Accounts

Spectroscopic Implications for Magnetic Interactions in Metal Complexes with Nitroxide Radicals

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The influence of the magnetic interaction between a paramagnetic metal ion and a radical ligand upon the spectroscopic (UV-vis and/or NMR) properties will be described and discussed mainly for the mixed ligand complexes, M(L)(X) (M = Ni(II), Cr(III); L = nitroxide radicals such as NIT2py (2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl) or IM2py (2-(2-(pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy), X = β-diketonates). For the Ni(II) and Cr(III) complexes, the spin-forbidden d–d bands demonstrated some intensity enhancement and the charge transfer band from the d orbital to the SOMO π^* newly appeared in the visible region. Their variable temperature UV-vis spectra substantiated the antiferromagnetic and ferromagnetic interactions as revealed by the magnetic susceptibility measurements. The spectroscopic behaviors with variation of the β-diketonates is examined in connection with magnetic interaction constant J values, exhibiting the coligand effect, e.g., in terms of the exchange mechanism. For the Mn(II), Co(II), Ni(II), and Ln(III) complexes with the NIT2py and/or IM2py or their derivatives and for the Cr(III) and diamagnetic Co(III) complexes with monodentate NIT3- or 4py and IM3- or 4py, the spectroscopic properties are also found to be influenced to the d orbitals from the coordinated nitroxides.

The effects of the intramolecular interactions on the magnetic and spectroscopic (UV-vis, MCD, EPR, NMR) properties in spin-coupled systems such as multinuclear paramagnetic metal complexes or paramagnetic metal complexes with radical ligands have been investigated from the viewpoint of coordination chemistry focusing on biological to material sciences especially including ferromagnets or optical devices.[1–16] In biological systems, metalloproteins that contain polynuclear active sites consisting of copper, iron and manganese clusters show peculiar magnetic and spectroscopic properties.[13] Intensive studies on metal complexes with phenoxyl radicals have been concerned with some copper enzymes such as galactose oxidase, which provide a relevant interest in one electron oxidation centered on either metals or ligands.[14] From the viewpoint of molecular materials, the transition metal clusters or radical complexes give a clue to construct molecular magnets[1–8] and molecular switches including the spin-crossover phenomena.[17] Studies on optical spectra in the spin-exchange systems have been focused on the doped compounds as well as exchange coupled polynuclear or one-, two-dimensional complexes[2] and the dihydroxo bridge Cr–Cr dimers.[1,19] For example, $Mn^{II}Cu^{II}_3$ tetranuclear[16] and $[L_3Cr(OH)_3CrL_3]$ dimeric[19] complexes exhibit some fairly strong formally spin-forbidden absorption bands. The variable temperature measurements of the intensities of these bands made it possible to elucidate the exchange-coupled behavior. For the (phenoxyl)chromium(III) complexes,[14] the spin-forbidden bands are too intense irrespective of the coligands to evaluate the exchange coupling. However, there has been no relevant report on nitroxide radical complexes, for which magnetic properties have been extensively explored for the purpose of molecular magnets in terms of the so-called radical approach.[6,7,20–25] The nitroxide complexes with another advantage of the intermediate magnetic interaction over the phenoxyl complexes are expected to exert some appropriate coligand effect on the magneto-optical properties.

In addition to the magnetic interaction between the ground states in the spin-coupled systems, the excited state in the one moiety of the multi-spin systems is magnetically influenced from the ground state in the other one. Such intramolecular interactions give the spectroscopic deviation from the simple superposition of each moiety; one case is UV-vis spectra where "dimer bands" due to the charge transfer (CT) transitions newly appeared in Cu(II) and Fe(II) dinuclear complexes[13] and the other case is "intensity enhancement of the spin-forbidden d–d transitions" observed for the Mn(II)Cu(II) tetramers[16] or $[Cr_3(\mu\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]Cl$ trimer.[26] The latter case is analogous in an inverted sense to the intensity enhancement of the singlet-triplet transition of the diamagnetic organic ligand such as aromatic imines or acetylacetonate in the paramagnetic Cr(III) complexes[27,28] as well as that of pyridine under perturbation of dissolved paramagnetic dioxygen molecule.[29]

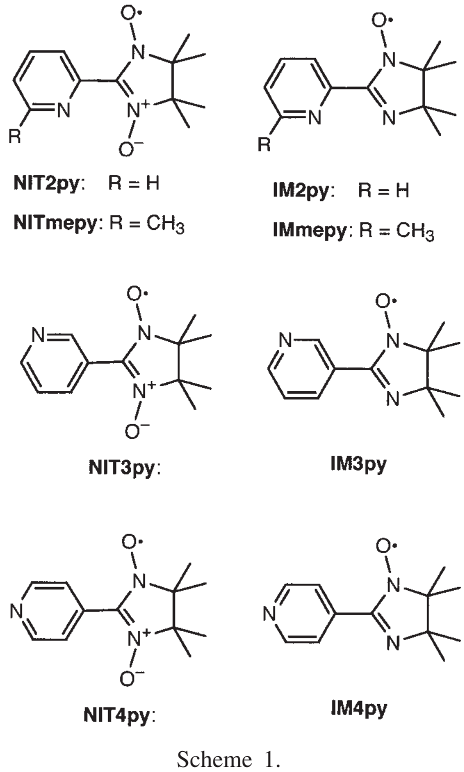
In the spin-forbidden d–d transitions of the dinuclear Cr(III) complexes, for instance, there are two cases: a single ion transition and a pair ion transition.[30] The former single ion case originates from the same borrowing mechanism as that for the mononuclear Cr(III) complexes; here the spin-forbidden $^4A_2$–^2E, $^2T_1$ transitions attain the intensity from the nearby spin-allowed $^4A_2$–$^4T_2$ transitions by the mixing of the $^4T_2$ state into the ^2E, $^2T_1$ states via the spin-orbit coupling. The latter pair ion case arises from the mixing of the CT state like "dimer bands"[13,31] with the ^2E, $^2T_1$ states, which gives the intensity enhancement. The intensity of the latter pair ion transition is generally much larger than that of the former single ion one with small mixing coefficients in the first transition metal series. This is because the spin coupling in the excited states for the pair ion transition makes the same spin multiplicity as the ground states. As a result, this leads to the formally spin-forbidden transition with the spin selection rule $\Delta S = 0$[16,18,19,26] through relatively large electron transfer integrals or orbital overlaps between the d orbital and the charge transferred ligand orbital.

On the other hand, the configurational interaction between the ground coupled levels and the CT levels results in the antiferromagnetic or ferromagnetic properties; in other words, the interaction reveals the direct mechanism, as exemplified for the metal-metal CT in polynuclear complexes by Anderson.[32] This description is equivalent to the consideration in terms of the Valence Bond Configurational Interaction (VBCI) model through the LMCT and/or metal-metal transitions developed by Solomon et al.[13,31] Recently, Güdel and Weihe[33] have claimed to elucidate the ferromagnetic interaction in terms of the kinetic exchange by applying the VBCI to the hydroxo bridged Cr(III) dinuclear complexes through taking consideration of the CT to the bridging moiety from the metal centers, in contradiction to the Anderson's earlier concept.[32]

So far, there have been only independent approaches to the spectroscopic differences from the superposition of the spin-coupled units, e.g., the newly appeared CT or the intensity enhancement of the spin-forbidden d–d transitions in this kind of complexes, but no example for the systematic examination in terms of their simultaneous observation, with the exception of only a few cases to which the proposed theoretical formulation were applied.[19] In this view, if there were available the nitroxide radical complexes, M(L)(X) (M = Cr(III) or Ni(II): L = NIT2py (2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl) or IM2py (2-(2-(pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy: X = β-diketonates), they would allow us to examine the coligand effect on the magnetic and spectroscopic properties. This is because they may give new CT and spin-forbidden transition intensity enhancement as well as intermediate intramolecular magnetic interactions, as expected from the corresponding (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel(II) complexes.[21a,24]

Apart from the optical spectra, the magnetic interactive contributions in the multi-spin coupled systems has been studied using magnetic resonance spectra from physical and biochemical viewpoints.[9–12,34,35] A number of studies on EPR spectra in multi-spin systems for paramagnetic transition metal ions with organic radicals[12,34] or polynuclear structures[12] have been extensively reviewed. In contrast, though NMR investigations for such dinuclear paramagnetic metal complexes have also been widely carried out, there have been no NMR study on the coligand effect in radical complexes. For radical nickel(II) complexes, the chemical shifts of the diamagnetic coligands would be influenced by exchange coupling with the radical spin as is true for the paramagnetic or diamagnetic metal ions. Therefore, such changes in chemical shift could be assessed by applying the theoretical formulation for the spin coupled NMR contact shifts, which are expressed through the uncoupled contact shifts for each constituent metal ions.[10,11,35] This is expected to be quite informative thanks to the coligand effect.

In these circumstances, the examinations of UV-vis spectra and NMR contact shifts in conjunction with magnetic exchange coupling constants are invaluable to acquire fundamental insights into the influences to the ground and/or excited state from the magnetic interactions between metal ions and radical ligands. From these aspects, the author's group has recently investigated systematically the magnetic and spectroscopic properties[36–50] for a series of the transition metal complexes as well as for the lanthanide complexes with nitroxide radical ligands; these are the chelated NIT2py or IM2py and NITmepy (4,4,5,5-tetramethyl-2-(6-methyl-2-pyridyl)imidazolin-1-oxyl 3-oxide) and IMmepy-(4,4,5,5-tetramethyl-2-(6-methyl-2-pyridyl)imidazolin-1-oxyl); the monodentate NIT3- or 4py (4,4,5,5-tetramethyl-2-(3- or 4-pyridyl)imidazolin-1-oxyl 3-oxide) or IMpy3- or 4py (4,4,5,5-tetramethyl-2-(3- or 4-pyridyl)imidazolin-1-oxyl) as shown in Scheme 1. Three series[37,45] of Ni(II) complexes were synthesized; these are [Ni(β-diketonato)$_2$(NIT2py or IM2py)] and [Ni(β-diketonato)(tmen)(NIT2py)]$^+$(tmen = N,N'-tetramethylethylenediamine), a pair of linkage isomers (κ-N and κ-O)[50] of [Ni(acac)(tmen)(IM2py)]$^+$ and two series of Cr(III) complexes, [Cr(β-diketonato)$_2$(NIT2py[41] or IM2py[45])]$^+$, where the β-diketones are Hacac (2,4-pentanedione), Hdbm (1,3-diphenyl-1,3-propanedione), Hbzac (1-phenyl-1,3-butanedione), HacaMe (3-methyl-2,4-pentanedione), HacaEt (3-ethyl-2,4-pentanedione), Haca^{n}Bu(3-*n*-buthyl-2,4-pentanedione), HacaPh (3-phenyl-2,4-



Scheme 1.

pentanedione), Hdpm (2,2,6,6-tetramethyl-3,5-heptanedione), HMehp (6-methyl-2,4-heptanedione), HacaPh (3-phenyl-2,4-pentanedione), Hhfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), Htfac (1,1,1-trifluoro-2,4-pentanedione) as shown in Table 1. *cis*(Cl)-*trans*(py)-$[MCl_2(IM2py)_2]$ (M(Ⅱ) = Mn,Co,Ni,Zn),[39] $[Ln(hfac)_3(IM2py)]$[44,47,48] (*T*-4)-$[MCl_2$(NITmepy or IMmepy)] (M(Ⅱ) = Co,Ni,Zn),[40] and the Cr(Ⅲ) complexes[46] of *cis*-[CrCl$(acac)_2$(NITnpy or IMnpy)], *cis*- and *trans*-[Cr$(acac)_2$(NITnpy or IMnpy$)_2]^+$ and the Co(Ⅲ) complexes[42] of [Co$(acac)_2$(NO_2 or PPh_3)(NITnpy or IMnpy)$]^{n+}$ ($n = 3$ and 4) were also described and discussed.

In this Account, the influence of the intramolecular interaction for these nitroxide complexes will be reviewed in three chapters; Magnetic Properties, UV-vis Absorption Spectra, and NMR Behavior.

