucher, J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.* **1965**, *27*, 1093–1097. [27b] L. J. Boucher, N. G. Paez, *Inorg. Chem.* **1970**, *9*, 418–421.

[28] R. H. Lee, E. Griswold, J. Kleinberg, *Inorg. Chem.* **1964**, *3*, 1278–1283.

[29] A. Yamazaki, *J. Coord. Chem.* **1991**, *24*, 211–260.

[30] [30a] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351–359. [30b] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473. [30c] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, **1997**. [30d] *teXsan*, Single Crystal Structure Analysis Software, Molecular Structure Corporation and Rigaku Corporation, MSC, The Woodlands, TX, USA, and Rigaku, Akishima, Tokyo, Japan, **1999**, ver. 1.10.

Received August 14, 2001
[I01309]