Magnetic Properties

1) General Trend. The magnetic properties of various kinds of transition metal and lanthanide complexes were examined by the temperature dependent magnetic susceptibilities. As have been revealed for the mono-NIT2py[21a] and IM2py[24] complexes with the corresponding hfac, the magnetic interactions in $[Ni(acac)_2(NIT2py)]$, $[Ni(acac)(tmen)(NIT2py)]^+$ and $[Ni(acac)_2(IM2py)]$, [Ni(acac)(tmen)(IM2py*κ*-N)$]^+$ are antiferromagnetic and ferromagnetic, respectively (Table 1). Very recently, we succeeded in isolating two linkage isomers for the (tmen)(IM2py) complex and found that the magnetic interactions in the five-membered IM2py*κ*-N and the six-membered IM2py*κ*-O Ni(Ⅱ) complexes are ferromagnetic and antiferromagnetic, respectively, confirming the importance of the orthogonality or overlap of the magnetic orbitals.[50] It was found for the first time that both $[Cr(acac)_2(NIT2py)]^+$ and $[Cr(acac)_2(IM2py)]^+$ show antiferromagnetic interaction (Table 1) in accordance with the prediction on the basis of the orthogonality between metal d(t_{2g}) and radical SOMO π^* magnetic orbitals.[45] For the monodentate IMnpy and NITnpy Cr(Ⅲ) complexes, *cis*-[CrCl$(acac)_2$(NITnpy or IMnpy)] and *cis*- and *trans*-[Cr$(acac)_2$(NITnpy or IMnpy$)_2$] are antiferromagnetic for $n = 3$ and ferromagnetic for $n = 4$.[46] This is a reverse situation to the 3- and 4-(*N*-oxy-*N*-*tert*-butylamino)pyridine Cr(Ⅲ) complexes, [Cr(TPP or TAP)Cl(3- or 4NOpy)],[51] which are ferromagnetic for $n = 3$ and antiferromagnetic for $n = 4$. The absolute values for the magnetic interaction constants for the NITnpy complexes are found to be ca. 1–6 cm^{-1}, an order of magnitude smaller than those of the *n*NOpy complexes. The sign and magnitude of *J* values reflect the differences in the number of the intervening atoms between the Cr(Ⅲ) and the radical moiety and can be interpreted by a spin polarization mechanism. The bis(IM2py) complexes *cis*(Cl)-*trans*(py)-$[MCl_2(IM2py)]$ are antiferromagnetic for Mn^{II}, and ferromagnetic for Co^{II} and Ni^{II}, as confirmed by the variable temperature absorption spectra (vide infra).[39] Both (*T*-4)-$[CoCl_2$(NIT2py or IM2py)] complexes even with the analogous ligand field ground state ($^4A_2$) to (*OC*-6)-Cr(Ⅲ) complexes show an antiferromagnetic interaction.[40] The magnetic interaction in $[Gd^{III}(hfac)_3(IM2py)]$[44] is antiferromagnetic as found for the other radical-Gd complexes,[52] irrespective of the confidence that Gd^{III}–Cu^{II}[53] or Gd^{III}(NIT-radical$)_2$[54] interactions are intrinsically ferromagnetic. For a series of the former lanthanide(Ⅲ) complexes $[Ln(hfac)_3(IM2py)]$, the products of the magnetic susceptibilities and the temperature in comparison with those of the corresponding nonradical $[Ln(hfac)_3(pybzim)]$ (pybzim = 2-(2-pyridyl)-benzimidazole) complexes were examined, in terms of Kahn's

Table 1. Magnetic and Optical data of the NIT2py or IM2py Ni(Ⅱ) and Cr(Ⅲ) complexes

	Compounds	J_{obsd} (g)[a)]	ε_{SF}[b)]	ε_{CT}[c)]	E_{CT}[d)]	ΔE_{CT}[e)]	$(\varepsilon_{SF}/\varepsilon_{CT})(\Delta E_{CT})^2/(E_{CT})$[f)]
1a	$[Ni(acac)_2(NIT2py)]$	−219.4 (2.34)	448	887	16.2	3.2	0.325
2a	$[Ni(bzac)_2(NIT2py)]$	−223.8 (2.38)	465	870	16.1	3.1	0.319
3a	$[Ni(dbm)_2(NIT2py)]$	−206.5 (2.06)	472	894	16.1	3.1	0.315
4a	$[Ni(tfac)_2(NIT2py)]$	−207.6 (2.24)	258	583	16.3	3.1	0.261
5a	$[Ni(hfac)_2(NIT2py)]$	−167.0 (2.27)	111	417	16.2	3.0	0.148
1b	$[Ni(acac)_2(IM2py)]$	41.2 (2.12)	11.6	107	17.0	4.32	0.119
2b	$[Ni(dbm)_2(IM2py)]$	0.397 (2.13)	8.91	79.9	17.1	4.34	0.123
3b	$[Ni(tfac)_2(IM2py)]$	95.3 (2.15)	4.86	44.9	17.5	4.64	0.133
4b	$[Ni(hfac)_2(IM2py)]$	71.2 (2.13)	4.92	43.9	17.3	4.46	0.129
1c	$[Cr(acac)_2(NIT2py)]PF_6$	−61.6 (2.00)	327	641	17.3	4.00	0.472
2c	$[Cr(dbm)_2(NIT2py)]PF_6$	−70.0 (2.00)	325	648	17.3	4.05	0.475
3c	$[Cr(bzac)_2(NIT2py)]PF_6$	−30.2 (2.01)	285	589	17.3	4.00	0.447
4c	$[Cr(acaMe)_2(NIT2py)]PF_6$	−9.05 (2.06)	230	504	17.1	4.01	0.429
5c	$[Cr(acaEt)_2(NIT2py)]PF_6$	−36.5 (2.02)	265	536	17.2	4.07	0.477
6c	$[Cr(aca^nBu)_2(NIT2py)]PF_6$	−12.3 (2.01)	279	567	17.1	4.01	0.462
7c	$[Cr(acaPh)_2(NIT2py)]PF_6$	−19.4 (2.02)	234	479	17.2	4.03	0.460
8c	$[Cr(dpm)_2(NIT2py)]PF_6$	−98.6 (2.00)	346	631	17.3	3.97	0.500
9c	$[Cr(Mehp)_2(NIT2py)]PF_6$	−49.0 (2.00)	337	660	17.3	4.02	0.478
1d	$[Cr(acac)_2(IM2py)]PF_6$	−188 (2.01)	146	923	19.1	4.96	0.203
2d	$[Cr(dbm)_2(IM2py)]PF_6$	−96.4 (2.05)	160	1044	19.2	5.13	0.210
3d	$[Cr(acaMe)_2(IM2py)]PF_6$	−102 (2.03)	191	1367	19.6	5.80	0.241
4d	$[Cr(acaPh)_2(IM2py)]PF_6$	−119 (2.01)	184	1160	19.6	5.60	0.255

a) Obserbed ***J*** values/cm^{-1}. b) and c) Molar absorption coefficient for the spin-forbidden and MLCT transition, respectively/mol^{-1} dm^3 cm^{-1}. d) MLCT transition energy/10^3 cm^{-1}. e) The energy difference between the spin-forbidden and MLCT transition/10^3 cm^{-1}. f) Eq. 3 $\propto \boldsymbol{J}_{AF}/10^3$ cm^{-1}. **1a** – **5a** in Ref. 37; **1b** – **4b** in Ref. 45; **1c** – **9c** in Ref. 41; **1d** – **4d** in Ref. 45.

approach,[53,54] e.g., $\Delta\chi_M{}^{\mathrm{Ln}}T = \chi_M{}^{\mathrm{Ln}}T$ (IM2py) $-$ $\chi_M{}^{\mathrm{Ln}}T$ (pybzim), Results demonstrated that the Ln(Ⅲ) complexes with 4f^n electrons show ferromagnetic interaction for $n < 7$ and antiferromagnetic interaction for $n > 7$, respectively.[47] This fact confirms applicability of Kahn's approach to the present simpler $\mathrm{Ln^{III}}$(IM2py) complexes in an exactly reverse situation to that found for the Ln–Cu[53] and [Ln(NitTRZ)$_2$(NO$_3$)$_3$][54a] complexes. The Kahn's approach was examined by the quantitative analysis to reveal a significant intramolecular magnetic interaction between the NIT radicals.[54b,54c] Recently, the antiferromagnetic interaction between the NIT radical and Gd(Ⅲ) were claimed due to the structural and ligand effects.[55] The review on the magnetisms characteristics of Ln complexes[56] was published.

2) Variation of Magnetic Interaction with β-Diketonate Ligands. In the course of the magnetic study on several metal complexes with NIT2py and IM2py radicals made from the viewpoint of molecular magnetism in terms of the so-called radical approach,[6,7,20–25] the coligands were always hexafluoroacetylacetonate in view of the strong Lewis acid around metal centers. Thus NIT derivatives as weak Lewis bases are more susceptible to coordination through an NIT N–O oxygen. Therefore, the magnetic properties were compared only among different types of complexes so far, but not examined in terms of the coligand effect for the same type. For chelated NIT2py or IM2py radical metal complexes with various kinds of β-diketonates as shown in Table 1, variation of β-diketonato coligands could afford modification of the Lewis acidity of a metal ion center, which would provide invaluable information not only on the spectroscopic behavior, our main interest, but also on the magnetic interactions between a paramagnetic metal ion and NIT2py or IM2py.

The magnetic coupling constants J between a nickel(Ⅱ) or chromium(Ⅲ) ion and NIT2py or IM2py obtained by fitting the magnetic susceptibilities to a two spin system ($S_1 = 1$ or 3/2 and $S_2 = 1/2$) are summarized in Table 1: $J_{\mathrm{obs}} = -207$ to -224 cm^{-1} for the bis(β-diketonato)(NIT2py)nickel(Ⅱ) complexes; $J_{\mathrm{obs}} = +0.400$ to $+95.3$ cm^{-1} for the bis(β-diketonato)(IM2py)nickel(Ⅱ) complexes; $J_{\mathrm{obs}} = -35$ to -150 cm^{-1} for the (β-diketonato)(tmen)(NIT2py)nickel(Ⅱ) complexes; $J_{\mathrm{obsd}} = -9.05$ to -98.6 cm^{-1} and -96.4 to -188 cm^{-1} for the NIT2py and IM2py Cr(Ⅲ) complexes, respectively. Observation of such a large range of the J values for the Ni(Ⅱ) and Cr(Ⅲ) complexes with various kinds of the β-diketonates prompts us to evaluate the substituent effect or how the J values are influenced by variation of the β-diketonate coligands. The $\mathrm{Ni^{II}}$(NIT2py) complexes give a linear relation between the J_{obsd} values and the sum of the Hammett constants for the substituents in the β-diketonates,[37] whereas the J_{obsd} values for the $\mathrm{Ni^{II}}$(IM2py),[45] $\mathrm{Cr^{III}}$(NIT2py)[41] and $\mathrm{Cr^{III}}$(IM2py)[45] complexes are fairly well related with the acid dissociation constants K_a of the β-diketones; increasing the J_{obsd} values with increasing K_a. This subject will be discussed in more detail in correlation with the spectroscopic behavior in the following section.

UV-Vis Absorption Spectra

1) Near-Infrared Absorption Spectra: Spin-Allowed d–d Transitions. For each two series of the NIT2py or IM2py complexes [Ni(β-diketonato)$_2$(NIT2py or IM2py)] and [Ni(β-diketonato)(tmen)(NIT2py)]$^+$ (Figs. 1–3), the first spin-allowed d–d transition bands of ($^3A_2 \rightarrow {}^3T_2$) around 10×10^3 cm^{-1} are not influenced by coordination of the nitroxide radicals from similarity in position and intensity to those of [Ni(β-diketonato)$_2$(tmen)] or [Ni(β-diketonato)(NO$_3$)(tmen)]. The absorption bands of the bis(β-diketonato)(NIT2py) complexes are always located at the lower frequency than those of the $\mathrm{Ni^{II}}$-(tmen)(NIT2py) complexes, as expected from the spectrochemical series. [Ni(β-diketonato)$_2$(IM2py-kN)] and [Ni(β-

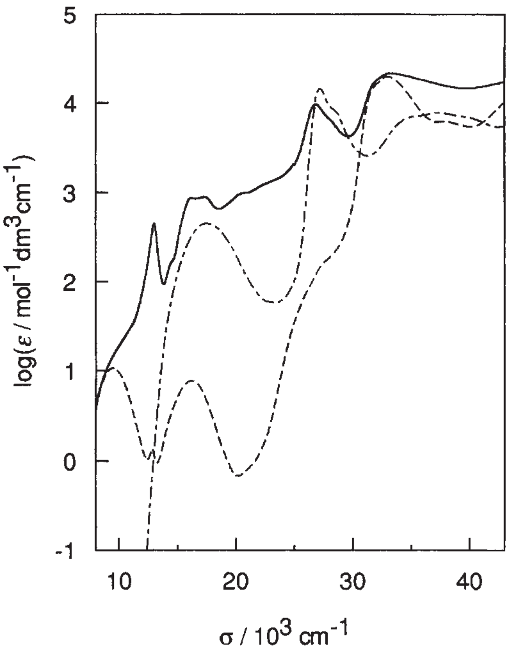


Fig. 1. Absorption spectra of [Ni(acac)$_2$(NIT2-py)] (——), [Ni(acac)$_2$(tmen)] (- - -), and NIT2-py (– – – – –) in CH$_2$Cl$_2$ (Ref. 37).

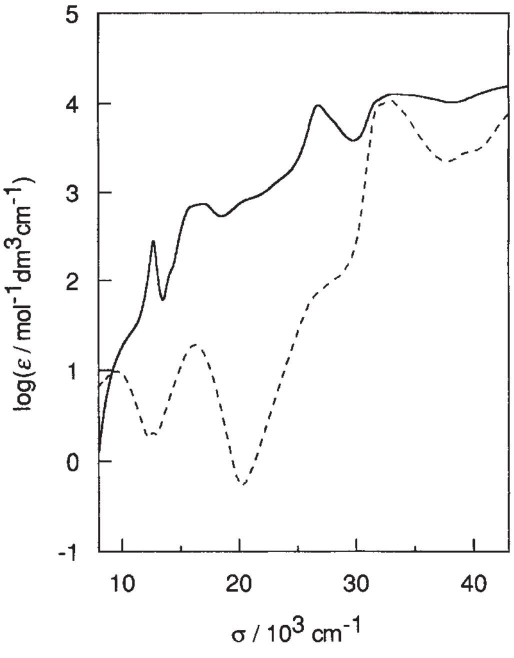


Fig. 2. Absorption spectra of [Ni(acac)(tmen)(NIT2-py)]PF$_6$ (——) and [Ni(acac)(NO$_3$)(tmen)] (- - -) in CH$_2$Cl$_2$ (Ref. 37).

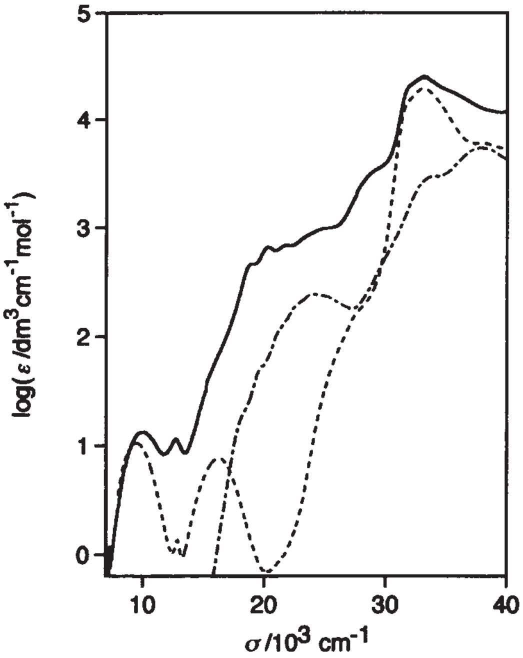


Fig. 3. Absorption spectra of [Ni(acac)$_2$(IM2py)] (——), [Ni(acac)$_2$(tmen)] (---------), IM2py (– – – – –) in CH_2Cl_2 at room temperature (Ref. 45).

diketonato)(tmen)(IM2py)]$^+$ give the lower frequency spin-allowed bands than the corresponding NIT2py complexes,[45,50] indicating that the ligand field of the IM2py is stronger than that of the NIT2py. A similar situation is also seen for (T-4)-[CoCl$_2$(NITmepy)] and -[CoCl$_2$(IMmepy)] complexes;[40] the $^4A_2$–$^4T_{1a}$ transition component for the IMmepy complex is located at the higher energy than the corresponding one for the NITmepy complex. Thus, the ligand-field of IMmepy via imino-N donor is stronger than NIT via nitroxide-O donor.

It is interesting to examine the variable temperature absorption spectra for the following bis(IM2py) complex. Of two weak NIR bands of *cis*(Cl)-*trans*(py)-[NiCl$_2$(IM2py)$_2$],[39] the lower energy band at 9670 cm^{-1} accompanied by a higher energy broad shoulder is assigned as the first spin-allowed ($^3A_2 \rightarrow {}^3T_2$) band. The temperature-dependence of this band gives some information about the magnetic interaction (J^*) at the $^3T_2$ excited state of Ni(II). The band position shows a significant blue-shift (by more than 450 cm^{-1}) and increases the band intensity by almost 1.5 times as the temperature decreases from 300 to 200 K. This larger blue-shift arises probably from the weaker ferromagnetic (or antiferromagnetic) interaction at the $^3T_2$ excited state as compared to that at the $^3A_2$ ground state. In such a situation, the spin-allowed quintet–quintet transition requires higher energy than the triplet–triplet or singlet–singlet transition, and the intensity of the quintet–quintet transition becomes larger at lower temperature in view of the ferromagnetic interaction in the ground state. This is not an unlikely assumption, since the magnetic coupling with two IM2py and an unpaired d-electron in each of the dσ(e$_g$) and dπ(t$_{2g}$) orbitals for the $^3T_2$ excited state would lead to some reduction of the ferromagnetic interaction and conversely to a new appearance of the antiferromagnetic one, respectively.

2) Visible Absorption Spectra: Charge-Transfer Transitions. In the energy regions corresponding to the n-π^* intraligand transitions of NIT2py or the second spin-allowed $^3A_2 \rightarrow {}^3T_1$ band for the nonradical Ni(II) complexes or the first spin-allowed $^4A_2 \rightarrow {}^4T_2$ band for the nonradical Cr(III) complexes, the visible absorption spectra of [Ni(β-diketonato)$_2$(NIT2py)], [Ni(β-diketonato)(tmen)(NIT2py)]$^+$ and [Cr(β-diketonato)$_2$-(NIT2py)]$^+$ at 16.0–19.0 × 10^3 cm^{-1} give different characteristics from those of the ligand itself and the nonradical complexes as shown in Figs. 1–2 and 4. A few components were observed with spacing of about 2000 cm^{-1} as a peak or a shoulder. Their intensities are much larger and the band widths are narrower than those of the ligand itself and of the nonradical complexes. The molar absorption coefficients in this region are found to be influenced by kinds of the substituent groups of the β-diketonato coligands (Table 1). For the IM2py complexes, on the other hand, new absorption shoulders are observed around 19.0–21.0 × 10^3 cm^{-1} for the Cr(III) complexes and around 17.0–18.0 × 10^3 cm^{-1} for the Ni(II) complexes (Figs. 3 and 5).

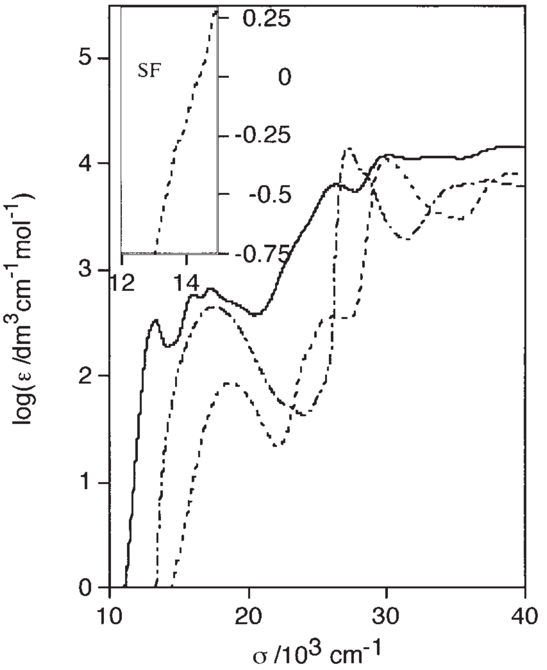


Fig. 4. Absorption spectra of [Cr(acac)$_2$(NIT2-py)]PF$_6$ (——), [Cr(acac)$_2$(en)]PF$_6$ (--------), NIT2-py (– – – – –) in CH_3CN at room temperature. Inset: Enlarged absorption curve with the logarithmic ordinate of [Cr(acac)$_2$(en)]PF$_6$ (--------) in CH_3CN at room temperature (Ref. 41).

The Raman spectra on resonance with these components in the corresponding region of the Ni^{II}(NIT2py or IM2py) and Cr^{III}(NIT2py or IM2py) complexes in solid state demonstrated significant intensity enhancements, especially for the bands due to the N–O stretching vibrations of the O–N=C moiety (around 1520 and 1468 cm^{-1} in the NIT2py and 1545 and 1480 cm^{-1} in the IM2py) and for those due to the M–O,N stretching(from 614 to 660 cm^{-1} in the NIT2py complexes) and due to the M–N,N one (340 cm^{-1} and 630 cm^{-1} of the Cr^{III}(IM2py) and 255 cm^{-1} of the Ni^{II}(IM2py)). Accordingly, these visible absorption bands or shoulders may be assigned to the CT transitions as supported by variable temperature UV-vis spectra as below. These CT bands are probably due to the metal-to-ligand SOMO π^* (MLCT) transition as suggested by the blue shift in more polar solvents.

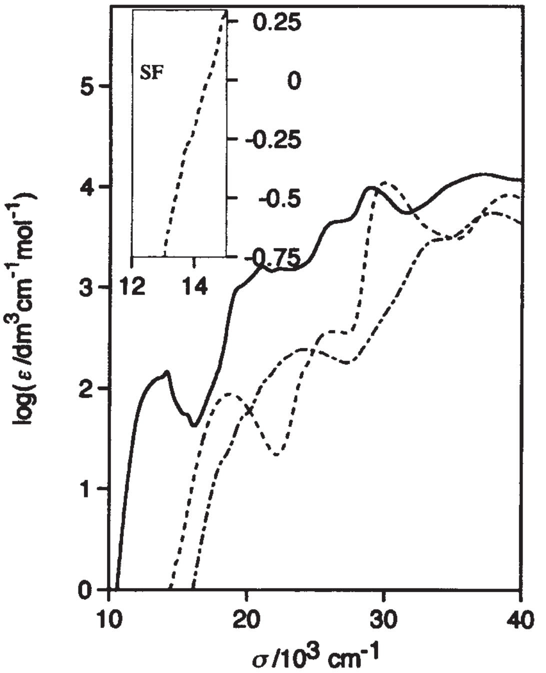


Fig. 5. Absorption spectra of [Cr(acac)$_2$(IM2py)]PF$_6$ (——), [Cr(acac)$_2$(en)]PF$_6$ (- - - - - - - -), IM2py (– – – – –) in CH$_3$CN at room temperature. Inset: Enlarged absorption curve with the logarithmic ordinate of [Cr(acac)$_2$(en)]PF$_6$ (- - - - - - - -) in CH$_3$CN at room temperature (Ref. 45).

The MLCT intensities of the $\mathrm{Ni^{II}}$(IM2py) complexes are much weaker than those of the $\mathrm{Ni^{II}}$(NIT2py) complexes. This is due to the depopulation of the doublet ground state for the ferromagnetically coupled $\mathrm{Ni^{II}}$(IM2py) complex as supported by the absorption band intensity decrease on lowering the temperature. This suggests that the MLCT is not a quartet (t_{2g}-π^*), but a doublet (e_g-π^*), similarly to the $\mathrm{Ni^{II}}$(NIT2py) complexes as shown from the energy level diagram in Fig. 6. The absorption intensity enhancement on lowering the temperature for [Cr(acac)$_2$(NIT2py)]$^+$ substantiates the rigorous assignment to the triplet–triplet metal t_{2g}-to-ligand SOMO π^* (MLCT) transition (Fig. 7). This is also supported by the blue shift in more polar solvents.

The Co(II) and Ni(II) complexes of [MCl$_2$(IM2py)$_2$] type gave a shoulder around 15000 and 16000 cm^{-1}, respectively. The intensity of each shoulder became weaker on cooling. This fact leads to the spin-allowed transition from the depopulated next-lowest ground quintet ($\mathrm{Co^{II}}$) and triplet ($\mathrm{Ni^{II}}$) state to the excited quintet ($\mathrm{Co^{II}}$) and triplet ($\mathrm{Ni^{II}}$) CT state or from dσ($\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$) to IM2py SOMO: π^*(N–O) CT, but the transition from the lowest sextet ($\mathrm{Co^{II}}$) and quintet ($\mathrm{Ni^{II}}$) state remains spin-forbidden. These results substantiate the ferromagnetic interaction as inferred from the magnetic susceptibility measurements. In contrast to the Ni(II) and Co(II) complexes, increase in the broad band intensity of the corresponding Mn(II) complex at 15710 cm^{-1} on cooling is in agreement with the antiferromagnetic interaction between Mn(II) and IM2py as demonstrated by the magnetic susceptibility measurements.

3) The Spin-Forbidden d–d Transitions. For the intensity enhancements of the spin-forbidden transitions characteristic of spin exchange coupled systems, the exchange mechanism[30] is exerted, where a pair ion transition is more effective than a single ion one. In the latter case for Cr(III) complexes, the spin-forbidden transition intensities are generally found to be only about 1% of the spin-allowed one estimated by an order of magnitude for $(\zeta/\Delta E)^2$ where ζ is the spin-orbit coupling constant for Cr(III) ion and ΔE the energy difference between the ^{2}E, ^{2}T$_1$ and ^{4}T$_2$ excited states. The intensity borrowing mechanism based on the double group theoretical correlations between the Kramers doublets in the doublet and quartet excited states (i.e., $E_{1/2}(^4A_2) \rightarrow (E_{1/2}(^2E) + \alpha(\zeta/\Delta E)E_{1/2}(^4T_2))$ gives the selection rule, which has been

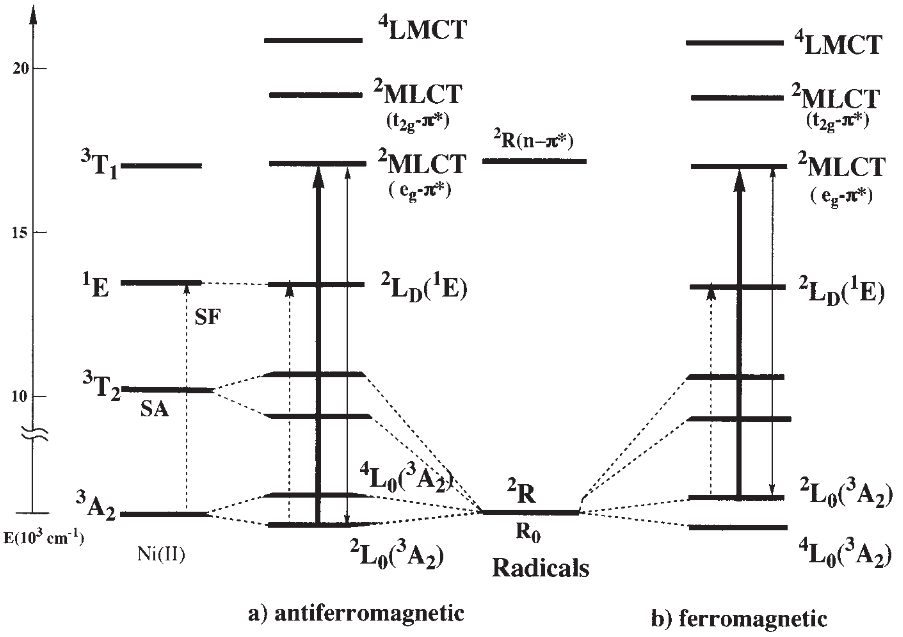


Fig. 6. Energy levels of the spin-allowed and spin-forbidden d–d transitions in the β-diketonato Ni(II) complexes with NIT2-py(a) and IM2py (b). (⟶) spin-allowed absorption; (⋯⋯→) spin-forbidden absorption; (⟷) configurational interactions between the ground and CT states with the same spin multiplicity.

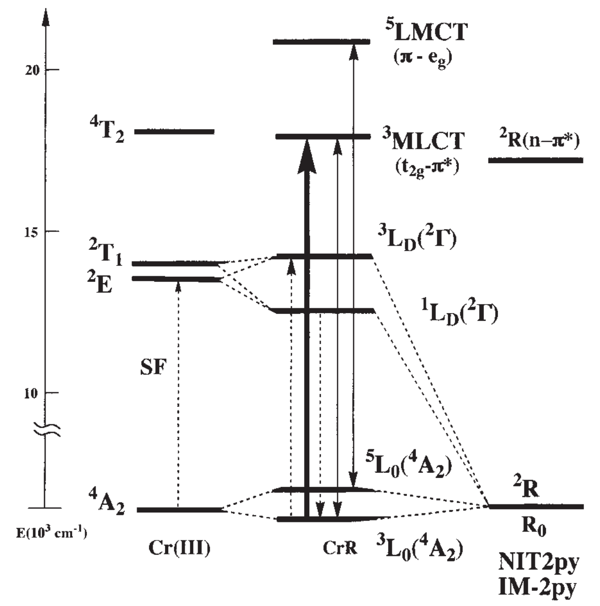


Fig. 7. Energy levels of the spin-allowed and spin-forbidden d–d transition in the β-diketonato Cr(III) complexes with NIT2-py and IM2py. (⟶) spin-allowed; (┈┈▸) spin-forbidden absorption and emission; (⟷) configurational interactions between the ground and CT states with the same spin multiplicity (Ref. 45).

substantiated experimentally and theoretically through the single crystal polarized or Zeeman spectra in the spin-forbidden transitions for ruby and chromium alums by Sugano, Tanabe, and Tsujikawa[57] and through solution circular dichroism (CD) for optically active trigonal tris(diamine) and tetragonal bis(diamine) chromium(III) complexes by the author.[58]

For the pair ion transition case, the magnetic interaction between the $^4A_2$ ground state in one ion and the ^2E or $^2T_1$ excited states in the other ion results in the common spin multiplets ($^4A_2{}^2E$ or $^4A_2{}^2T_1$ making triplet and quintet levels) with the coupled ground state ($^4A_2{}^4A_2$ making singlet, triplet and quintet levels), thus breaking down the $\Delta S = 0$ restriction by which the quartet–doublet spin-forbidden transitions become spin-allowed for the coupled triplet–triplet and quintet–quintet transitions. The combined measurements of the absorption and emission spectra provide information about the magnetic interaction in the excited state. On the other hand, strongly spin-coupled extremes have been known for the Cr(III) semiquinone or phenoxyl radical complexes[14a,c,20] which have demonstrated large intensity enhancements of the spin forbidden d–d transitions. In these cases, the magnetic interactions are so strong (more than 400 cm^{-1}) that they give temperature-independent magnetic moments. The intensities ($\varepsilon \sim 10^3$ $\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$) in the spin-forbidden transitions for this kind of Cr(III) complexes were too large to receive significant influence from the coligands. In the Ni^{II}(NIT2py or IM2py) and Cr^{III}(NIT2py or IM2py) complexes, on the other hand, the magnetic interactions are found to be in a range from 1 to 100 cm^{-1} as shown in Table 1. Such a moderately spin-coupled system is expected to give some quantitative relations between the intensity enhancement and the magnetic exchange interaction, which have seldom been examined with variation of the coligands so far. For this purpose, systematic comparisons for the spin-forbidden transitions of Ni^{II}(NIT2py), Ni^{II}(IM2py), Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes with various kinds of β-diketonato coligands are made as follows.

3-1) Ni(II) Complexes: For the NIT2py[37] and IM2py[45] complexes of the types of [Ni(β-diketonato)$_2$(NIT2py or IM2py)] and [Ni(β-diketonato)(tmen)(NIT2py)]$^+$, intense bands around 13.0×10^3 cm^{-1} are observed in the region corresponding to the spin-forbidden $^3A_2 \rightarrow {}^1E$ transition of Ni(II) in [Ni(β-diketonato)$_2$(tmen)] (Figs. 1–3). These band intensities of the Ni^{II}(NIT2py) complexes are significantly enhanced by about 100 – 350 times as compared with those of the corresponding nonradical complexes. MCD(magnetic circular dichroism) bands around 13.0×10^3 cm^{-1} of the NIT2py complexes are almost the same in position and bandwidth as those of the nonradical Ni(II) complexes, but the intensities ($\Delta\varepsilon_M$) are larger by several times than those of the nonradical complexes. Accordingly, such MCD behavior suggests that the absorption bands around 13.0×10^3 cm^{-1} of the NIT2py complexes originate from the spin-forbidden $^3A_2 \rightarrow {}^1E$ transition of Ni(II). For [Ni(β-diketonato)$_2$(IM2py)], the absorption intensity in the spin-forbidden $^3A_2 \rightarrow {}^1E$ transition around 13×10^3 cm^{-1} was enhanced by more than ten times as compared with those of the nonradical complex [Ni(acac)$_2$-(tmen)] as shown in Fig. 3. As compared with the Ni^{II}(NIT2py) complexes, the intensity of the $^3A_2 \rightarrow {}^1E$ transition for the Ni^{II}(IM2py) complexes were much smaller. The large difference (ε_{SF}(IM2py) = 4.86–11.6 versus ε_{SF}(NIT) = 111–465) between two series reflects the difference in magnetic interaction.

The remarkable spectral behavior around 13.0×10^3 cm^{-1} in the Ni^{II}(NIT2py or IM2py) complexes results from the exchange interaction between a paramagnetic nickel(II) ion and the NIT2py or IM2py radical as discussed for semiquinone Cr(III) complexes.[20] The exchange coupled ground state $^3A_2{}^2L_0$ consists of the doublet and quartet, whereas the excited state $^1E^2L_0$ generates only the doublet as shown in Fig. 6. Therefore, the triplet-singlet spin-forbidden transitions become formally spin-forbidden or actually spin-allowed between the exchange coupled doublets as a result of the breakdown of the $\Delta S = 0$ restriction. This assignment is supported by enhancement and diminution in the absorption band intensity with lowering the temperature, which results from the Boltzmann population and depopulation of the doublet level in the ground state, respectively, for the Ni^{II}(NIT2py) and Ni^{II}(IM2py) complexes. This is in accordance with the antiferromagnetic and ferromagnetic interaction observed by the magnetic susceptibility measurements as mentioned above. The different tendencies of the magnetic and the spectroscopic properties between the Ni^{II}(NIT2py) and Ni^{II}(IM2py) complexes with variation of the β-diketonates are elucidated in terms of the exchange mechanism for the intensity enhancement in the formally spin-forbidden transition region.

3-2) Cr(III) Complexes: For the radical complexes [Cr(β-diketonato)$_2$(NIT2py)]$^{+}$[41] and [Cr(β-diketonato)$_2$(IM2py)]$^+$,[45] the absorption peaks around 13.3×10^3 cm^{-1} and 14×10^3 cm^{-1} were intensified, respectively, by several hundred times compared with those in the corresponding region of the nonradical Cr(III) complex, [Cr(acac)$_2$(en)]$^+$, as shown in Figs. 4 and 5. The MCD sign in this region is similar to that of [Cr(acac)$_2$(en)]$^+$, though their intensities were different from each other along with small peak shifts. The CD peaks of the Cr^{III}(en) complex were observed in the same region as for the near infrared band of the NIT complexes.[58a] These facts indicate that they originate from the spin-forbidden $^4A \rightarrow {}^2E$, ^2T transitions of Cr(Ⅲ). Such enormous enhancement in the spin-forbidden transition intensity is ascribed to the exchange coupling between the Cr^{3+} and the NIT2py or IM2py radical. However, the extent of the enhancement is much smaller as compared with the strong coupling case for the semiquinone and phonoxyl radical complexes.[14a,c,20] Such less enhanced intensities are inferred from the moderate magnetic couplings.

The exchange coupled ground quartet state consists of the triplet $^3L_0(^4A_2)$ and quintet $^5L_0(^4A_2)$ states, whereas the excited doublet state $^2\Gamma$ ($\Gamma = E$ and/or T_1) generates the triplet $^3L_D(^2\Gamma)$ and singlet $^1L_D(^2\Gamma)$ states as shown in Fig. 7. Therefore, the quartet–doublet spin-forbidden d–d transitions of $[\mathrm{Cr}(\beta\text{-diketonato})_2(\mathrm{NIT2py})]^+$ and $[\mathrm{Cr}(\beta\text{-diketonato})_2(\mathrm{IM2py})]^+$ become substantially spin-allowed between the exchange coupled triplets as a result of the breakdown of the $\Delta S = 0$ restriction. This is substantiated by the enhancement in the absorption band intensity with lowering the temperature, as a result of the Boltzmann population of the triplet level in the ground state, in accordance with the antiferromagnetic interaction derived from the magnetic susceptibility measurements.

The differences in the magnetic and optical properties among the $\mathrm{Cr^{III}}$(NIT2py or IM2py) and $\mathrm{Ni^{II}}$(NIT2py or IM2py) complexes with various kinds of the β-diketonates are examined in terms of the exchange mechanism for the intensity enhancement in the formally spin-forbidden d–d transition region as discussed below.

3-3) Luminescence Spectra:[41] The luminescence peak of $[\mathrm{Cr(acac)_2(NIT2py)}]^+$ at 11350 $\mathrm{cm^{-1}}$ is located at a lower frequency than the lowest frequency absorption peak corresponding to the formally spin-forbidden transition ($^3L_0(^4A_2) \rightarrow {}^3L_D(^2\Gamma)$) around 13300 and 14000 $\mathrm{cm^{-1}}$, as shown in Fig. 8.[41] Apart from the recent claim that the NIR luminescence in the Ln(Ⅲ) complexes with two chelating NITBzImH radicals arises from the ligand-centered transitions,[59] this may show a large Stokes shift involving the $^1L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ emission in view of the band width, of which the corresponding absorption bands should be too weak to observe owing to the definitely spin-forbidden triplet–singlet transitions like a single ion mechanism (Fig. 7). Thus, the antiferromagnetic couplings are suggested between the lowest excited doublet state of the Cr(Ⅲ) moiety and the ground doublet state of the NIT2py radical, which are larger than that in the ground state, as expected and as observed for the dimeric transition metal complexes.[13,18,19] Similar results for the corresponding IM2py complexes are also observed.[49] However, until this assignments would be verified by the CD or MCD observation in the singlet–triplet transitions, the possibility of the triplet–triplet emission with large anti-Stokes shift could not necessarily be eliminated.

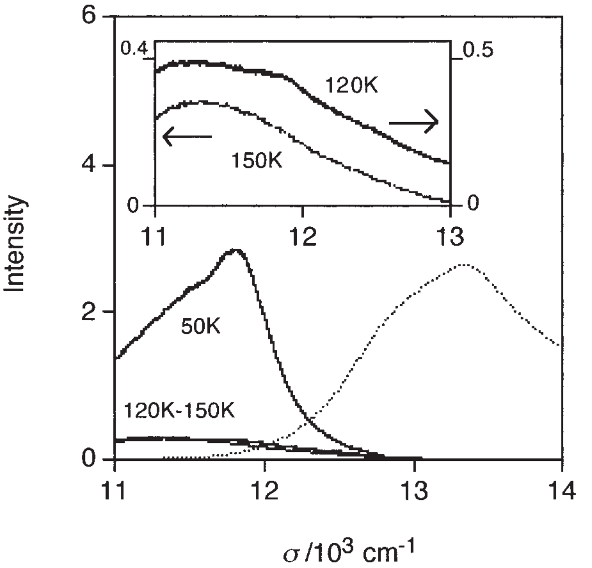


Fig. 8. Luminescence (solid lines) in the solid at 150, 120, 50 K and absorption spectra (dotted line) in CH_3CN at room temperature of $[\mathrm{Cr(acac)_2(NIT2\text{-}py)}]\mathrm{PF_6}$. Inset: Enlarged luminescence spectra at 120 K and 150 K (Ref. 41).

3-4) Correlation between the Absorption Intensity and the Magnetic Coupling Constant through the Substituent Effect:[37,41,45] For the $\mathrm{Ni^{II}}$(NIT2py) and $\mathrm{Ni^{II}}$(IM2py) complexes, varying ranges of the intensities of the formally spin-forbidden $^3A_2{}^2L_0 \rightarrow {}^1E^2L_0$ transition ($\varepsilon_{\max}(\mathrm{SF}) = 120$–$480$ and 4.8–11.6, respectively) can be compared with those ($\varepsilon_{\max}(\mathrm{CT}) = 417$–$872$ and 44–107, respectively) of the MLCT band (Table 1). Similarly, the $\mathrm{Cr^{III}}$(NIT2py) and $\mathrm{Cr^{III}}$(IM2py) complexes give ranges of $\varepsilon_{\max}(\mathrm{SF}) = 234$–$346$ and 146–191, respectively, for the $^3L_0(^4A_2) \rightarrow {}^3L_D(^2\Gamma)$ transition, which can also be compared with those of the MLCT band intensity ($\varepsilon_{\max}(\mathrm{CT}) = 479.0$–$630.9$ and 923–1367, respectively) as in Table 1. And the $\varepsilon_{\max}(\mathrm{SF})$ values increase with increasing the $\varepsilon_{\max}(\mathrm{CT})$. These facts strongly suggest to give some connection among the $\varepsilon_{\max}(\mathrm{CT})$, $\varepsilon_{\max}(\mathrm{SF})$ and J_{obsd} values in the multi-spin coupled systems; in other words, the formally spin-forbidden transition of $^3L_0(^4A_2) \rightarrow {}^3L_D(^2\Gamma)$ can attain the integrated intensity I_{SF} by borrowing the integrated intensity I_{CT} of the t_{2g}-π^* SOMO CT through the exchange mechanism.

According to the exchange mechanism,[30] the formally spin-forbidden transitions due to $^3L_Q(^4A_2) \rightarrow {}^3L_D(^2\Gamma)$ and $^2L_T(^3A_2) \rightarrow {}^2L_S(^1E)$ for the $\mathrm{Cr^{III}}$(NIT2py or IM2py) and $\mathrm{Ni^{II}}$(NIT2py or IM2py) complexes, respectively, are made allowed by the mixing of the MLCT excited states through the perturbation, i.e., the electron transfer integral between the Cr(t_{2g})-IM2py(SOMO π^*) and the Ni(e_g)-IM2py(SOMO π^*). The spin-forbidden transitions attain the transition intensity or the integrated intensity I_{SF}, by acquiring a small part ($b = h_{\mathrm{CT}}/\Delta E_{\mathrm{CT}}$) of that of the spin-allowed MLCT. h_{CT} is the electron transfer integral, $\langle \Psi_0(^3L_Q(^4A_2))|h^{\mathrm{Cr}}|\Phi(^3\mathrm{MLCT})\rangle$ for Cr(Ⅲ) and $\langle \Psi_0(^2L_T(^3A_2))|h^{\mathrm{Ni}}|\Phi(^2\mathrm{MLCT})\rangle$ for Ni(Ⅱ). ΔE_{CT} is the difference ($E_{\mathrm{CT}} - E_{\mathrm{SF}}$) between the transition energies where E_{CT} and E_{SF} refer to the transition energies from the triplet ground state to the $^3\mathrm{MLCT}(E_{\mathrm{CT}})$ and the $^3L_D(^2\Gamma)(E_{\mathrm{SF}})$ for Cr(Ⅲ) or those from the doublet ground state to the $^2\mathrm{MLCT}(E_{\mathrm{CT}})$ and the $^2L_S(^1E)(E_{\mathrm{SF}})$ for Ni(Ⅱ). Then, the following equation is given.

$$I_{\mathrm{SF}} = b^2 I_{\mathrm{CT}} = (h_{\mathrm{CT}}/\Delta E_{\mathrm{CT}})^2 I_{\mathrm{CT}} \tag{1}$$

The configurational interaction with the triplet (Cr) or doublet (Ni) excited MLCT state level results in stabilizing the triplet (Cr) or the doublet (Ni) ground state level by $h_{\mathrm{CT}}{}^2/E_{\mathrm{CT}}$ (Figs. 6, 7 and Eq. 2).

$$\begin{aligned} J_{\mathrm{AF}} &= h_{\mathrm{CT}}{}^2/E_{\mathrm{CT}} \qquad (2) \\ &\approx J_{\mathrm{AF}} = (I_{\mathrm{SF}}/I_{\mathrm{CT}})(\Delta E_{\mathrm{CT}})^2/E_{\mathrm{CT}} \end{aligned}$$

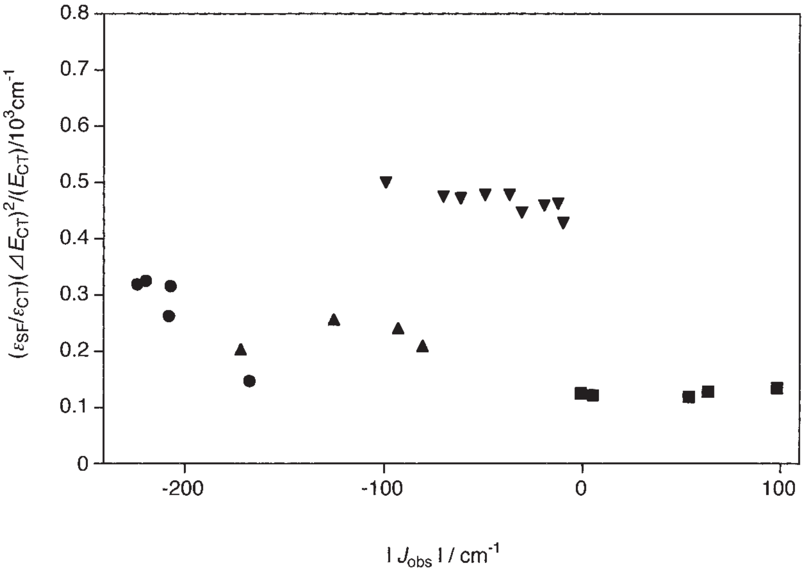


Fig. 9. Plots of $(\varepsilon_{SF}/\varepsilon_{CT})(\Delta E_{CT})^2/(E_{CT})$ vs. $|J_{OBSD}|$ for the bis(β-diketonato) complexes NIT2py Ni(II) (●), IM2py Ni(II) (■), NIT2py Cr(III) (▼), IM2py Cr(III) (▲) (Ref. 37).

$$\propto (\varepsilon_{SF}/\varepsilon_{CT})(\Delta E_{CT})^2/E_{CT} \tag{3}$$

Thus, in terms of the ratio of the spin-forbidden transition intensities to the MLCT ones from Eqs. 1 and 2 by considering the antiferromagnetic interaction through the charge transfer integral h_{CT}, one can express the exchange coupling constant J_{AF} is expressed as in Eq. 3.

The integrated intensity I_{SF} in Eq. 3 may be approximated by the product of the molar absorption coefficient (ε) and the half-bandwidth ($\Delta_{1/2}$). The ratios $\varepsilon_{SF}/\varepsilon_{CT}$ are almost constant, and the MLCT transition energy E_{CT} and the energy difference (ΔE_{CT}) between the MLCT and the spin-forbidden transition energy change with different kinds of β-diketonates in the Ni^{II}(NIT2py) complexes, but not in the Ni^{II}(IM2py) complexes, the Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes (Table 1). Accordingly, $(\varepsilon_{SF}/\varepsilon_{CT})(\Delta E_{CT})^2/E_{CT}$) or J_{AF} varies with β-diketonates in the Ni^{II}(NIT2py) complexes, whereas this is almost constant for variation of β-diketonates in the Ni^{II}(IM2py), Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes, in contrast to the large difference of the J_{obsd} values (Table 1 and Fig. 9). That is, the antiferromagnetic interaction is affected by the coligands in the Ni^{II}(NIT2py) complexes, but not in three series of the Ni^{II}(IM2py), Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes. Since the J_{obsd} values are the sum of the antiferromagnetic and ferromagnetic contributions, i.e., $J_{obsd} = J_{AF} + J_{F}$, the variation of the J_{obsd} values seems to reflect that of the J_{AF} values for the Ni^{II}(NIT2py) complexes, but that of the J_{F} values for the Ni^{II}(IM2py), Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes. In other words, the coligand effect may be operative in the antiferromagnetic interaction for the Ni^{II}(NIT2py) complexes and in the ferromagnetic interaction for the Ni^{II}(IM2py), Cr^{III}(NIT2py) and Cr^{III}(IM2py) complexes. In order to reveal how the coligand effect is exerted on the antiferromagnetic or ferromagnetic interaction, relations of J_{obsd} or the right member of Eq. 3 with the Hammett's constant σ_m for the 1 and 3 substituents in the β-dikentonates or the acid dissociation exponent pK_a of the β-diketones were examined. For the Ni^{II}(NIT2py) complexes, a plot of the right member of Eq. 3 against $\sum\sigma_m$ (the sum of each for the substituents in the complexes) results in a linear correlation for the mono(β-diketonato)(NIT2py)nickel(II) complexes and a nearly linear one for the bis- and mono(β-diketonato)(NIT2py)nickel(II) complexes as shown in Fig. 10. That is, the larger the electron withdrawing of the substituents, the smaller the right member of Eq. 3 or the antiferromagnetic coupling is. On the other hand, the J_{obsd} values of the Cr^{III}(NIT2py), Cr^{III}(IM2py) and Ni^{II}(IM2py) complexes tend to increase with decreasing the acid dissociation exponent pK_a of the β-diketones except the Cr^{III}(dbm) complex. Thus, the J_F values increase with decreasing the pK_a or increasing Lewis acidity of the metal sites in the M(β-diketonate)$_2$ moiety which makes the interaction between IM2py and metal ions

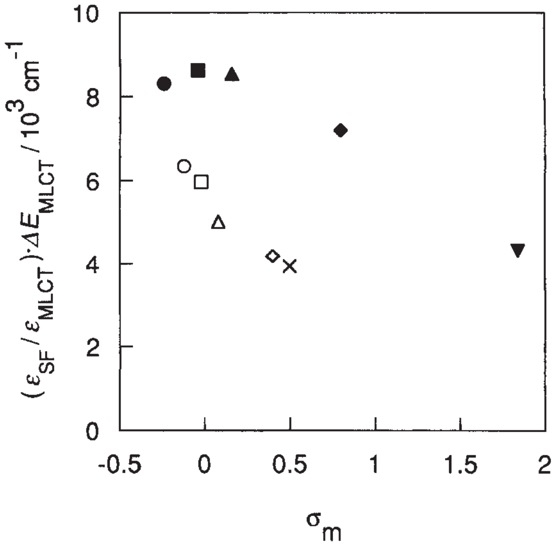


Fig. 10. Plots of $(\varepsilon_{SF}/\varepsilon_{MLCT})\cdot\Delta E_{MLCT}$ vs σ_m for [Ni(β-diketonato)$_2$(NIT2py)] complexes (acac (●), bzac (■), dbm (▲), tfac (◆), hfac (▼)) and for [Ni(β-diketonato)(tmen)(NIT2y)]PF$_6$ complexes (acac (○), bzac (□), dbm (△), tfac (◇), bztfac (×)) (Ref. 37).

stronger. This may result in the increase of the orbital overlap between the $e_g(d_\sigma)$ and the HOMOπ^+ in the nitroxide radicals for Cr(Ⅲ) or the $t_{2g}(d_\pi)$ and the SOMO(π^*) for Ni(Ⅱ), leading to the increase of the ferromagnetic interaction J_F.

The hypothetical variation of the J_F values depending on coligands may be accounted for theoretically by considering the lowest quintet LMCT for Cr(Ⅲ) and the quartet MLCT for Ni(Ⅱ). The highest and lowest spin multiplet levels of the ground state are stabilized due to the configurational interaction, leading to the ferromagnetic and antiferromagnetic interaction or varying the J_F and J_{AF} values, respectively.[4,13] That is, the ferromagnetic interaction appears with the quintet ^{5}LMCT(HOMOπ-e_g) for Cr(Ⅲ) and quartet ^{4}MLCT(t_{2g}-π^*) for Ni(Ⅱ), whereas the antiferromagnetic interaction appears with the triplet ^{3}MLCT(t_{2g}-π^*) for Cr(Ⅲ) and the doublet ^{2}MLCT(e_g-π^*) for Ni(Ⅱ). Consequently, the variation in J_{obsd} values with the coligand effect can be interpreted by considering the J_F and J_{AF}, namely, both the magnetic orbital orthogonality and overlap. The difference in degree of the electron transfer integral or overlap integral between the IM2py and NIT2py with the metal d orbitals is compared on the basis of the chelate ring planarity (IM2py being more planar than NIT2py) as revealed by the X-ray analysis. J_F and $|J_{AF}|$ depend on $h_{e\pi}{}^{Cr} = \langle |e_g{}^+|h|\pi^+|\rangle$ and $h_{t\pi^*}{}^{Cr} = \langle |t_{2g}{}^+|h|\pi^{*+}|\rangle$, respectively, for Cr(Ⅲ) and $h_{t\pi^*}{}^{Ni} = \langle |t_{2g}{}^-|h|\pi^{*-}|\rangle$ and $h_{e\pi^*}{}^{Ni} = \langle |e_g{}^+|h|\pi^{*+}|\rangle$,[33] respectively, for Ni(Ⅱ), assuming that the respective factors $1/E_{CT}$ in Eq. 3 for J_{AF} and in the analogous equation for J_F are not so much different on going from the Ni$^{\rm II}$(NIT2py) or the Cr$^{\rm III}$(NIT2py) complexes to the corresponding Ni$^{\rm II}$(IM2py) or Cr$^{\rm III}$(IM2py) complexes.

For Cr(Ⅲ), the overlap between the $e_g(d_\sigma)$ and π orbitals ($h_{e\pi}{}^{Cr} = \langle |e_g{}^+|h|\pi^+|\rangle$) or between the $t_{2g}(d_\pi)$ and the π^* orbitals ($h_{t\pi^*}{}^{Cr} = \langle |t_{2g}{}^+|h|\pi^{*+}|\rangle$) leads to the relations $h_{e\pi}{}^{Cr}(\mathrm{NIT}) > h_{e\pi}{}^{Cr}(\mathrm{IM})$ or $h_{t\pi^*}{}^{Cr}(\mathrm{NIT}) < h_{t\pi^*}{}^{Cr}(\mathrm{IM})$, which gives $J_F(\mathrm{NIT}) > J_F(\mathrm{IM})$ and $-|J_{AF}(\mathrm{NIT})| > -|J_{AF}(\mathrm{IM})|$, respectively.

For Ni(Ⅱ) with the $e_g(d_\sigma)$ magnetic orbital, the situations are completely reverse in terms of the relations $J_F(\mathrm{NIT}) < J_F(\mathrm{IM})$ and $-|J_{AF}(\mathrm{NIT})| < -|J_{AF}(\mathrm{IM})|$ from $h_{e\pi^*}{}^{Ni}(\mathrm{NIT}) < h_{e\pi^*}{}^{Ni}(\mathrm{IM})$ and $h_{t\pi^*}{}^{Ni}(\mathrm{NIT}) > h_{t\pi^*}{}^{Ni}(\mathrm{IM})$, respectively.[34] The addition of the respective inequalities leads to the following ones; $-|J_{AF}(\mathrm{NIT})| + J_F(\mathrm{NIT}) > -|J_{AF}(\mathrm{IM})| + J_F(\mathrm{IM})$ for Cr(Ⅲ) and $-|J_{AF}(\mathrm{NIT})| + J_F(\mathrm{NIT}) < -|J_{AF}(\mathrm{IM})| + J_F(\mathrm{IM})$ for Ni(Ⅱ), which are in accordance with the following findings; $J_{obsd}(\mathrm{NIT}) > J_{obsd}(\mathrm{IM})$ for the Cr(Ⅲ) and $J_{obsd}(\mathrm{NIT}) < J_{obsd}(\mathrm{IM})$ for the Ni(Ⅱ). This accounts for the differences in magnetic behavior among the Cr(Ⅲ) and Ni(Ⅱ) complexes with IM2py and NIT2py by considering both the antiferromagnetic and ferromagnetic contributions to the J_{obsd} through the exchange mechanism. It is seen that the reverse behavior in the inequal relations results from the difference in magnetic orbitals, $t_{2g}(d_\pi)$ of Cr(Ⅲ) and $e_g(d_\sigma)$ of Ni(Ⅱ), which are orthogonal to each other.

The differences in magnetic behavior among the Cr(Ⅲ) and Ni(Ⅱ) complexes with IM2py and NIT2py are elucidated by considering the overlaps between the magnetic orbital (t_{2g} or e_g) and the SOMO π^*, LUMO π^* or HOMO π in the nitroxide radicals.

3-5) Tetrahedral Co(Ⅱ) Complexes: Next, one should examine the influence from the coordinated radical ligands (NITmepy and IMmepy) to the spin-forbidden $^4A_2$–^2E, $^2T_1$ transitions in (T-4)- $\mathrm{CoCl_2(L)}$.[40] In view of the chelate coordination of the radical ligand in these Co$^{\rm II}$ complexes, there is expected to be notable effect on the spin-forbidden transition intensity in the spin coupled systems for transition metal complexes with the analogous mono(NIT2py or IM2py)chromium(Ⅲ) complexes.[41,45] However, the spectral patterns of the spin-forbidden transitions overlapped with the third $^4A_2$–$^4T_{1b}$ transition are similar to those of the non-radical (T-4) Co$^{\rm II}$ complexes; the molar absorption coefficients are not much changed on radical coordination as shown in Fig. 11. Since the intensification of the sharp components is not always linearly correlated with the observed magnetic coupling constants estimated from the magnetic susceptibility, it appears that the intensity enhancement due to the radical coordination is very small for the present (T-4)-Co$^{\rm II}$(NITmepy) and -Co$^{\rm II}$(IMmepy) complexes even with the observed considerable antiferromagnetic interactions. Since the extent of the intensity enhancement depends on the CT transition energy and intensity as does the antiferromagnetic interaction in the ground state (vide infra), the absence of appreciable enhancement of the IMmepy and NITmepy complexes probably arises from the high energy position (large ΔE_{CT}) and low intensity of the CT (small $\varepsilon_{max}{}^{CT}$) concerned, though the CT position and intensity are not clearly identified so far.

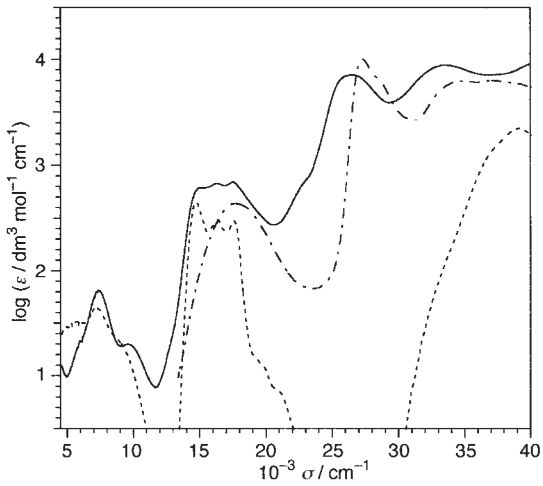


Fig. 11. UV-vis-NIR absorption spectra of $[\mathrm{CoCl_2(NITmepy)}]$ in dichloromethane (——), $\mathrm{CoCl_2 \cdot 6H_2O}$ in acetonitrile (-----) and NITmepy in dichloromethane (– – – – –) at room temperature (Ref. 40).

3-6) Diamagnetic Co(Ⅲ) Complexes: In this case, there is no magnetic interaction in the ground state owing to the diamagnetic low spin Co(Ⅲ) complexes. However, it is interesting to see whether the lowest excited triplet state of Co(Ⅲ) complexes is influenced by the coordinated NIT or IM radicals. This is a reverse situation to the magnetic interaction between the excited triplet state in diamagnetic ligands and nearby paramagnetic species such as central metal ions[27,28] or dissolved dioxygen molecule.[29] For the latter case, the intraligand singlet–triplet transition intensities of the coordinated acetylacetonates and aromatic imines in Cr(Ⅲ) complexes are found to be intensified through borrowing the CT intensities, on the basis of the MCD spectra and the semi-quantitative theoretical consideration.[28]

For $[\mathrm{Co^{III}(acac)_2(NO_2\ or\ PPh_3)(NITnpy\ or\ IMnpy)}]^{n+}$ complexes,[42] it is expected that the intensity in the spin-forbidden $^1A_1 \to {}^3T_2$, $^3T_1$ transitions of Co(Ⅲ) near 12500 cm^{-1} will be enhanced by the spin exchange coupling with the doublet ground state of the nitroxide radical and the excited triplet state of the Co(Ⅲ) complexes. However, it is found that the lowest frequency shoulder belongs to one of the vibronic components of the n $\rightarrow \pi^*$ NITnpy intraligand transition. The spin exchange coupling in this kind of the (nitroxide)cobalt(Ⅲ) complexes is not large enough to observe the spin-forbidden transition intensity enhancement as observed for the corresponding monodentate Cr$^{\text{III}}$(NITnpy or IMnpy) complexes,[46] of which the J_{obsd} values are found to be several cm^{-1} (vide supra). The chelated Co$^{\text{III}}$(NIT2py or IM2py) complexes may be such candidates to give observable intensity enhancement. However, it is noted that the electron transfer integral ($h_{\mathrm{e}\pi^*}{}^{\mathrm{Co}} = \langle|\mathrm{e_g}^+|\mathrm{h}|\pi^*|\rangle$) from the triplet ligand field state with the $\mathrm{t_{2g}}^5\mathrm{e_g}^1$ configuration to the SOMO π^* or the overlap between the $\mathrm{e_g}(\mathrm{d}_\sigma)$ and π orbitals would be negligibly small, predicting little or no intensity enhancement of the singlet–triplet d–d transitions even for the chelated Co$^{\text{III}}$(NIT2py) complexes according to the above theoretical consideration in terms of the exchange mechanism.

4) Intraligand Absorption Band. Another influence on coordination of the NIT2py and IM2py ligands is seen in the intraligand transitions. They give a broad vibronic band at 17500 cm^{-1} and a sharp strong band following the higher energy component around 27200 cm^{-1} for the nitronyl nitroxide (NIT) moiety and two bands at 22000 cm^{-1} and 33300 cm^{-1} for the imino nitroxide (IM) moiety. These are due to the n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions from the longer wavelength, respectively.[60]

4-1) Ni(Ⅱ) and Cr(Ⅲ) Complexes:[37,41,45] The UV bands of the Cr$^{\text{III}}$(NIT2py) and Ni$^{\text{II}}$(NIT2py) complexes show the NIT2py and β-diketonate intraligand or CT transitions, respectively, at 27×10^3 and 33.3×10^3 cm^{-1} as in Figs. 1, 2, 4. There seem to be the almost superposition of the nonradical (β-diketonato) complexes and NIT2-py ligand or little influence from the NIT2-py coordination in contrast to the spin-forbidden d–d transitions. However, definite comparison with each other is difficult owing to the overlap with the newly appeared CT . As for the ultraviolet spectral characteristics of the Cr$^{\text{III}}$(IM2py) and Ni$^{\text{II}}$(IM2py) complexes, the vibronic structure around 20.0×10^3 cm^{-1} as shown in Figs. 3 and 5 may originate from the intraligand n $\rightarrow \pi^*$ transition, in view of the similarities in intensity and shift behaviors for variation of the β-diketonates as well as for the Ln$^{\text{III}}$(IM2py) complexes as mentioned below.

4-2) Ln(Ⅲ) Complexes:[44] As compared with the intraligand n-π^* transition of IM2py in the region from 19×10^3 cm^{-1} to 24×10^3 cm^{-1}, the corresponding bands of [Ln(hfac)$_3$(IM2py)] (Fig. 12) are shifted to lower frequency as observed in [Gd(NITBzIMH)$_2$(NO$_3$)$_3$].[59] These Ln$^{\text{III}}$(IM2py) complexes give much larger molar absorption coefficients of each component as well as clearer appearance of the vibrational structure than the free IM2py ligand. Two causes of this behavior may be considered: (i) the chelation stabilizes slightly the radical SOMO π^* energy level due to increase in planarity between N=C–N=O moiety and pyridine ring leading to expansion of the conjugated system; (ii) the coordination bond formation with lanthanide(Ⅲ) ion affects the electronic state of the ligand considerably as found for Schiff base complexes.[61]

4-3) Co(Ⅲ) Complexes:[42] We have also observed significant influences on the n-π^* absorption bands for the diamagnetic Co(Ⅲ) complexes bearing NITnpy and IMnpy(3- or 4-pyridyl substituted NIT and IM) as monodentate ligands through pyridyl coordination, in spite of giving weaker (magnetic) interaction between the pyridine of the nitroxides and metal ions, as seen for the corresponding Cr(Ⅲ) complexes.

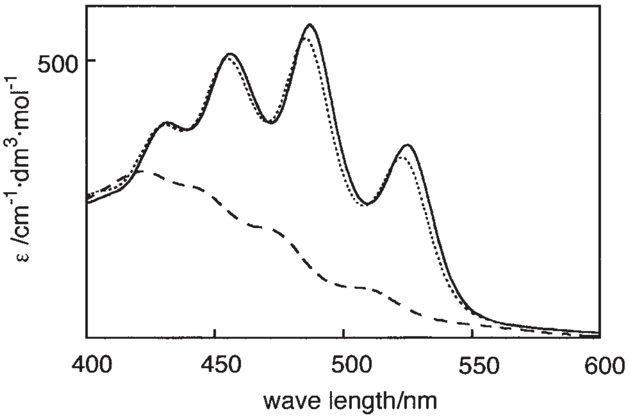


Fig. 12. Absorption spectra of [Sm(hfac)$_3$(IM-2py)] (solid line), [Yb(hfac)$_3$(IM-2py)] (dotted line) and IM-2py (dashed line) in CHCl$_3$ (Ref. 44a).

For [Co(acac)(tdmme)(NIT4py)](PF$_6$)$_2$ (tdmme = 1,1,1-tris-(dimethylphosphino-methyl)ethane), the n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are red-shifted by 1300 and 1100 cm^{-1}, respectively. In contrast, the corresponding NIT3py complex gives a slightly red-shifted (500 cm^{-1}) n $\rightarrow \pi^*$ transition band, and a negligibly shifted but remarkably broad $\pi \rightarrow \pi^*$ band. Such influences on the radical coordination are confirmed for *trans*-[Co(acac)$_2$(NO$_2$-κN or PPh$_3$)(L)] (L = NIT4py, NIT3py). These differences in perturbation between the NIT4py and NIT3py complexes may result from the differences in spin density (and sign) at the pyridyl-N atom as found in the ^{59}Co NMR chemical shifts of the NIT4py and NIT3py nitrito-*k*N complexes (vide infra).

Since the corresponding Co$^{\text{III}}$(IMnpy) complexes gave quite complicated absorption spectra, the results are not so clear.

NMR Behavior

1) Ni(Ⅱ) Complexes.[38] **1-1) Contact Shifts in Spin Coupled Systems:** The methine C–H contact shifts of β-diketonato ligands were observed in the order of hfac, tfac, acac, bzac and dbm from the lower magnetic field with variation of the β-diketonate ligands in two series of the NIT2py complexes similarly to the order in the nonradical complexes. Such a tendency of NMR contact shifts is examined by considering both J and the C–H contact shifts of [Ni(β-diketonato)$_2$(tmen)] as follows.

In general, NMR contact shifts in magnetically-electron spin-coupled systems are expressed by the following Eq. 4. Here the spin coupled contact shifts $\delta_i{}^{\text{con}}(T, J)$ are separately expressed in terms of a product of the fractional contributions ($\mathrm{h}_i(T, J)$) from each part in paramagnetic moieties (j) and the uncoupled spin density A$_j$ or chemical shifts ($\delta_j{}^{\text{con}}(T, 0)$) through the theoretical approach employed for the dinuclear metal complexes.[11,35]

$$\delta_j{}^{\text{con}}(T, J) = \frac{\Delta\nu}{\nu_0} = \frac{g_{\mathrm{e}}\mu_{\mathrm{B}}}{3h\gamma_{\mathrm{N}}kT}\sum_j A_j C_{ij} S_i(S'_i + 1)$$

$$\times \frac{(2S_i + 1)\exp(-E_i/kT)}{\sum\limits_i (2S_i + 1)\exp(-E_i/kT)}$$

$$= \sum_j \delta_j{}^{\mathrm{con}}(T, 0)\mathrm{h}_j(T, J) \tag{4}$$

Here each coefficient C_{ij} equals $\langle S_{jZ}\rangle_{ij}/\langle S'_Z\rangle_{ij}$ which relates the hyperfine coupling of S_j spin systems in each uncoupled paramagnetic moiety to that in a coupled system for each S'_i level; the other symbols have the usual meanings. A more practical form for contribution from paramagnetic centers ($j = 1$) is given in Eq. 5, where the fractional contribution from coupled paramagnetic origins, Ni(II) ($S_1 = 1$) is expressed by functions of the exchange magnetic coupling constant J.

$$\delta_1{}^{\mathrm{con}}(T, J) = \delta_1{}^{\mathrm{con}}(T, 0)\mathrm{h}_1(T, J) \tag{5}$$

where

$$\mathrm{h}_1(T, J) = \frac{1 + 5\exp(3J/kT)}{2 + 4\exp(3J/kT)}$$

Then, these contact shifts $\delta_1{}^{\mathrm{con}}(T, J)$ of the radical complexes are given by $\delta_1{}^{\mathrm{con}}(T, 0)\mathrm{h}_1(T, J)$ in relation with the exchange coupling constants J, where $\delta_1{}^{\mathrm{con}}(T, 0)$ refers to the contact shifts of nonradical Ni(II) complexes. In the present case, $\delta_1{}^{\mathrm{con}}(T, J)$ and $\delta_1{}^{\mathrm{con}}(T, 0)$ correspond to δ^{con}(C–H) of [Ni(β-diketonato)$_2$(NIT2py)] and [Ni(β-diketonato)$_2$(tmen)] or those of [Ni(β-diketonato)(tmen)(NIT2py)]$^+$ and [Ni(β-diketonato)(NO$_3$)(tmen)], respectively. A plot of the $\delta_1{}^{\mathrm{con}}(T, J)$ against $\delta_1{}^{\mathrm{con}}(T, 0)\mathrm{h}_1(T, J)$ at 303.15 K according to Eq. 5 exhibits a good linear correlation for the mono- and bis(β-diketonato) complexes as shown in Fig. 13, leading to the following eqs.

$$\delta^{\mathrm{con}}(303, J) = 0.507 \times \delta^{\mathrm{con}}(303, 0)\mathrm{h}_1(303, J) + 6.52 \tag{6}$$

$$\delta^{\mathrm{con}}(303, J) = 1.28 \times \delta^{\mathrm{con}}(303, 0)\mathrm{h}_1(303, J) + 1.09 \tag{7}$$

for [Ni(β-diketonato)$_2$(NIT2py)] and [Ni(β-diketonato)(tmen)(NIT2py)]$^+$, respectively. It is seen that the C–H contact shifts of [Ni(β-diketonato)(tmen)(NIT2py)]$^+$ and [Ni(β-diketonato)$_2$(NIT2py)] at room temperature are determined by the contribution from the contact shifts of the nonradical complexes [Ni(β-diketonato)(NO$_3$)(tmen)] and [Ni(β-diketonato)$_2$(tmen)], respectively, and the exchange coupling constant J between a nickel(II) ion and NIT2py. Furthermore, it is found that this relationship is appropriate for the low temperature case. Since it is difficult to determine the positions of the ^{1}H-NMR signals due to line broadening on lowering temperature, ^{2}H-NMR contact shifts with narrower linewidths are used for this case. $\delta_1{}^{\mathrm{con}}(T, J)$ and $\delta_1{}^{\mathrm{con}}(T, 0)$ correspond to the contact shifts δ^{con}(C–D) of [Ni(β-diketonato-d)$_2$(NIT2py)] and [Ni(β-diketonato-d)$_2$(tmen)], respectively. A plot of the $\delta_1{}^{\mathrm{con}}(T, J)$ against $\delta_1{}^{\mathrm{con}}(T, 0) \times \mathrm{h}_1(T, J)$ at low temperature according to Eq. 5 gives a fairly good linear correlation for the bis complexes as similarly to the room temperature case.

By using the above relations (Eqs. 6 and 7), one can estimate the exchange coupling constant J through knowledge of the contact shifts of both the radical and nonradical complexes with the identical β-diketonato ligands. This offers an alternative semi-empirical means to simply estimate the J value only from the NMR measurements at room temperature. This is applicable only to these types of complexes so far, but it is more advantageous over the elaborate traditional one obtained from variable temperature magnetic susceptibility measurements.

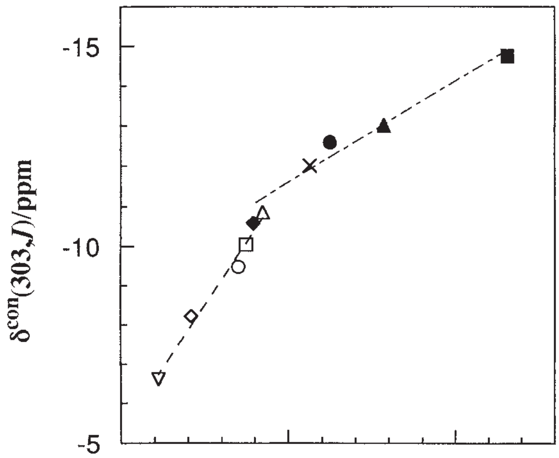


Fig. 13. Plots of ^{1}H-NMR contact shifts in the form of $\delta^{\mathrm{con}}(303, J)$ vs $\delta^{\mathrm{con}}(303, 0)\mathrm{h}(303, J)$ at 303 K for [Ni(β-diketonato)$_2$(NIT2-py)] (acac(○), bzac(□), dbm(△), tfac(◇) and hfac (▽)) and [Ni(β-diketonato)(tmen)(NIT2-py)]PF$_6$ (acac(●), bzac(■), dbm(▲), tfac(◆), bztfac(×)). Lines for [Ni(β-diketonato)$_2$(NIT2-py)] (- - -) and [Ni(β-diketonato)(tmen)(NIT2-py)]PF$_6$ (– - – - –) are the least-squared-fits (Ref. 38).

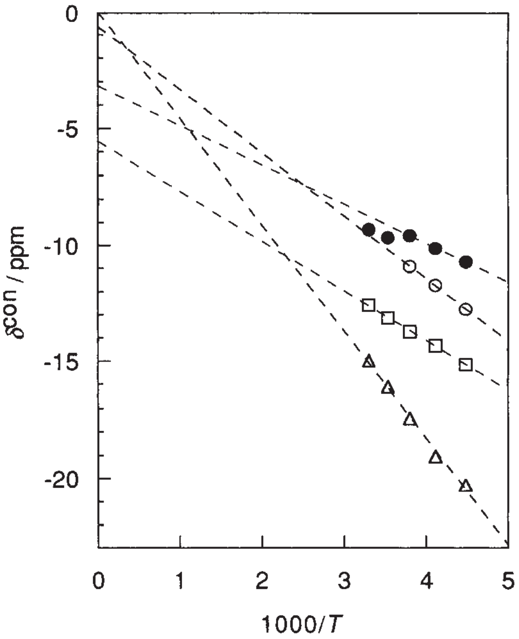
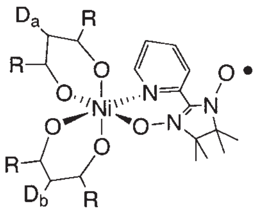


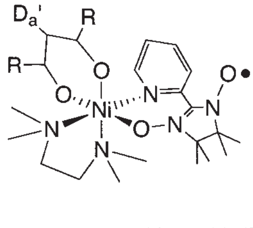
Fig. 14. Inverse temperature dependence of ^{2}H-NMR for [Ni(acac-d)$_2$(NIT2-py)]; C–D$_a$ (○), C–D$_b$ (●), [Ni(acac-d)(tmen)(NIT2-py)]PF$_6$; C–D$_a{}'$ (□) and [Ni(acac-d)$_2$(tmen)]; C–D$_b{}'$ (△). Lines are the least-squared-fits (Ref. 38).

1-2) Discrimination of the acac Methines in [Ni(acac-*d*)$_2$(NIT2py)]: A plot of the C–D contact shifts for the acac complexes against the reciprocal of temperature gives straight lines with negative slopes as shown in Fig. 14. One of two lines for [Ni(acac-*d*)$_2$(NIT2py)] is similar in slope and intercept to that of the radical complex [Ni(acac-*d*)(tmen)(NIT2py)]$^+$, whereas the other is similar to the nonradical complex [Ni(acac-*d*)$_2$(tmen)]. The former gives slower slopes in contrast to the steeper slopes for the latter. One of the oxygens of the acetylacetonate in [Ni(acac-*d*)(tmen)(NIT2py)]$^+$ binds at the *trans* position of the NIT2py N–O group. Therefore, the signal giving a slower slope for the C–D contact shifts of [Ni(acac-*d*)$_2$(NIT2py)] corresponds to the methine deuteron (C–D$_a$) in the acac bound at the *trans* position of the NIT2py coordinated oxygen as found by the X-ray analysis (Scheme 2). It is plausible that the slopes become slower due to the antiferromagnetic interaction with the coordinated NIT2py. This distinct behavior arises from the difference in the magnetic interactions between NIT2py and two different e$_g$ orbitals. That is, the NIT2py coordinated oxygen exerts a larger influence on the C–D$_a$ than on the C–D$_b$ (Scheme 2) probably in terms of *trans* influence, implying a topological discrimination of the acac ligands with respect to the disposition of the NIT2py oxygen ligator.

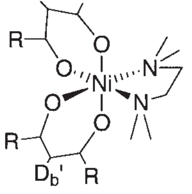
2) Co(Ⅲ) Complexes.[42] **2-1) ^{1}H NMR Spectra:** The ^{1}H NMR signals of the acac or PPh$_3$ moiety in [Co(acac)$_2$(NO$_2$-κN or PPh$_3$, NITnpy or IMnpy)]$^{n+}$ were found to become broad. Since the observed broad signals did not show any shift from those of the parent complexes, the line-broadening upon coordination of NITnpy or IMnpy via 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 shorter distance from the radical moiety in NIT3py to the protons in the coligands than that in NIT4py accounts for the difference in line broadening in terms of the dipolar relaxation. For the IMnpy Co(Ⅲ) complexes, the ^{1}H NMR shifts of the IM radical moiety ranges from δ 0 to δ 10, as if the IMnpy were diamagnetic, as found for the Ln(Ⅲ) complexes (vide infra).



[Ni(β-diketonato-d)$_2$(NIT2-py)]



[Ni(β-diketonato-d)(tmen)(NIT2-py)]$^+$



[Ni(β-diketonato-d)$_2$(tmen)]

Scheme 2.

2-2) ^{59}Co NMR Spectra: The ^{59}Co NMR signals of the nitroxide complexes are relatively broader than the py complexes. For the NITnpy complexes, [Co(acac)$_2$(NO$_2$ or PPh$_3$)(NIT3- or 4py)]$^{n+}$, the ^{59}Co NMR signals on the coordination of NIT3py and NIT4py shift to higher and lower field, respectively, from those of the corresponding py complexes. The line-broadening is little for the NIT3py complex and considerable for the NIT4py complex. These observations coincide with the ^{1}H NMR behaviors of the *meta* and *para* protons in the phenyl group of NITPh[62] and NITPhOH[63] and also with the experimental spin density (and sign) at the positions.[64]

The ^{59}Co NMR resonances of the IMnpy complexes, [Co(acac)$_2$(NO$_2$ or PPh$_3$)(IM3- or 4py)]$^{n+}$, show slightly higher field shifts with less broadening than the corresponding NITnpy complexes. This also coincides with the difference in the spin density between the imino and nitronyl nitroxides. Thus, the ^{59}Co NMR chemical shifts reflect the spin density and sign on the pyridyl-N atom of NITnpy or IMnpy, although the shift values are relatively small in accordance with the small spin density on the N atom as evidenced by the magnetic interaction for the Cr^{III}-(NITnpy) complexes (vide supra).

3) Lanthanide(Ⅲ) Complexes.[48] The ^{1}H NMR signals are observed for the hfac methine proton (δ 6.0) and the pyridine protons (from δ 7.5 to δ 8.5) in the diamagnetic range associated with line-broadening as observed for the Co^{III}(IMnpy) complexes. The paramagnetic radical containing a diamagnetic lanthanide and/or transition metal ion may inhibit shifting of the NMR signals in the radical compounds and makes it possible to analyze as if it were diamagnetic. This means the complete quenching of the unpaired electron around the protons in the IM radicals with respect to the NMR spectra. This was supported by analyzing the lanthanide induced shift for the hfac methine proton and pyridine protons in the paramagnetic Ln(Ⅲ) complexes. Accordingly, the paramagnetic shifts of the IM2py ligand in the paramagnetic Ln(Ⅲ) ion, e.g., for [Yb(hfac)$_3$(IM2py)] are induced only by unpaired 4f electrons in the Yb(Ⅲ) ion, but not by the paramagnetic IM2py itself.

It should be noted that the paramagnetic shifts in ^{1}H NMR are *hardly affected* by the unpaired spin in IM2py.

Concluding Remarks

The nitroxide radical ligands have been found to exert various influences on the spectroscopic properties of the metal complexes, depending on the direct coordination of the nitroxide moiety or the indirect coordination through the pyridyl moiety.

The absorption band intensities in the spin-forbidden transitions are enhanced for the Cr(Ⅲ) and Ni(Ⅱ) complexes with IM2py and NIT2py and a new CT appeared in the visible region for the

Cr(Ⅲ), Ni(Ⅱ), Mn(Ⅱ), and Co(Ⅱ) complexes. The absorption behavior in the spin-forbidden d–d transitions is elucidated in terms of the pair ion transition for the exchange mechanism; the formally spin-forbidden transitions and the MLCT between the same spin-multiplets. The variable temperature (VT) spin-forbidden absorption bands and the MLCT show qualitative but not quantitative accordance with the antiferromagnetic or ferromagnetic interaction estimated from the magnetic susceptibilities measurements. The quantitative discussion for the magnetic interaction constants J must wait for further spectroscopic study such as VT variable magnetic field (VH) MCD or VT CD . On the other hand, for the Cr(Ⅲ) and Ni(Ⅱ) β-diketonato complexes with IM2py and NIT2py, the observed larger difference of the $J_{\rm obsd}$ values associated with change of the β-diketonate coligands made it feasible to examine the origin of the magnetic interaction in relation with the variation of the absorption spectral intensity and positions in terms of the exchange mechanism. For the Ni$^{\rm II}$(IM2py), Cr$^{\rm III}$(NIT2py) and Cr$^{\rm III}$(IM2py) complexes, a large variation of the $J_{\rm obsd}$ is found to originate from the ferromagnetic interaction ($J_{\rm F}$), but not from the antiferromagnetic interaction ($J_{\rm AF}$) as found for the corresponding Ni(Ⅱ) complexes. This coligand effect on $J_{\rm F}$ or $J_{\rm AF}$ arises from the electronic effect of the β-diketonates as revealed from the correlation with the sum of the Hammett constant ($\sigma_{\rm m}$) of the substituents for the Ni$^{\rm II}$(NIT2py) complexes or the Lewis acidity (p$K_{\rm a}$) of the β-diketones themselves for the Ni$^{\rm II}$(IM2py), Cr$^{\rm III}$(NIT2py) and Cr$^{\rm III}$(IM2py) complexes. In order to confirm the constancy of the $J_{\rm F}$ for the Ni$^{\rm II}$(NIT2py) complexes for which there is no direct evidence, further collection of the magnetic and optical data for complexes with other types of coligands would be needed. The differences in magnetic behavior among the Cr(Ⅲ) and Ni(Ⅱ) complexes with IM2py and NIT2py are elucidated by considering the overlaps between the magnetic orbital ($\rm t_{2g}$ or $\rm e_g$) and the SOMO π^*, LUMO π^* or HOMO π in the nitroxide radicals in terms of the VBCI description. A more direct relation between the magnetic interaction constants J and the spectroscopic data could be found for the NMR contact shifts of [Ni(β-diketonato)$_2$(NIT2-py)] or [Ni(β-diketonato)(tmen)(NIT2-py)]$^+$, which are determined by the contribution of the antiferromagnetic interaction between Ni(Ⅱ) ion and NIT2-py radical as well as the methine C–H contact shifts of the nonradical β-diketonato complexes. The linear relation affords a new method to estimate the exchange coupling constants only from the ^{1}H NMR contact shifts at room temperature. Topological discrimination for two C–D NMR contact shifts in [Ni(acac-d)$_2$(NIT2py)] from VT NMR measurements could give a clue to reveal the magnetic interaction through different paths from the NIT2py SOMO.

Unlike the intensity enhancement of the spin-forbidden transitions of the NIT2py or IM2py Cr$^{\rm III}$ complexes, no apparent influence from the radical coordination to the analogous spin-forbidden $^4\rm A_2$–$^2\rm E$, $^2\rm T_1$ transitions in the UV region of (T-4)-[CoCl$_2$(NITmepy or IMmepy)] overlapped with the $^4\rm A_2$–$^4\rm T_{1b}$ transition were seen, even though these Co(Ⅱ) complexes gave considerable antiferromagnetic interation. Future elucidation for this curious fact together with the predicted spin-forbidden transition intensity behavior of the chelated Co$^{\rm III}$(NIT2py or IM2py) complexes (*vide supra*) would provide invaluable information to reveal the intensity borrowing mechanism for the radical complexes.

Besides the d–d and CT transitions, the intraligand transitions are also influenced by the radical coordination. For the chelated radicals, little change of the intraligand transitions from those of the NIT2py and IM2py ligands themselves are seen in the Ni$^{\rm II}$(NIT2py), Ni$^{\rm II}$(IM2py), Cr$^{\rm III}$(NIT2py) and Cr$^{\rm III}$(IM2py) complexes, whereas [Ln(hfac)$_3$(IM2py)] gave the red shift and/or intensity enhancement with vibronic structure in the n-π^* intraligand transition of the IM2py. For the monodentate radicals, there are found to be explicit perturbations on the n → π^* and $\pi \rightarrow \pi^*$ transition bands of the nitroxide moieties in Co$^{\rm III}$(NITnpy) and Co$^{\rm III}$(IMnpy) complexes even with no significant structural and magnetic changes from the corresponding pyridine complexes and/or from free nitroxides. These perturbed properties reflect the radical spin density and sign on pyridyl-N atom of NITnpy or IMnpy and/or the Co(Ⅲ)-py π backbonding, which may be related with the unusual diamagnetic NMR behavior of the radical ligands in the Co$^{\rm III}$(IM3- or 4py) and Ln$^{\rm III}$(IM2py) complexes.

More spectroscopic studies for various types of the nitroxide radical complexes must be completed to understand electronic and magnetic properties or bonding in metal complexes with radical ligands by exploring the influences from the radical ligands to the central metal ion with the d and/or f electrons or vice versa.

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